The 29th International Conference on Photochemistry

Boulder, Colorado • July 21 – 26, 2019

ABSTRACTS

The 29th International Conference on Photochemistry
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PLENARY SPEAKER ABSTRACTS

Code: Plenary

Presenter: Hiroshi MASUHARA (TWN)

Abstract Title: Optical Manipulation in Chemistry

Co-Author(s):

Abstract: Photochemistry and spectroscopy study various dynamics and mechanism of molecules and materials induced by their interaction with light. Optical force is another interaction between light and matter, which was experimentally confirmed by Lebedev in late 19th century. Utilizing this force Ashkin proposed as “Optical Tweezers” in 1986 and demonstrated high potential in application to bio-science, which was awarded Nobel Prize Physics last year. Optical force was also expected to control molecular motion in solution and eventually chemical reaction. In 1988 we started to explore new molecular phenomena characteristic of optical force by combining optical trapping with fluorescence, absorption, electrochemical, and ablation methods. We have studied on microparticles, microdroplets, nanoparticles, polymers, supramolecules, micelles, amino acids and proteins in solution and reported their unique behavior. The remarkable achievement was performed in 2007 when the trapping laser was focused at solution surface. Various amino acids are crystalized, giving one single crystal at the position where trapping laser is focused and at the time when irradiated. This optical manipulation at solution surface is extended to dielectric and gold nanoparticles and to glass/solution interface. The initially trapped polystyrene nanoparticles at the focus form their periodical structure and scatter/propagate the trapping laser, shifting trapping site outside of the focus and forming a single large circle assembly. Due to intense scattering of the laser by gold nanoparticles, their assembly evolves to swarming where the nanoparticles dynamically fluctuating like bees. These dynamics and mechanism are considered as “Optically Evolved Assembling”. In this lecture we will summarize these developments and show high potential of optical manipulation at solution surface and interface in photochemistry and spectroscopy.

Institution: National Chiao Tung University

Code: Plenary

Presenter: Barbara J. Finlayson-Pitts (USA)

Abstract Title: Photochemistry in the Gas and Condensed Phases as Drivers of Environmental Change

Co-Author(s):

Abstract: Most issues involved in recent years in environmental change, including air and water quality, acid deposition, toxic compounds and climate change, are driven by photochemistry either directly or indirectly. In the atmosphere, there are thousands of individual compounds encompassing both the gas and condensed phases, where the latter includes liquids, solids and multiphase mixtures. This complexity presents special challenges in relating sources and chemistry to impacts. However, understanding the fundamental, molecular processes that occur in such systems is essential for developing reliable predictive models that can be used to develop policy and regulatory options. While important problems remain to be explored in the gas phases, much less is know about processes in and on solids (so-called "heterogeneous chemistry"), in liquids and at interfaces between the phases. This talk will explore some current challenges in elucidating mechanisms of heterogeneous and multiphase chemistry that play a role in air quality, toxic compounds and climate change.

Institution: Department of Chemistry, University of California Irvine

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Code: Plenary

Presenter: Helen Fielding (GBR)

Abstract Title: UV photoelectron spectroscopy of biochromophores in the gas-phase and in aqueous solution

Co-Author(s):

Abstract: Photoelectron spectroscopy is an attractive technique for probing the electronic structure and relaxation dynamics of biochromophores in the gas-phase and in solution. However, the interpretation of solution-phase photoelectron spectra is complicated by inhomogeneous broadening and inelastic scattering of photoelectrons causing the measured electron kinetic energies to be lower than their true values. In this presentation, we will discuss how comparing analogous UV photoelectron spectroscopy measurements in the gas-phase and in aqueous solution can help us to unravel the role of an aqueous environment on electronic structure.

Institution: University College London

Code: Plenary

Presenter: Stefan Haacke (FRA)

Abstract Title: Ultrafast photo-isomerisation in microbial retinal proteins and biomimetic molecular switches

Co-Author(s):

Abstract: The ultrafast trans/cis photo-isomerization dynamics and reaction quantum yield of protonated retinal Schiff bases (PRSB) in microbial retinal proteins is known to depend critically on the amino acid composition, but a detailed understanding is still lacking. Through a combined experimental and theoretical investigation of the reaction dynamics of all-trans PSBR in Anabaena Sensory Rhodopsin and its mutants(1-2), we propose that non-adiabatic mixing of the first two excited states (S1 and S2) determine the excited state energy profile (PES), and thus controls the isomerization speed. Since only the reactive S1 has charge transfer character, the reaction dynamics are modulated via the electrostatic properties of the protein environment or by mutation-induced steric effects (3).

Remarkably, the same mechanism is operative for the PRSB-mimicking N-alkylated indanylidene-pyrroline (NAIP) photoswitches in methanol (4). Here, substituting the pyroline moiety with a methyl group introduces a ≈15° twist of the ground state conformation for Z-1. Quantum chemistry calculations show that S1 and S2 are separated, allowing for a barrierless and ballistic isomerization, leading to low-frequency wavepackets in the ground state.

aken together, both model systems provide now a generalized mechanism for ultrafast photo-isomerization, and confirm predictions for rhodopsin, the visual photoreceptor of vertebrates (5).

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Institution: University of Strasbourg & CNRS, IPCMS, F-67034 Strasbourg Cedex

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Code: Plenary

Presenter: Graham Richard Fleming (USA)

Abstract Title: Two Dimensional Electronic Vibrational (2DEV) Spectroscopy A New Method to Observe the Conspiracy of Electrons and Nuclei in Motion

Co-Author(s):

Abstract: Two-dimensional electronic vibrational (2DEV) spectroscopy includes two optical interactions (UV/Vis) and two infrared interactions. Because of the two different sets of transition moments involved, 2DEV spectroscopy is very sensitive to electronic coupling within molecular complexes, can reveal rapid changes in electronic structure during large amplitude motion such as motion to, and through a conical intersection, and explore whether multi-component reactions such as proton-coupled electron transfer are truly concerted. Because the method, associated theory, and methods of analysis are still being developed this talk aims to illustrate both the potential and complexity of 2DEV spectroscopy via examples taken from photosynthetic light harvesting, a conical intersection system, and a proton-coupled electron transfer system (the latter being a collaboration with T. Moore, A. Moore, D. Gust and co-workers) and a strongly vibronically coupled dimer system along with associated theory and modeling.

Institution: University of California at Berkeley, Lawrence Berkeley National Lab, Kavli Energy Nanoscience Institute

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Code: Plenary

Presenter: Michael R Wasielewski (USA)

Abstract Title: Quantum Coherence in Photo-driven Electron Transfer Processes

Co-Author(s):

Abstract: Quantum coherence has been implicated in natural and artificial photosynthesis and is central to the emerging field of quantum information science (QIS). We will present examples from our recent work in both contexts. First, we will discuss photo-driven electron transfer in donor-acceptor (D-A) compounds that link one donor to one or two equivalent acceptors. Sub-picosecond ET from the lowest excited singlet state of the donor to both acceptors is about 2.5 times faster than ET to one acceptor at room temperature, but about 5 times faster at cryogenic temperatures, resulting from ET to a superposition state of the two acceptors with correlated system-bath fluctuations. Second, we will present our recent results on electron spin state teleportation in an ensemble of covalent organic donor-acceptor-stable radical (D-A-R•) molecules. Following preparation of a specific electron spin state on R• in a magnetic field using a microwave pulse, photoexcitation of A results in the formation of an entangled electron spin pair D•+-A•-. The spontaneous ultrafast chemical reaction D•+-A•--R• -> D•+-A-R- constitutes the quantum measurement step necessary to carry out spin state teleportation. Quantum state tomography of the R• and D•+ spin states using pulse electron paramagnetic resonance spectroscopy shows that the spin state of R• is teleported to D•+ with high fidelity. This result affords the possibility that chemical synthesis can create complex nanostructures for QIS applications.

Institution: Northwestern University

Code: Plenary

Presenter: Christy F. Landes (USA)

Abstract Title: Super-Resolved Protein Dynamics at Nanoscale Interfaces

Co-Author(s):

Abstract: Understanding nanoscale protein dynamics at interfaces is crucial for topics ranging from disease inception to drug delivery to separations science. Recent efforts by our group and others have shown the promise of applying single molecule methods to link mechanistic detail about protein adsorptions to macroscale observables. Although the best super-resolution methods achieve high 2D spatial resolution, the temporal resolution remains low. We developed a new phase mask that provides 3D super-localized spatial information while simultaneously improving the temporal resolution of traditional cameras by 20 times. This improvement is achieved by rotating a new stretching phase mask in the Fourier plane during data acquisition and then recovering the temporal information by fitting the PSF orientations. The feasibility of this technique is verified with both simulated and experimental adsorption/desorption and transport. When STReM is applied to measure protein adsorption/desorption at a nanostructured interface, previously unresolvable dynamics are revealed.

Institution: Rice University

Code: Plenary

Presenter: Paul Mulvaney (AUS)

Abstract Title: Surface Plasmon Spectroscopy of Gold Nanocrystals

Co-Author(s):

Abstract:

In this talk, I will discuss the emergence of nanocrystals for applications in optical switching, sensing and signal modulation. These potential applications arise from the unusual nature of surface plasmon resonances (SPRs). Surface plasmon resonance frequencies or wavelengths depend on the electron density of the gas, particle size and shape, and also the medium refractive index.
I will show that we can modulate the particle response by altering the electron density, through hydrostatic loading and by modifying the refractive index of the medium. We also demonstrate how electro-optical effects lead to a method for direct modulation of light, that could be used in high speed signal processing. I will demonstrate detection of 100 electrons using single gold rods as sensors [1-4] and that directed assembly of nanocrystals into arrays opens up single nanocrystal spectroscopic sensing.

[1] T. Kawawaki, H. Zhang, H. Nishi, P. Mulvaney, T. Tatsuma, “Potential-Scanning Localized Plasmon Sensing with Single and Coupled Gold Nanorods,” J. Phys. Chem. Lett. 8, (2017) 3637.
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Acknowledgements: The author acknowledges funding from the ARC through grant CE170100026.

Institution: University of Melbourne

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FUNDAMENTAL PHOTOCHEMISTRY & PHOTOPHYSICS (FUNDPhoto) ABSTRACTS

INVITED TALKS

Code: FUNDPhoto_I1

Presenter: Timothy W. Schmidt (AUS)

Abstract Title: The Role of Excimer Formation in Singlet Fission

Co-Author(s): Shyamal K. K. Prasad, Miroslav Dvorak, Joseph K. Gallaher, Cameron B. Dover, Laszlo Frazer, John E. Anthony

Abstract:

Singlet fission (SF) is a bichromophoric process in which an excited singlet state separates into independent triplet states on separate chromophores. It is presently a subject of intense interest, due to its potential applicability to excitonic solar cells which circumvent the Shockley-Queisser limit by creating more than one excited electron-hole pair for each incoming high-energy photon.

Endothermic SF is desired for maximum energy-conversion efficiency,[1] and such systems have been considered to form an excimer-like state with multiexcitonic character prior to the appearance of triplets. We show, using TIPS-tetracene in solution, that, rather than acting as an intermediate, the excimer serves to trap excited states, to the detriment of SF yield.[2]

Pentacene chromophores exhibit high-efficiency singlet fission approaching 200% quantum yield. The highly soluble TIPS-pentacene was shown to exhibit SF in highly concentrated solutions. It was argued, on the basis of the appearance of steady-state spectra, that excimer formation occurred as part of the SF process.

We revisited the steady-state spectroscopy at high concentrations using an excitation set-up which exploits the shallow penetration-depth of the evanescent wave in total-internal reflection. We show that with such an experimental geometry, there is no evidence for excimer formation, contrary to literature reports.

[1] M. J. Y. Tayebjee, A. A. Gray-Weale and T. W. Schmidt, J. Phys. Chem. Lett. 3, 2749-2754, 2012.
[2] C. B. Dover, ,J. K. Gallaher, L. Frazer, P. C. Tapping, A. J. Petty, M. J. Crossley, J. E. Anthony, T. W. Kee and T. W. Schmidt, Nature Chem. 10, 305-310, 2018.

Institution: UNSW Sydney

Code: FUNDPhoto_I2

Presenter: Dirk M. Guldi (DEU)

Abstract Title: Towards Breaking the Barrier to 100% Charge Transfer

Co-Author(s): N/A

Abstract:

Chemistry affects almost every aspect of our existence, so that it will be an essential component of solutions in global issues in health, materials, and energy. For this reason, the design and synthesis of novel molecular materials lies at the forefront of transformative research and has game-changing character. A leading example for such shifts in existing scientific paradigms is surpassing the Shockley-Queisser limit, which places an upper bound on solar conversion efficiency for a single p-n junction solar cell at slightly more than 30%, by means of singlet fission (SF) in molecular acenes, the molecular analog to multiple exciton generation (MEG). In an optimal SF process, the lowest singlet excited state of one molecule (S1) that is positioned next to a second molecule in its ground state (S0) is down-converted into two triplet excited states (T1) each residing on one of the two adjacent molecules. The two triplet states initially form a correlated pair state 1(T1T1), which then evolves into two separated triplet states (T1 + T1). As such, the energetic requirement for SF is E(S1) ≥ 2 × E(T1). Shifting the focus to intramolecular SF in dilute solutions rather than intermolecular SF in crystalline thin films enabled the following important breakthroughs:

Firstly, we demonstrated that in a series of pentacene dimers, which were linked by a myriad of molecular spacers, SF takes place with quantum yields of up to 200%.

Secondly, we identified all key intermediates in the SF process, including the formation and decay of a quintet state that precedes formation of the pentacene triplet excitons.

Thirdly, we employed those parts of the solar spectrum, in which pentacene dimers lack absorptions, in non-resonant, indirect excitation of the SF materials via two-photon absorptions or intramolecular Förster resonance energy transfer.

Finally, we succeeded in showcasing the use of up to 200% triplet quantum yields by the realization of 130% carrier multiplication in solar cells for pentacene dimers immobilized onto semiconductors.

Institution: University of Erlangen

Code: FUNDPhoto_I3

Presenter: Stephen Bradforth (USA)

Abstract Title: Symmetry Breaking Charge Transfer for Rapid, Long-Lived Charge Separation

Co-Author(s): Mark Thompson, Laura Estergreen, Mike Kellogg, Ali Akil

Abstract: The approach we have taken is to couple strongly absorbing chromophores into orthogonal dimers to drive Symmetry Breaking Charge Transfer (SBCT) and form charge-separated excited states from the initially localized excited (LE) state. A key design criterion for the SBCT studies is that they are capable of chelating to a metal center or being fused into a dimer by linking two dyes at their meso carbons. We have found that for both Zn(dipyrrin)2 and meso bridged BODIPY and DIPYR compounds excitation initially gives an inter-chromophore charge separated state on the ps time scale, and that the charge-separated state lives for 0.5-2 ns.

Both BODIPY and DIPYR dimers involve an intermediate partial charge transfer state where charge density is pushed onto the meso-bridge of the dimer complex as observed in 9,9'-bianthryl. The partial charge transfer state is facilitated by the positive overlap of the LUMO and HOMO orbitals, respectively, at the meso carbons. The HOMO orbital of the BODIPY dimer has a node at the meso carbon, so no such interaction exists, thus the BODIPY dimer is expected to transfer an electron to form the SBCT; for the DIPYR dimers it is the LUMO that has a node and therefore a hole should be transferred to form the SBCT state in this case. Polarized pump-probe measurements are being used investigate the directionality of the electron transfer reactions in the three types of dimer studied here.

Institution: University of Southern California

Code: FUNDPhoto_I4

Presenter: Amanda Morris (USA)

Abstract Title: Spin-Orbit Coupling Induced Energy Transfer in UiO-67 MOFs Doped with Photoactive Transition Metal Complexes

Co-Author(s): Arnab Chakraborty; William Maza

Abstract: Metal-organic frameworks (MOFs) are a diverse class of highly ordered and tunable nanoscale materials that are increasingly employed in several solar energy conversion schemes. Investigation of light-harvesting and energy transfer processes within the three-dimensional framework of such nanoscopic materials results in the efficient design of biomimetic chromophore arrays for artificial photosynthesis. Here we present the synthesis and photophysical investigation of Ru(II), Os(II), and Ir(III) polypyridyl complexes doped into the 3D framework of UiO-67 MOF. MOFs were synthesized by following well established one-pot solvothermal synthetic protocol, and the powders were structurally characterized with the help of X-ray powdered diffraction (PXRD) patterns and scanning electron microscopy (SEM) images. Steady-state and time-resolved spectroscopic techniques aided in exploring the photophysical behavior in MOFs as a function of dopant concentration. The MOFs exhibited unmatched stability under photo-excitation. As an extension of our previously reported study of dipole-dipole energy transfer in RuDCBPY doped UiO-67 MOF, here we further explore the energy transfer process with systematic variation of MOF-incorporated chromophore as a function of spin-orbit coupling. Our recent study reveals a substantial increase of Förster distance (R0 = 88±12Å) in OsDCBPY doped UiO-67 MOF in comparison to our previously reported RuDCBPY doped UiO-67 MOF (R0 = 22±5Å).

Institution: Virginia Tech

Code: FUNDPhoto_I5

Presenter: Julia Weinstein (GBR)

Abstract Title: Towards Directing Photoprocesses with Bond-Specific Infrared Excitation

Co-Author(s): M Delor, P Scattergood, S Archer, T Keane, A Sadler, I Sazanovich, G Farrow, A Auty, D Chekulaev, H Carson, A Meijer, M Towrie

Abstract: One of the challenges in the field of photoinduced charge separation - a fundamental process at the heart of natural and artificial systems powered by the energy of light – is how to control reaction pathways. Nuclear-electronic (vibronic) coupling can offer the means of such control: due to ultrafast timescales of the initial photoprocesses, perturbing vibronic coupling in the course of charge transfer may drastically affect the outcome of photochemical reactions. Experimentally, such perturbation can be achieved by introducing a narrow-band IR pulse after initial population of an excited state to selectively affect vibration(s) that are coupled to electron transfer processes, in the pulse sequence {UVpump-narrowband IRpump - broadband IRprobe }. Yet it has long been perceived that IR-perturbation was unlikely to have any effect on reactions in solution phase, due to ultrafast vibrational relaxation. Recent work on IR-perturbation of photoinduced charge separation in transition metal Donor- Bridge-Acceptor complexes showed that selective excitation of bridge-localised vibrational modes in the excited state can drastically change the yield of the product states, up to 100%.[Science 2014, 1492] Further, it has also been shown that in a "fork-type" system D- B-A-B-D, which have competing, parallel electron transfer pathways differing only by
isotopic labelling of the bridge, 13C vs. 12C, selective IR-excitation of either bridge affects the yield of charge-separation along both 'arms'.[NatChem 2017, 1099] This effect potentially offers the means to direct electron flow along a pre-selected reaction pathway. The suggested mechanisms, and potential applications of the fundamental effects observed will be discussed.

Institution: Department of Chemistry, University of Sheffield, UK

Code: FUNDPhoto_I6

Presenter: Eric Vauthey (CHE)

Abstract Title: Looking at Ion-Pair Dynamics upon Photoinduced Electron Transfer Using Ultrafast Spectroscopy

Co-Author(s): Joseph Beckwith, Alexander Aster, Marius Koch Bernhard Lang

Abstract: Bimolecular photoinduced electron transfer (PET) between two neutral molecules produces radical ions in polar solvents. However, the exact nature of the primary product, tight/loose ion pair, excited ions, or exciplex, remains debated, due to the difficulty to find specific spectroscopic signatures of these species. We will present several of our efforts to answer this longstanding question using various ultrafast spectroscopic techniques. For example, clear spectroscopic signatures of exciplexes could be obtained using time-resolved IR spectroscopy [1]. Similarly, by combining transient electronic absorption with an external magnetic field, we found that the ion pairs remain correlated during several tens of nanosecond even in non viscous solvents.[2] Finally, we will show that the excited-state dynamics of radical ions, measured using pump-pump-probe transient absorption spectroscopy, report on the presence of a nearby counter-ion and, thus, can be used to differentiate paired and free ions.

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(2) S. V. Feskov, M. V. Rogozina, A.I. Ivanov, A. I., A. Aster, M. Koch, E. Vauthey, J. Chem. Phys. 150 (2019), 024501.

Institution: Dpt. of Physical Chemistry, University of Geneva, Switzerland

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Code: FUNDPhoto_I7

Presenter: Dongho Kim (KOR)

Abstract Title: Spectroscopic Diagnosis of Excited-state Aromaticity: Capturing Electronic Structures and Conformations upon Aromaticity Reversal

Co-Author(s): N/A

Abstract: Aromaticity, the special energetic stability derived from cyclic [4n+2]π-conjugation, has been the topic of intense interest in chemistry. Recently, the pioneering work by Colin Baird on aromaticity reversal, postulating that aromatic (antiaromatic) character in the ground state reverses to antiaromatic (aromatic) character in the lowest excited triplet state, has attracted much attention. The completely reversed aromaticity in the excited states provides direct insight into understanding the properties of photoactive materials. However, most studies on excited state aromaticity have been based on the theoretical point of view. The experimental evaluation of excited state aromaticity is still challenging and strenuous because the assessment of aromaticity with conventional magnetic, energetic, and geometric indices is difficult in the excited states.

Time-resolved optical spectroscopies can provide a new and alternative avenue to experimentally evaluate excited state aromaticity. With monitoring ultrafast changes in the excited states, they can provide valuable information for excited state aromaticity. In this regard, recent breakthroughs in experimentally assessing aromaticity reversal in the excited states with time-resolved optical spectroscopic measurements are introduced. To scrutinize this intriguing and challenging scientific issue, expanded porphyrins have been utilized as the ideal testing platform because they exhibit perfect aromatic and antiaromatic congener pairs, having the same molecular framework but with different numbers of π-electrons, which facilitates the study of the pure effect of aromaticity. Time-resolved electronic and vibrational absorption spectroscopies capture the change of electronic structure and molecular conformations driven by the change of aromaticity and provide clear evidence for aromaticity reversal in the excited states.

Institution: Yonsei University

Code: FUNDPhoto_I8

Presenter: Ferdinand C. Grozema (NLD)

Abstract Title: Quantum Interference Effects in Charge Transfer and Single Molecule Conductance

Co-Author(s): Nicolas Renaud, Natalie Gorzcak, Rajeev Dubey

Abstract: In most current designs of single molecule devices, quantum mechanical effects that are operative on the molecular scale, such as wave function interference, are disregarded. In this work we explore ways to use these interference effects in a functional way by a combination of theoretical and experimental methods. This should lead to single- molecule devices with more functionality than is currently achieved.

The current consensus is that destructive quantum interference occurs in cross-conjugated molecules, while linearly conjugated molecules exhibit constructive interference. In a combined experimental and theoretical study of photoinduced charge transfer in donor- bridge-acceptor systems we show that the reality is more complex and the specific design of the donor-bridge acceptor system plays an important role in the trends in charge transfer that are observed. We demonstrate that the specific molecular orbital symmetry of the involved donor and acceptor states leads to interference conditions that are different from those valid in single molecule conduction experiments. The results indicate that by utilizing molecular orbital symmetry in a smart way new opportunities of engineering charge transfer emerge.

In addition, quantum interference effects do not only appear when considering transport through a single conjugated molecule, but are also encountered in pi-stacked systems. In a single-molecule conductance experiment, we have shown the occurrence of clear quantum interference effect in the conductance through a dimer of two conjugated molecules connected between two electrodes. These interference effects can be manipulated by mechanically altering the pi-stacking configuration by moving the electrodes with respect to each other.

Institution: Delft University of Technology

Code: FUNDPhoto_I9

Presenter: Eberhard Riedle (DEU)

Abstract Title: Determination of Reaction Quantum Yields: LED based Setup with Better 5% Accuracy

Co-Author(s): Henrieta Volfova, Qi Hu

Abstract: Chemical actinometers were introduced about hundred years ago to permit photochemists to measure reaction quantum yields with some accuracy. The problem at the time was the lack of availability of stable, easily usable and properly calibrated devices to measure the power of light absorbed within a reaction vessel. This problem has now been solved by the commercial availability of power meters with a large aperture, high sensitivity from mWs to Watts and a calibration to better than 3 % compared to NIST standards. We suggest to therefore replace the chemical actinometry by a combination of controlled illumination from high power LEDs with such an absolute light detector.

In our quantum yield determination setup QYDS we image the LED light with high numerical aperture optics into spectroscopic cuvette, typically 10x10 mm^2. The wide selection of LEDs allows work from 265 nm to over 1000 nm. The power going into the sample can be freely varied between sub-100 µW to well above 1 W. The lower range is used for photochemical work, the higher one for photocatalysis.

We have measured quantum yields for a wide range of substances and photoinitiated processes to validate the new setup and method. The problem that arises is there are no really reliable reference values that can compete with the sub-5 % accuracy found in our experiments. Only the direct estimation of the residual errors in the experiments and the direct comparison to a few available values published recently can establish this margin.

Institution: LMU München, LS für BioMolekulare Optik

Code: FUNDPhoto_I10

Presenter: Hiroshi Miyasaka (JPN)

Abstract Title: Photosynergetic Responses Induced by Multiple Excitation and Multiphoton Absorption

Co-Author(s): Tatsuhiro Nagasaka, Hikaru Sotome

Abstract: Molecules in the electronic excited state take important roles in various photo-functional systems. Three general restrictions, however, limit the efficient utilization of light energies. First, large molecules in higher excited states usually very rapidly relax to lower electronic states (Kasha’s rule) and subsequent vibrational relaxation leads to the thermally equilibrated S1 state in the condensed phase. Second, a large number of the molecules excited in assemblies undergo fast annihilation and only a small number of excited state molecules can remain, leading to the loss of the number of photons absorbed in the system. In addition, the electronic state accessible through the one-photon absorption is limited by the optical selection rule and we cannot access to various dark electronic excited states of molecules. Research outcomes beyond these restrictions have been recently reported by several groups including us in the field of photochemistry. Based on these backgrounds, we have started a new project, “Photosynergetics”, as a research program supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT). In the present talk, we will introduce several topics relating to Photosynergetics project, such as multiple and multiphoton excitation responses in photochromic molecules [1-3].

[1] H. Sotome et al., J. Am. Chem. Soc. 139 (2017) 17159.
[2] H. Sotome et al., J. Phys. Chem. Lett., 8 (2017) 3272.
[3] T. Nagasaka et al., J. Phys. Chem. C, 122 (2018) 24987.

Institution: Graduate School of Engineering Science, Osaka University

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CONTRIBUTED TALKS

Code: FUNDPhoto_T1

Presenter: Jacqueline Cole (GBR)

Abstract Title: Molecular Engineering of Crystalline Nano-optomechanical Transducers

Co-Author(s):

0 **Abstract:**

Abstract
Crystalline materials that behave as optical actuators and proceed via some form of solid-state nano-optomechanical mechanism are of particular interest for optical data storage[1] or quantum computing[2]. Nonetheless, the field is facing a dearth of suitable functional materials for applications. One possible material option is a series of compounds based on the generic formula, [Ru(SO2)(NH3)4X]Y, whose SO2 group manifests solid-state linkage photo-isomerization (X is the trans-ligand to SO2; Y is a counterion). This light-induced phenomenon causes these materials to act as photo-induced molecular switches [3-6] or molecular transducers [7-9] whose nano-optomechanical properties exist in the single-crystal state: a high-quality solid-state medium for single-photon control.

This talk will present the development of this family of materials towards such applications, via a range of advanced in situ 'photo-crystallography' and in-situ imaging experiments that capture the phenomenon in their light-induced state [10-12]. Results are enabling our understanding of the light-induced molecular structure and nano-optomechanical properties of these light-induced solid-state actuators. Establishing this knowledge-base of structure-to-function relationships leads to the ultimate goal of being able to molecularly engineer these materials for a given device application.

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Institution: University of Cambridge, UK

Code: FUNDPhoto_T2

Presenter: Jean-Hubert Olivier (USA)

Abstract Title: Tuning Electronic Properties of Well-Defined Nanoscale Objects by Locking-in π-Conjugated Superstructures

Co-Author(s): Adam Ashcraft, Victor Paulino, Kaixuan Liu

Abstract:

As a product of the dynamic equilibrium between solubilized building blocks and self-assembled structures, supramolecular architectures are fragile compositions where minor changes in temperature, solvent dielectric, and building-block concentration can trigger the dismantlement of superstructures and a concomitant loss of the emergent properties associated with them. Undeniably, developing molecular strategies to covalently polymerize superstructures can provide entirely new nanoscale platforms with which to elucidate structure-function properties that remain elusive by current supramolecular methodologies. We will introduce the design principles to tether 1-dimensional supramolecular polymers built from π-conjugated subunits using molecular lockers that differ in length and structural rigidity. Confirmed by atomic force microscopy and transmission electron microscopy, organic nanomaterials created in this manner are best characterized by a nanowire morphology than span the nano-to-mesoscale dimensions suggesting that conformation of supramolecular 1D assemblies can be captured. We will show that modifying the structure of molecular locks provides new avenues to regulate excitonic coupling between neighboring units by design. Furthermore, investigation of the electronic properties of length-sorted nanowires exploiting spectroelectrochemical measurement methods reveals a non-negligible stabilization of the energy of the conduction band with respect to that of the parent, non-polymerized self-assembly. The presented strategy delivers a new tool to not only capture conformation of supramolecular assemblies but also to enforce the formation of emergent electronic properties not accessible in pristine, non-covalent assemblies.

Institution: University of Miami

FUNDPhoto_T3

Presenter: Nadia Korovina (USA)

Abstract Title: Endothermic Singlet Fission in Perylene Oligomers

Co-Author(s): Justin Johnson

Abstract: Organic chromophores undergoing singlet fission, in which an absorbed photon of visible light yields a pair of triplet excitons, have the potential to enhance the efficiency of solar energy harvesting and may find applications in quantum computing. Endothermic singlet fission is particularly desirable to photovoltaic applications, as this process results in minimal energy losses and results in high energy triplet excitons that could be used to sensitize efficient photovoltaic materials such as silicon or perovskites. To take advantage of this process, it is crucial to thoroughly understand its mechanism and develop design criteria for molecules to undergo this process efficiently. We employed the photochemically stable and highly absorbing perylene chromophores and designed a series of covalently coupled oligomers that provide insights into the role of exciton delocalization, size of the system, and chromophore coupling on the rate and yield of endothermic intramolecular singlet fission.

The excited state dynamics of the oligomers (ranging from dimer to tetramer) in solution and solid state, obtained by transient absorption and time resolved fluorescence spectroscopies will be described. We observed faster rate of singlet fission in longer oligomers compared to dimers, and a substantial increase of the singlet fission rate in thin films of all oligomers. These results suggest that spatial separation of the triplet excitons after singlet fission is a key step that enables endothermic singlet fission. Additionally, varying the electronic coupling between the chromophores within the oligomers provided insight about the rate of intramolecular triplet energy transfer, and its effect on singlet fission.

Institution: NREL

Code: FUNDPhoto_T4

Presenter: Christian Ley (FRA)

Abstract Title: New Insight into Photoinitiator Photochemistry for Free Radical Photopolymerization

Co-Author(s): Julien Christmann, Xavier Allonas,* Christian Ley, Céline Croutxé-Barghorn

Abstract: The conversion of photon into chemical energy, i.e. radicals, is of prime interest for application in free radical photopolymerizatio, a green chemistry without solvent, enabling energy savings, spatio-temporal control of the reaction, etc. Photopolymerization is used many applications, such as graphics arts, coatings, adhesives, microelectronics, automotive, etc.[1] In this presentation, the photochemistry of a type II photinitiating [2] system is studied by transient absorption experiments and results are combined with kinetic modeling of the all polymerization reaction. It reveals the role of the ketyl radicals produced by the abstraction of a hydrogen from an amine by the photoinitiator system. These ketyl radicals are able to react with oxygen, decreasing the extent of oxygen inhibition during the polymerization. Moreover, it is shown by kinetic modeling that the photoproduced ketyl radicals act as a terminating agent of the polymerization reaction [3], reducing the photopolymerization rate. The robustness of the model is finally assessed by modifying the incident light intensity as well as the initial amounts of photoinitiator and amine. The results of this study bring new perspectives in the topic of photopolymerization.

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Code: FUNDPhoto_T5

Presenter: Fengling Song (CHN)

Abstract Title: Harnessing Triplet Energy of Fluorescein Derivatives with Thermally Activated Delayed Fluorescence

Co-Author(s): Zhiwei Liu, Wenlong Chen, Xiaoqing Xiong, Xiaojun Peng

Abstract: Fluorescein is one of the two FDA proved fluorescence dyes to be used in clinic use. Its derivatives have been developed in the last decades as chemosensors and probes for biological related ions and small molecules. In this study, the 4',5' derivation in the parent dye of 2',7'-dichlorofluorescein extend the fluorescence wavelength up to red and near-infrared region where the background signal from biological auto-fluorescence becomes weak. Importantly, these new derivatives were found to have a long-lived triplet excited state and thermally activated delayed fluorescence (TADF). Besides being used in the time-resolved luminescence bioimaging, these TADF fluorescein derivatives has become a kind of particular photosensitizers and showed great potentials in photodynamic therapy and photon upconversion.

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Institution: Dalian University of Technology

Code: FUNDPhoto_T6

Presenter: Ksenija Glusac (USA)

Abstract Title: Light Harvesting by Graphene Quantum Dots

Co-Author(s): Varun Singh

Abstract: The co-assembly of light-harvesting chromophores with efficient fuel-forming electrocatalysts to form organized 3D supramolecular architectures represents a significant challenge in the field of artificial photosynthesis. Our approach toward such photocatalysts involves the utilization of molecular building blocks composed of graphene quantum dots (GQDs) and their catalyst-grafted derivatives. Molecular tunability of such structures is expected to enable the discovery of supramolecular photoelectrodes with exceptional efficiencies. Here, we present a study of exciton size and dynamics in two graphene quantum dot assemblies with different aromatic cores. Using a combination of time-resolved laser spectroscopy and molecular mechanics/DFT calculations, we obtain insights into the aggregation and excited-state behavior of GQDs. Subsequently, we investigate model catalyst-grafted GQDs that contains Co-based electrocatalysts for the hydrogen-evolution reaction. The electrochemical behavior of the Co-center in GQDs is investigated and compared to that of a simple model. The results of our work represent an important step toward light-responsive and electrocatalytic supramolecular assemblies.

Institution: UIC/ANL

Code: FUNDPhoto_T7

Presenter: Guoqiang Yang (CHN)

Abstract Title: A New Mitochondria Responsive and Activatable Red-Emissive photosensitizer for Cancer Cell Photoablation

Co-Author(s): Chenlin Yang, Rui Hu, Xudong Guo

Abstract: A couple of dibenzylideneacetone derivatives have been designed and synthesized. MPS presents environment-sensitive on-off fluorescence and activatable photosensitizing abilities. Under the guidance of pyridinium unit, MPS mainly accumulates on mitochondrial components with bright red emission and silent photoablation. Upon light irradiation, copious ROS are generated from mitochondria which causes MMP loss and cell apoptosis. Then the red emission on mitochondrial components turns off and the ROS generation is ceased due to the MMP disruption induced MPS leakage from mitochondria to cytosol. The integrated functionalities of target-controlled photoablation and self-efficacy traceability offer MPS a new opportunity for visualized and hazard-free cancer PDT with synchronous evaluation of the therapeutic responses.

Institution: Key Laboratory of Photochemistry, Institute of Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences

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Code: FUNDPhoto_T8

Presenter: Bryan Kudisch (USA)

Abstract Title: Magnetoexcitonic Effects on Organic Semiconductors at High Magnetic Fields Probed by Ultrafast Spectroscopy

Co-Author(s): Margherita Maiuri, Luca Moretti, Belen Oviedo, Leon Wang, Robert K. Prud'homme, Stephen A. McGill, Gregory D. Scholes

Abstract: Molecular organic semiconductors are an important subset of the emerging field of organic electronics which serve to both complement and improve upon state-of-the-art inorganic semiconductor technologies. For organic optoelectronic applications, it is paramount that we understand how these organic materials interact with light to the extent to which we can predict, design, and optimize new molecular building blocks to improve device performance. The photophysical properties of these systems, though, are heavily dependent not only on the electronic architecture on the molecular level, but also the degree of electronic coupling between neighboring molecules. This interplay gives rise to the outstanding issue in the comprehension of organic semiconductor photophysics: experiments that attempt to establish cause-effect relationships are undermined because of the inability to selectively perturb electronic structure without affecting intermolecular interactions. Here we show using steady state and ultrafast optical spectroscopies that magnetic fields as high as 25 T explicitly modulate the electronic properties of model phthalocyanine (Pc) aggregates. We deduce that this novel magnetic field effect arises from the interaction between the magnetic field and the orbital angular momentum of the molecular wavefunctions through the generation of coupled ring currents in the Pc π-system, manifesting experimentally as a magnetic field-dependent optical cross-section and intersystem crossing rate in CuPc nanoparticles. Our findings suggest that high magnetic fields can be used as a powerful and general tool for establishing direct cause-effect relationships between the electronic structure and the optoelectronic properties of organic materials.

Institution: Princeton University

Code: FUNDPhoto_T9

Presenter: Leah M. Rader Bowers (USA)

Abstract Title: It’s Good to be Flexible: Energy Transport Facilitated by Conformational Fluctuations in Light-Harvesting Polymers

Co-Author(s): Egle Puodziukynaite, Li Wang, Zachary A. Morseth, Kirk A. Schanze, John R. Reynolds, John M. Papanikolas

Abstract: The mechanism of energy transfer between Ruthenium (II) (Ru) and Osmium (II) (Os) polypyridyl complexes affixed to a polyfluorene backbone (PFRuOs) is investigated using a combination of time-resolved emission spectroscopy and coarse-grained molecular dynamics (CG MD) simulations. Photoexcitation of a Ru chromophore initiates Dexter-style energy hopping along isoenergetic complexes followed by sensitization of a lower energy Os trap. While we can determine the total energy transfer rate within an ensemble of solvated PFRuOs from time-dependent Os emission spectra, heterogeneity of the system and inherent polymer flexibility give rise to highly multiexponential kinetics. To determine how energy transfer is influenced by conformational motion, we developed a two-part computational kinetic model to supplement our spectroscopic results: 1) CG MD model of PFRuOs that simulates molecular motions out to 800 ns and reduces computational time by ~400x compared to all atom MD and 2) Energy transfer kinetic simulations in CG MD PFRuOs that produce time-resolved Ru and Os excited state populations. Good agreement between simulated and experimental emission transients reveals our kinetic model accurately simulates the molecular motion of PFRuOs during energy transfer. Simulated results indicate that pendant flexibility significantly increases transfer efficiency. When pendants on our CG PFRuOs model keep their inherent motions, energy transfer is 80% efficient, while a 62% efficiency is achieved when pendants are treated statically.

Institution: University of North Carolina at Chapel Hill

Code: FUNDPhoto_T10

Presenter: Svenja Neumann (CHE)

Abstract Title: Quantitative Insights into Charge-separated States from One- and Two-pulse Laser Experiments

Co-Author(s): Christoph Kerzig, and Oliver S. Wenger

Abstract: Photosynthesis relies on charge-separated states as key intermediates to perform efficient multi-electron transfer reactions.[1] However, the desired charge accumulations compete with light-induced electron-hole recombinations as main deactivation pathways, which are largely unexplored.[2] Moreover, the factors that govern the formation efficiencies of charge-separated states are still poorly understood.[3] Our study provides a systematic investigation of two donor-sensitizer-acceptor triads[4] capable of storing as much as 2.0 eV in their charge-separated states. The triads have different donor-acceptor distances which enabled us to include distance-dependence investigations. Using quantitative one-pulse laser flash photolysis, we provide deep insights into the charge-separated state formation quantum yields, which can reach up to 80%. Two-pulse laser flash photolysis experiments[5] elucidate the fate of the charge-separated state upon further (secondary) excitation with green photons. One key finding of our study is that thermal and light-induced charge recombinations show opposite behaviors in terms of their distance dependences.[6]

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Code: FUNDPhoto_T11

Presenter: Supattra Panthai (JPN)

Abstract Title: White-Color Luminescence Emitted from Liquid-Crystalline AIEgens

Co-Author(s): Maruoka Yui, Sami H. Alijuzayri, Osama Yousin, Kyohei Hisano, Osamu Tsutsumi

Abstract: Highly luminescent materials are of great interest for use in light-emitting devices. However, the luminescence intensity of most organic molecules is abruptly reduced in concentrated solutions or condensed phases owing to concentration quenching or aggregation-caused quenching. Recently, some types of organic molecules have shown strong photoluminescence in the condensed phase, where the aggregation enhanced the photoluminescence through a phenomenon called an aggregation-induced emission (AIE). The structure of their molecular aggregates, as well as their own molecular structure, must strongly affect the luminescence of AIE materials. We have developed liquid-crystalline (LC) luminophores with the AIE property (AIEgen). Some useful characteristics of LCs that lend themselves to efficient aggregate control include their self-assembled nature, fluidity, and responsivity to external stimuli. Since the aggregated structure of luminophores can be easily manipulated in the LC phase, their luminescence behavior can be controlled.
Herein, we have developed three novel LC AIEgens. We found that all molecules emitted blue- color emission with proper quantum yields in a crystalline phase through AIE. Interestingly, 6T-H displayed pure white-color emission in an LC phase. The results indicated that emission color can be tuned by the aggregated structure of AIEgens, and that pure white-color emission can be obtained from the single compound.

Institution: Department of Applied Chemistry, Graduate School of Life Sciences, Ritsumeikan University, Japan

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Code: FUNDPhoto_T12

Presenter: Sanchita Sengupta (IND)

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Abstract Title: Regioisomeric Dual Emissive BODIPY-BDT Dyads and Triads as Ratiometric Temperature Sensors and Viscosity Sensors.

Abstract: An acceptor-donor-acceptor rotor triad (p-ADA) was synthesized based on BODIPY dye as electron acceptor and Benzodithiophene electron donor decoupled with a para-phenyl spacer. The compound showed dual emission with efficient twisted intramolecular charge transfer (TICT) band at ~ 700 nm with Stokes shift of ~ 194 nm. Prominent fluorescence solvatochromism in solvents of increasing polarity was observed for p-ADA. Efficient aggregate induced emission and a reasonable charge carrier mobility of p-ADA in thin films of ~ 10-4 cm2/Vs was obtained.1 Furthermore, to elucidate structure property relationships, meta regioisomer, m-ADA was synthesized that showed well-defined aggregation in solution evident from absorption and emission studies. On the other hand, the dyad counterparts, p-AD and m-AD showed distinct optical properties whereby the dyad p-AD showed three emissions with TICT band at 660 nm characterized by a Stokes shift of ~ 149 nm and prominent solvatochromism. Notably, all compounds showed temperature tunable and viscosity dependent emission changes. The temperature dependence of emission intensities of p-AD and p-ADA render these molecules useful ratiometric sensors. On the other hand, viscosity dependence of fluorescence is indicative of their potential applications as viscosity sensors for biologically or material science relevant micro-environments. Interestingly, solvent polarity dependent fluorescence of dyad m-AD (in 10/90 v/v THF/water) showed a near white light emission with CIE chromaticity coordinates (x,y) of 0.32,0.28. Such multifunctional rotor molecules with readily tunable emission properties are potential temperature and viscosity sensors for bio(medical) and material applications.

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Institution: Indian Institute of Science Education and Research (IISER) Mohali

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Code: FUNDPhoto_T13

Presenter: Jacek Waluk (POL)

Co-Author(s): -

Abstract Title: Photodestruction of Porphyrinoids

Abstract: Our studies focus on the mechanisms of photodegradation and the methods which could control and improve photostability of various organic chromophores [1-3]. In this work, we investigate photoinduced decomposition of selected porphyrins and their constitutional isomers, porphycenes. Photostability has been compared for the regimes of single molecules and molecular ensembles. Various strategies have been used in order to modify photodecomposition quantum yields: (i) substitution with electron donor or acceptor groups; (ii) lowering the triplet formation efficiency; (iii) introduction of a triplet quenching moiety; (iv) placing a molecule on a plasmonic nanostructure; (v) altering the chromophore environment. Due to the crucial role of oxygen in photodegradation, quantum yields of singlet oxygen generation have been determined for differently substituted porphyrins and porphycenes. The results indicate that several different channels may be responsible for the photodestruction of porphyrinoids.

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Code: FUNDPhoto_T14

Presenter: Aurimas Vysniauskas (LTU)

Co-Author(s): Stepas Toliautas, Jelena Dodonova, Sigitas Tumkevicius

Abstract Title: Improving the Viscosity Sensitivity of BODIPY-based Molecular Rotors

Abstract: Fluorescent viscosity sensors – molecular rotors – provide one of the most convenient ways for measuring viscosity in aerosols, model membranes and living cells [1]. However, despite the increasing usage of molecular rotors, the relation between their molecular structure and sensitivity to viscosity or parameters, such as temperature and solvent polarity is not well examined. We have varied the molecular structure of BODIPY-C10 – one of the most popular molecular rotors – and examined how this impacts the sensitivity of the fluorophore to viscosity, temperature and solvent polarity [2,3]. While the viscosity-sensitive range of BODIPY-C10 is approximately from 5 cP to 1500 cP, a new BODIPY rotor with –NO2 group was viscosity-sensitive up to 50 000 cP, which makes it much more suitable viscosity probe for high viscosity environments than BODIPY-C10. To our knowledge, this is the first hydrophobic fluorophore capable of viscosity sensing in such viscous environments. Furthermore, by using theoretical calculations we have determined the photophysical mechanism of BODIPY molecular rotors, which explains why the inclusion of -NO2 group extends the viscosity-sensitive range and why BODIPY molecular rotors suffer from undesirable dependence on temperature.

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Institution: Center for Physical Sciences and Technology

Code: FUNDPhoto_T15

Presenter: Natalia Kiseleva (DEU)

Abstract Title: Heavy Atom-free Donor/Acceptor Photosensitizers for Efficient Triplet-triplet Annihilation Up-conversion

Co-Author(s): Dmitry Busko, Marius Jakoby, Ian A. Howard, Bryce S. Richards, Mathias O. Senge, Mikhail A. Filatov, Andrey Turshatov

Abstract: Triplet-triplet annihilation up-conversion (TTA-UC) is a photophysical process which has attracted significant interest in recent years. For performing TTA-UC two molecules are needed: a sensitizer – a molecule with very efficient intersystem crossing (ISC) – which absorbs photons and an emitter which emits photons with higher energy. TTA-UC occurs after energy transfer from a triplet state of the sensitizer to a triplet state of the emitter and TTA with two emitter molecules. Nowadays one of the major challenges of TTA-UC is to design heavy atom free photosensitizers with high intersystem crossing. Recently, it was reported that heavy atom free anthracene-BODIPY-dyad (ABD) shows the photoinduced electron transfer(1) that allows ABD to play a role of the sensitizer in TTA-UC(2). Here we present photophysical investigation of novel BODIPY-dyads with high ISC. These dyads act as the sensitizer demonstrating efficient green-to-blue UC. We characterized TTA-UC via measuring absolute photoluminescence quantum yield (PLQY), time resolved UC luminescence, and transient absorption. On the whole, the results demonstrate dependency of TTA-UC on the electron donor part of the dyad (naphthalene, anthracene, pyrene, perylene) and the structure of the electron acceptor part (BODIPY).

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Code: FUNDPhoto_T16

Presenter: Abbey Meprathu Philip (NLD)

Abstract Title: Decoding the Curious Tale of Atypical Intersystem Crossing Dynamics in Regioisomeric Acetylanthracenes

Co-Author(s): Abbey M. Philip, Mahesh Gudem, Ebin Sebastian and Mahesh Hariharan*

Abstract: Mapping the primary photochemical dynamics and transient intermediates in functional chromophores is vital for crafting archetypal light-harvesting materials.1,2 Although the excited state dynamics in 9-acetylanthracene is well explored, the origin of near-quantitative triplet population and the atypical intersystem crossing (ISC) rate as compared with the regioisomeric analogs (1-/2-acetylanthracene) have rarely been scrutinized.3 We present a comprehensive account of the photoinduced dynamics in three regioisomeric monoacetylanthracenes using ultrafast transient absorption and quantum chemical calculations.4 The conjoint experimental and computational investigations suggest that (i) greater stabilization of the 1nπ* relative to 1ππ* state, (ii) dissimilar 1ππ* → 1nπ* crossover barriers, and (iii) the strong spin−orbit coupling (vSO) of the 1nπ* state with the receiver 3ππ* state command the divergent triplet population in 1-/2-/9-acetylanthracenes.4 A tacit understanding of the subtle structural-alteration-facilitated contrasting ISC dynamics in carbonylated arenes can help design novel organic photofunctional materials.

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Institution:
OM, Chemical Engineering
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Code: FUNDPhoto_T17

Presenter: Clémence Allain (FRA)

Abstract Title: Mechano-responsive Fluorescent Materials: Studies from the Macroscale to the Nanoscale

Co-Author(s): Luca Polacchi, Marine Louis, Jan Patrick Dela Cruz Calupitan, Cristian Pinero-Garcia, Arnaud Brosseau, Rémi Métivier

Abstract: Fluorescent materials can be used to detect a wide range of stimuli with excellent sensitivity. In particular, a mechano-responsive fluorescent material is sensitive to mechanical forces (compression, shear, etc.). This type of material, whether molecular or polymeric, is attracting increasing attention and various mechano-responsive fluorescent compounds have been prepared. [1] However, studies of this phenomenon at the nanoscale remain very limited.

We are interested in different families of molecular materials, which give different responses under mechanical stimulus. Thus, we synthesized a series of boron difluoride complexes with diketonate ligands, [2] and polydiacetylenes functionalized with tetrazines. [3] The photophysical properties of these molecular materials, in the form of thin films and nanoparticles, before and after mechanical stress, will be presented. Their specific behavior at the nanoscale, studied by AFM coupled with fluorescence microscopy, will be discussed.

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Code: FUNDPhoto_T18

Presenter: Melissa K. Gish (USA)

Abstract Title: Balancing Competitive Pathways in Singlet Fission Dye-Sensitized Solar Cells using Self-Assembled Acene Multilayers

Co-Author(s): Justin Johnson

Abstract: Singlet fission dye-sensitized solar cells (SF-DSSCs) combine the excitonic multiplication properties of visible light-absorbing SF molecules with semiconducting metal oxide nanoparticles to potentially double the low efficiencies of conventional DSSCs. In an ideal SF-DSSC, light absorption by the SF chromophore (e.g. functionalized acenes) creates a singlet exciton that undergoes SF to produce two low energy triplet excitons followed by triplet injection into the conduction band of a wide-band gap semiconductor (e.g. TiO2), thereby producing two charges per one photon. Realistically, competitive and parallel processes including rapid singlet injection preclude triplet formation on the surface. Constructing self-assembled multilayers on the metal oxide surface may circumvent some competition by increasing distance between chromophores and the interface, and open up a pathway towards triplet formation via singlet fission. Using ultrafast transient absorption spectroscopy, we studied the photophysics of an SF-DSSC consisting of an anthradithiophene derivative functionalized with two carboxylic acid binding groups, one of which attaches to the metal oxide. A Zn2+ ion coordinated to the unbound carboxylic acid facilitates binding of additional chromophore layers. Differences monolayer and bilayer dynamics uncover important design principles to consider when constructing a functional SF-DSSC.

Institution: National Renewable Energy Laboratory

Code: FUNDPhoto_T19

Presenter: Yoichi Kobayashi (JPN)

Abstract Title: Stepwise Two-Photon-Induced Photochromic Reactions via Higher Triplet Excited States of Rhodamine Derivatives

Co-Author(s): Tsuji Kanna, Katsuya Mutoh, Jiro Abe

Abstract: Stepwise two-photon absorption processes, which is defined as an absorption of another photon from a photogenerated transient state, have been received particular attention these days because of their low power thresholds and drastic enhancements of photochemical reaction yields in some systems (Kobayashi et al. J. Phys. Chem. Lett. (Perspective), 2016, 7, 3666-3675., and J. Photochem. Photobiol. C (Review), 2018, 34, 2-28.). However, these reactions were reported only in specific molecules such as diarylethene, fulgide, bridged-imidazole dimer, and these systems still require high power pulse lasers to induce the nonlinear processes.

In this study, we developed a novel stepwise two-photon-induced photochromic materials based on rhodamine framework. This molecule gives the blue emission upon irradiation of continuous wave UV light (365 nm, 500 mW cm−2) and no photochromic reaction proceeds even prolonged irradiation for 20 sec. On the other hand, the photochromic reaction quickly proceeds upon irradiation of a nanosecond pulse laser (3.3 mJ pulse-1). The excitation power to induce the nonlinear reaction (< 1 MW cm−2) is much smaller than those of conventional two-photon absorption systems. The low power threshold enables to induce the reaction by a CW laser under microscope. Wide ranges of time-resolved spectroscopies revealed that this nonlinear photochromic reaction proceeds via a higher triple excited states produced by the stepwise two-photon absorption process.

Institution: Ritsumeikan University

Code: FUNDPhoto_T20

Presenter: Aurelie Perrier (FRA)

Abstract Title: Aggregation-Induced Emission: A Challenge for Computational Chemistry

Co-Author(s): Laura LE BRAS, Laure DE THIEULLOY, Stéphane ALOISE, Claire LEMARCHAND, Nicolas PINEAU, Carlo ADAMO

Abstract: In the last decade, the aggregation-induced emission (AIE) and crystallization-induced emission (CIE) photophysical phenomena were observed in a series of non-emissive luminogens. Contrary to the "classical" behaviour of organic fluorophores, these molecules emit weakly or moderately in dilute solutions but become very efficiently emissive when aggregated in concentrated solutions or in crystal. The understanding and optimization of the luminescent properties of AIEgen molecules and materials is now crucial, with challenging applications in high-tech innovative devices such as light-emitting diode (OLED) or luminescent solar concentrators (LSC). To incorporate these fluorophores into such opto-electronic devices, luminescent molecules should be dispersed into thin films or polymer matrix. Controlling and optimizing the AIE phenomenon in these different environments thus represents a real challenge and computational chemistry along with molecular modelling methods (from TD-DFT to Molecular Dynamics) is appropriate for the investigation of such phenomena. We propose here a full study of the emission properties of a triphenylamine-substituted fluorophore [(Z)-4-benzylidene-2-methyloxazol-5(4H)-one] (TPABMO, J. Mater. Chem. C, 2017, 5, 7191), in solution, crystal, aggregated phase and within a polybutadiene matrix. This molecule exhibits different behaviors depending of the considered environment, both the color and the efficiency of this emission process depending on the environment. We will show that an appropriate modeling of the environmental effects is crucial to predict the behavior of AIE/CIE candidates and to pave the way towards the development of novel CIE functional materials.
References: Phys. Chem. Chem. Phys, 2019,21, 46 ; J. Phys. Chem. C, 2017, 121, 45, 25603

Institution: Institute of Chemistry for Life and Health Sciences (i-CLeHS) , FRE 2027 (CNRS / Chimie Paris Tech) - Universite Paris Diderot

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Code: FUNDPhoto_T21

Presenter: Philipp Wilhelm (DEU)

Abstract Title: Optical Properties of Curved Chromophores

Co-Author(s): Jan Vogelsang, Nina Schönfelder, Sigurd Höger, John M. Lupton

Abstract: In π-conjugated polymers a strong connection between morphology and function exists. Not only the arrangement of the chromophores influences the optical characteristics, but rather the morphology of the single chromophore itself can change the overall properties. Barford et al. showed theoretically [1] that bending of a chromophore on the one hand reduces the oscillator strength of transitions. On the other hand, vibrational transitions can also gain oscillator strength via the Renner-Herzberg-Teller (RHT) effect. In this case, light emission arising from the vibrational transitions is, in contrast to the electronic 0-0 transition, not perfectly linearly polarized anymore. Therefore, one should be able to demonstrate the RHT effect experimentally by looking at the polarization characteristics. To avoid ensemble averaging, we employ single-molecule spectroscopy. Unfortunately, the chromophore number of a π-conjugated polymer is too large to carry out meaningful experiments, since interchromophoric energy transfer will influence the emission polarization. However, looking at oligomers, which consist only of few chromophores, is challenging, because the bending arising in these systems is minor. We therefore introduce polygonic model systems [2], which all consist of a certain number of the same chromophoric unit. If we reduce this number, the degree of bending increases, which makes the investigated molecules ideal candidates to study the impact of chromophore bending and verify the RHT effect experimentally [3].

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Institution: University of Regensburg

Code: FUNDPhoto_T22

Presenter: Steven M. Sartor (USA)

Abstract Title: Charge-Transfer Mediated Intersystem Crossing in Highly Reducing Organic Photoredox Catalysts

Co-Author(s): Yisrael M. Lattke, Blaine G. McCarthy, Ryan M. Pearson, Garret M. Miyake, Niels H. Damrauer

Abstract: In the design of new organic photoredox catalysts (PCs), access to long-lived triplet excited states via intersystem crossing (ISC) is key for ensuring efficient excited-state intermolecular electron transfer in homogeneous catalytic systems. However, for organic PCs, promoting efficient ISC can be challenging. This is particularly the case for highly reducing PCs, since typical methods of promoting ISC, such as the addition of carbonyls or heavy halogens, present stability and reactivity issues. In this presentation, I will demonstrate how time-resolved visible spectroscopic techniques can inform design principles for maximizing ISC in such systems. In particular, I will discuss a design exploiting orthogonal π-systems and an intermediate-energy charge-transfer excited state, consisting of a phenoxazine donor and a naphthyl acceptor, which greatly improves the yield of ISC in a highly reducing, visible-light-absorbing PC.[1] The impacts of altering the naphthyl connectivity on photophysical dynamics relevant to ISC will also be explored.[2] Spectroscopic investigation reveals that these effects, ranging from subtle to dramatic, originate in the change of donor-acceptor distance upon altering the connectivity of the naphthyl substituent.

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Institution: University of Colorado Boulder

Code: FUNDPhoto_T23

Presenter: Trevor A. Smith (AUS)

Abstract Title: Steady-State and Time-Resolved Spectroscopic Studies of Tetrapyrrole-Based Compounds

Co-Author(s): Yee X. Wong, Christopher R. Hall, Andrew J. Tilley, Wallace W.H. Wong, A. Anda and Jared H. Cole

Abstract: Bilirubin is an archetypal member of the open chain bichromophoric tetrapyrrole class of compounds, that acts as a molecular exciton, as observed in its UV-visible and circular dichroism spectra.[1,2] The structure of bilirubin consists of two nearly identical dipyrrinone subunits, bridged by a methylene group that allows flexible rotation, which in turn facilitates extensive hydrogen bonding that influences the structure and properties of bilirubin. Despite its importance in a biological context, surprisingly few ultrafast laser spectroscopy studies have been performed on bilirubin,[3,4] perhaps due to its weak emission and solvent dependent photophysics. We have synthesised analogues of bilirubin, with and without extended conjugation between the two dipyrrinone groups, that permit the excitonic coupling between the two halves to be investigated and provide control over the hydrogen bonding. In this paper we will present results of steady-state absorption and emission spectral measurements and femtosecond transient absorption spectroscopy to investigate hydrogen bonding and excitonic coupling within bilirubin and the synthetic derivatives, compared with the equivalent dipyrrinone model molecule. These measurements are supported by energy and excitonic modelling calculations.

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Institution: ARC Centre of Excellence in Exciton Science, School of Chemistry, The University of Melbourne

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Code: FUNDPhoto_T24

Presenter: Alexandre Fuerstenberg (CHE)

Abstract Title: Mechanism of Universal Fluorescence Quenching by Water: Towards Counting Solvent Molecules with Organic Fluorophores

Co-Author(s): Kathrin Klehs, Jimmy Maillard, Christopher A. Rumble, Amalia Poblador Bahamonde, Mike Heilemann

Abstract: The understanding of biological processes has largely benefited from the development of fluorescence spectroscopy and imaging. Extrinsic fluorescent probes are typically selectively attached to a biomolecule of interest in order to enable its detection. In this context, the ideal fluorophore should usually absorb light efficiently and display a high fluorescence quantum yield. When it comes to the choice of the fluorophore, it is however often overlooked that water, which is ubiquitous in biological environments, is a well-known quencher of the fluorescence of many organic and inorganic emitters. Frequently, the emission is restored in aprotic and deuterated solvents and we have previously shown that single-molecule based super-resolution imaging significantly benefits from replacing H2O by D2O.

Whereas the mechanism leading to fluorescence quenching by water has been discussed in detail for inorganic ions in coordination complexes in which water is bound as ligand, its exact nature remains elusive for organic fluorophores surrounded by water as the (loose) solvent. In this contribution, we systematically explore the quenching of 40 organic fluorophores by water and other solvents. We observe that quenching by the solvent is stronger for red-emitting fluorophores and depends on the spectral overlap between fluorophore emission and overtones of solvent O-H vibrational stretching modes. We further relate the quenching efficiency to the number of water molecules in the first fluorophore coordination sphere and show that this strategy can be used to quantify the amount of water in the direct environment of the fluorophore, for example when it is bound to a protein.

Institution: Department of Inorganic and Analytical Chemistry, University of Geneva

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Code: FUNDPhoto_T25

Presenter: Shun-Fa WANG (TWN)

Abstract Title: Arbitrary Control of Aggregation-Induced Emission Enhancement of a Tetraphenylethene Derivative by Optical Trapping

Co-Author(s): Jhao-Rong Lin, Fumitaka Ishiwari, Takanori Fukushima, Hiroshi Masuhara, Teruki Sugiyama

Abstract: We have reported unusual optical trapping-induced phenomena such as outwardly-expanded assembling of nano-colloids and molecular crystallization of amino acids. Systematic investigation on dynamics and mechanism of these trapping behaviors is indispensable, and here we present a new phenomenon of aggregation-induced emission enhancement (AIEE). One tetraphenylethene derivative molecule is optically trapped with a continuous-wave 1064 nm-laser and we have succeeded in demonstrating arbitrary control of its fluorescence emission by changing laser power.

Initially a single sub-micrometer-sized aggregate was confined by optical trapping for a couple of minutes, when its fluorescence was hardly detectable. The continuous irradiation into the trapped aggregate led to its rapid growth with a mature size of around 3-4 micrometers, and the resultant aggregate showed bright yellow fluorescence. Also we measured the fluorescence spectra during the aggregation using a confocal system and found that its intensity was drastically enhanced during the growth. Amazingly, the fluorescence emission intensity at the peak wavelength was arbitrarily changeable in a repetitive manner by alternating the laser power, whereas the aggregate size was almost kept. This result clearly indicates that optical trapping changes the aggregate structure, probably overcoming the electrostatic repulsion between the protonated molecules. The dynamics and mechanism in optical trapping-induced aggregation will be discussed from the viewpoint of AIEE.

Institution: Department of Applied Chemistry, National Chiao Tung University

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Code: FUNDPhoto_T26

Presenter: Teruki Sugiyama (TWN)

Abstract Title: Optical Trapping-induced Crystallization and Polymorphism Toward Chirality Chemistry

Co-Author(s): No

Abstract: We present optical trapping-induced crystallization and polymorphism of amino acids, cyclodextrins, and inorganic compounds toward chiral chemistry [1-3]. When an intense, continuous-wave laser is focused at an air/solution interface of their solutions, the local solute concentration at the laser focus is increased by optical trapping, eventually leading to crystallization. Optical trapping also controls the arrangement of their molecules/clusters at the laser focus, by which their polymorphs are determined. We also confirmed that the crystallization is triggered even from their unsaturated solutions when polymorphism becomes strongly dependent on laser polarization. From some experiments, localized surface plasmon resonance (LSPR) of metal particles is utilized to trigger crystallization. LSPR produces a strong electromagnetic field with a steep gradient, especially in the nano-scaled gap between the particles, which can manipulate nano-scaled substances beyond the diffraction limit (plasmonic optical trapping). Optical trapping with a circularly-polarized light produces chiral reaction fields, where chirality in asymmetric photoreaction and chiral crystallization is demonstrated.

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Institution: National Chiao Tung University and Nara Institute of Science and Technology

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Code: FUNDPhoto_T27

Presenter: Naoto Tamai (JPN)

Abstract Title: Intramolecular Singlet Fission in Acene Dimers and Trimers: Rate Difference Exists?

Co-Author(s): Li Wang, Sunna Jung, Tetsuro Katayama, Kenji Kamada, Toshiyuki Hamura

Abstract: Intramolecular singlet fission (iSF) is an efficient strategy of multiexciton generation for their applications of solar cells via one singlet exciton splitting into a correlated triplet pair in one organic molecule. Tetracene (Tc) and pentacene (Pc) dimers and polymers have been reported to be high quantum yields of iSFs.1) However, there is no report on iSF of triangle acene derivatives in which one more available triplet site adjacent to the requisite two chromophores.

Steady-state absorption spectra of Tc and Pc monomers, dimers, and trimers represented similar spectra with several-nm red-shift in the oligomers, which indicates a negligible electronic coupling between the acene chromophores. Fluorescence quantum yields of Tc and Pc dimers and trimers were significantly reduced as compared with their counterpart monomers. In both Pc and Tc derivatives, the fluorescence dynamics showed ~6 ps decay components as compared with their long-lifetime monomers. Transient absorption (TA) spectra of Pc trimers represent fast relaxations at absorption peaks of 463 and 1400 nm with rising signals at 518 and 971 nm, which correspond to the relaxation of singlet state and the formation of triplet pair. The formation and annihilation of the triplet pair in the trimers were almost the same to those in the dimers, which might be induced by similar rates of exciton delocalization through the same bridge before iSF process. The available iSF sites, that is the chromophore numbers, give less influence on the reaction rates. Moreover, solvent effects on iSF in Tc derivatives were examined. With increasing of solvent polarity from 0.1 (hexane) to 4.6 (benzonitrile), rate of iSF in Tc trimers reduced from (5.7 ps)-1 to (3.0 ps)-1. Our results proved that the intermediate processes limit the reaction rates of iSF in both Tc and Pc derivatives.

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Institution: Department of Chemistry, Kwansei Gakuin University

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Code: FUNDPhoto_T28

Presenter: Anita C. Jones (GBR)

Abstract Title: Pulse-shaped Two-photon Excitation of Fluorescent Base Analogues for Single-molecule Spectroscopy of DNA

Co-Author(s): Rachel S. Fisher, David Nobis, L. Marcus Wilhelmsson, Yitzhak Tor, Steven W. Magennis

Abstract: Fluorescence spectroscopy and imaging are powerful techniques for studying the structure, dynamics and interactions of DNA. As the naturally occurring nucleic acids are virtually non-emissive, an extrinsic fluorophore is required. The most common approach is to covalently attach external dyes, but these are generally insensitive to local base interactions. An alternative is the use of a fluorescent base analogue (FBA) to replace one of the natural nucleobases, maintaining hydrogen bonding and leaving the overall conformation of the duplex unaffected. Numerous FBAs have been developed, notably 2-aminopurine (2AP), the archetypal analogue of adenine. Although ensemble measurements using 2AP have provided a wealth of information on DNA conformation and DNA-enzyme interactions [1], single-molecule spectroscopy could provide unprecedented insight into the mechanistic detail of DNA modification, at the individual base level. However, FBAs that are currently available are not suitable for single-molecule measurements, due to their short excitation and emission wavelengths (often in the UV), and their tendency to photobleach. Recently we have been exploring the possibility of using 2-photon excitation, in the 800-nm region, to overcome these difficulties [2, 3]. We will report our progress towards achieving single-molecule detection sensitivity, using pulse-shaped two-photon excitation of new FBAs with unprecedentedly high 2-photon brightness.

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Institution: The University of Edinburgh

Code: FUNDPhoto_T29

Presenter: Chavdar Slavov (DEU)

Abstract Title: Thiophenylazobenzene vs. Azobenzene – Beyond the Hula-twist Isomerization Mechanisms

Co-Author(s): Chong Yang, Andreas H. Heindl, Hermann A. Wegner, Andreas Dreuw, Josef Wachtveitl

Abstract: Azobenzenes are photochromic compounds that undergo reversible E ↔ Z photoisomerization which results in substantial geometrical and spectral changes.[1] This makes azobenzenes a favored group of photoswitches for control of molecular structures and reactions. The ultrafast dynamics of azobenzene is well characterized. The photoisomerization proceeds from the first excited state (ES) via an inversion-assisted rotation mechanism.[1]
Recently, azoheteroarenes have been investigated as an alternative to azobenzene photoswitches.[2] Azopyrroles and azopyrazoles show high isomerization quantum yields and photoconversion levels and have largely tunable thermal relaxation rates. Furthermore, their (Z)-isomers adopt unusual orthogonal or twisted conformations due to non-covalent intramolecular interactions. These strongly altered properties of azoheteroarenes, as compared to azobenzene, raise the question of what mechanism guides their photoisomerization reaction.
In this respect, we combined ultrafast spectroscopy and quantum chemical calculations to investigate the E ⇄ Z photoisomerization dynamics of thiophenylazobenzene, a novel azoheteroarene photoswitch. Thiophenylazobenzene shows impressive photoisomerization quantum yields and fatigue resistance. Moreover, the two isomers can be nearly completely interconverted. The ultrafast dynamics of thiophenylazobenzene resembles that of azobenzene. However, the ES relaxation of the (Z)-isomer shows a strong spectral shift dynamics indicative of significant conformational changes. Our quantum chemical calculations reveal the conformations adopted by the two isomers in the ground state. Furthermore, unconstrained optimizations delivered striking details on the isomerization pathway, which for the (Z)-isomer differs significantly from that in azobenzenes.

Funding: DFG (WA 1850/4-2, WE 5601/6-1)
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Institution: Institute of Physical and Theoretical Chemistry, Goethe University, Frankfurt, Germany

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Code: FUNDPhoto_T30

Presenter: Maxim Ivanov (USA)

Abstract Title: Towards a Rational Design of Molecules for Quantum Information Science: Insights from Equation-of-Motion Coupled-Cluster Theory

Co-Author(s): Anna Krylov

Abstract: An ability to laser-cool polyatomic molecules to sub-millikelvin temperatures could open new research avenues in quantum information science (QIS), cold chemistry, precision measurements, etc. A crucial requirement for a molecule to reach such low temperatures via laser cooling is the ability to undergo multiple absorption and emission cycles without dissipation of energy over multiple degrees of freedom. This requirement imposes tight restrictions on the Franck-Condon factors for the transition involved in optical cycling, thus only a specific set of molecules can be considered as candidates for various QIS applications. Here, we use equation-of-motion coupled-cluster (EOM-CC) methods, which enable robust and accurate treatment of the electronically excited and open-shell systems, to screen a pool of promising candidates for their potential application in QIS. We perform calculations on a series of molecules based on the alkali earth metal derivatives with the general chemical formula MR, where M = Ca, Sr, Ba and R is a substituent with varied electron-withdrawing strength, starting from R = H and up to superhalogen BO2, which has the largest known electron affinity. To quantify the extent of electronic excitation, we perform wave-function analysis based on the reduced quantities, such as one-particle reduced transition density matrix and Dyson orbitals. By combining the data from high-level electronic structure calculations with the model based on the effective Hamiltonian, we explain the observed trends in the optical properties of MR molecules and pave the way towards a rational design of novel candidates for QIS applications.

Institution: University of Southern California

Code: FUNDPhoto_T31

Presenter: Alberto Mezzetti (FRA)

Abstract Title: Solvent Effects on Fluorescence and Photochemistry of Flavonols. A Combined Spectroscopic and Computational Study

Co-Author(s): Stefano Protti, Ari P. Seitsonen, Daniele Loco, Benedetta Mennucci

Abstract: Flavonols are naturally-occurring molecules with a fluorescence spectrum very sensitive to the surrounding environment. This behavior relies mainly on an excited-state intramolecular proton transfer (ESIPT) producing a green fluorescent tautomeric form. When ESIPT is partially or totally hampered, fluorescence from the normal state occur. Ground-state deprotonation of OH groups also strongly modify fluorescent properties [1,2].

Several synthetic flavonols have been developed and are used as environment-sensitive fluorophors [1]. Similarly, natural flavonols are used as endogenous fluorophors in biochemistry[1] .

We have investigated by UV-Vis, fluorescence, flash photolysis and Raman spectroscopy the excited-state and ground-state proton transfer in 3-hydroxyflavone and quercetin[2,3]. Spectroscopic data obtained in several solvents were interpreted through TD-DFT [4] and Car-Parrinello molecular dynamics [5,6]. We stidied also the solvent effect on the photochemistry of flavonols [7].

For quercetin, deprotonation of OH group(s) was found to be the key parameter in transforming a weakly fluorescent neutral molecule to strongly emitting anionic species[3].

Other flavonoids like luteolin have been studied [8].

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Institution: Sorbonne Université

Code: FUNDPhoto_T32

Presenter: Anuradha Das (CHE)

Abstract Title: Probing Excited State Dynamics of Charge Transfer Reactions in Ionic Deep Eutectic Solvents

Co-Author(s): Egmont J. Rohwer, Hans- Martin Frey, Ping Zhou, Shi-Xia Liu, Thomas Feurer

Abstract: An interesting puzzle of Nature is how plants in extreme condition (droughts/frozen zones) sustain chemical/physiological reactions. Recent developments show, plants contain solvents composed of sugars, ions, amides and water, similar to deep eutectic solvents (DES) (Plant Physiology 2011,156, 1701). DES are formed by mixing multiple room temperature solids at appropriate ratio to get a liquid at temperature, lower than their individual melting points. The main driving force of bringing the constituents to liquid state is extensive interspecies H-bonding. Experiments and simulations have indicated, these systems have microdomains which are spatially and temporally heterogeneous.

To understand how heterogeneous dynamics of DES affect simple chemical reactions (to be extended to biochemical reactions), we have carried out the first pump-probe investigation of excited state dynamics of a series of charge transfer molecules, changing their size/complexity, in DES and compared to conventional solvents. The line shapes of steady state and transient absorption spectrum for the electron transfer reaction of DMABN [4-(Dimethylamino)benzonitrile] (J. Phys. Chem. A 2001, 105, 5768) in acetonitrile resembles DES, but the dynamics differs. However, for MV2+/methyl viologen (1,1’-dimethyl-4,4’-bipyridinium)(J. Phys. Chem. A 2006, 110, 2955) and APM [4,4’-azobis(pyridinium) methylsulfate], both, spectral shape and excited state dynamics in DES vary from conventional solvents. The significant retardation in reaction dynamics of these molecules under the influence of DES, may provide a pathway to analyse the molecular basis behind the alteration of courses of biochemical reactions in extreme nature.

Institution: Institute of Applied Physics, University of Bern

Code: FUNDPhoto_T33

Presenter: Vanessa Huxter (USA)

Abstract Title: Ultrafast Dynamics of Novel Tripyrrolic Molecular Systems

Co-Author(s): Byungmoon Cho, Alicia Swain

Abstract: Using ultrafast nonlinear spectroscopy, we have studied the dynamics of a novel series of tripyrrindione molecules. These molecules are related to linear or macrocyclic oligopyrroles, such as tetrapyrrolic porphyrins as well as bilins, chlorophylls and bacteriochlorophylls. Tripyrroles are uncommon in nature, however, they possess many of the desirable properties of tetrapyrroles while also being attractive platforms for redox chemistry. These systems have optical and material properties that make them of interest for the development of new redox-active materials, for catalytic applications and as optical sensors. Our ultrafast experiments have shown that the optical properties and ultrafast dynamics of the tripyrrindiones studied here are tuned by hydrogen-bonding interactions between the solute and the solvent. In solvents with low hydrogen-bonding affinity, these molecules preferentially form hydrogen-bonded dimers, whereas in solvents that can either donate or accept hydrogen bonds the molecules are present as monomers. The distinction between dimer and monomer determines the dynamics of the system, with faster internal conversion observed in the dimer form, providing a reversible pathway for tuning the excited state dynamics of the system.

Institution: University of Arizona

Code: FUNDPhoto_T34

Presenter: Roland Wilcken (DEU)

Abstract Title: Full Photophysical Characterization of the Hemithioindigo Motor Rotation Mechanism

Co-Author(s): Monika Schildhauer, Ludwig Huber, Manuel Guentner, Florian Ross, Regina de Vivie-Riedle, Henry Dube, Eberhard Riedle

Abstract: Light-powered molecular motors convert photon energy into unidirectional mechanical motion on the molecular scale and are essential building blocks for artificial molecular machines. Recently hemithioindigo (HTI)-based motors became available performing a full rotation in four steps via two photoisomerizations followed each by an irreversible thermal ratcheting step.

To elucidate the inner workings of these motors UV/Vis transient absorption spectroscopy was applied covering 11 orders of magnitude in time from fs to ms. This allowed directly following a complete rotation cycle under the exact same experimental conditions. On the fs/ps timescale the photoisomerization dynamics were observed and photoisomerization quantum yields could be retrieved by thorough spectral analysis. High level quantum chemical calculations improved understanding of the excited state mechanism and confirmed a spectroscopically identified yet unproductive triplet state. Both thermally labile intermediates were observed on the ns to ms timescale. Their thermal helix inversions were proven to be fully quantitative.

Three motor molecules with different substitutions were compared regarding their excited and ground state properties. The motor rotation efficiency was studied under realistic experimental conditions using a kinetic model. For one of the motor derivatives quantitative in-situ NMR measurements at low temperature were performed with an LED-based illumination setup. This experiment allowed studying the hitherto unknown effects of photoexciting the thermally unstable intermediates completing the mechanistic analysis of HTI-based molecular motors.

With this quantitative analysis new generations of motor molecules can now consciously be designed and improved.

Institution: LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München, Oettingenstr. 67, D-80538 München, Germany

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POSTERS

Code: FUNDPhoto_P1

Presenter: Daniel E. Cotton (USA)

Abstract Title: The Interfacial Density of States in Perylene Diimide Thin Films

Co-Author(s): Aaron P. Moon, Jon A. Bender, Sean T. Roberts

Abstract: Perylene diimide (PDI) dyes are known for their pronounced crystallochromism, photophysical stability, tunability, and propensity for singlet fission. Recently, our group has studied how to control PDI's singlet fission kinetics by controlling PDI intermolecular couplings to optimize their use for multi-exciton generation photovoltaics. Not only do these couplings dictate singlet fission rates, but also the resulting triplet propagation through the film. However, the substrate-PDI interface presents a different environment than the bulk film, which provides the possibility of differing transport properties and band structure. Thus, to create a functional hybrid device, the PDI-substrate interface must be tuned to preferentially enhance triplet transfer. To resolve the density of states and describe the average geometry of the PDI stack near its interface, we have studied the PDI thin films using polarization resolved electronic sum-frequency generation (ESFG). Spectrally resolved ESFG studies suggest an optical band gap narrowing at the interface. These changes are qualitatively reproduced by a site-basis Holstein-style hamiltonian electronic structure calculation that reinforces the close interplay between molecular crystal structure and photophysical properties. Moreover, the polarization resolved experiments allow us to map this spectral response to a net PDI orientation near the PDI-substrate interface that is dependent on the derivative of PDI used. These findings suggest excitations might migrate towards the PDI-substrate interface and affirm that derivatization might be an avenue for interfacial engineering.

Institution: University of Texas, Austin

Code: FUNDPhoto_P2

Presenter: Alexander T. Gilligan (USA)

Abstract Title: Rigid Covalent Dimers as Tool for Investigating the Mechanistic Landscape of Singlet Fission

Co-Author(s): Ethan G. Miller, Tarek Sammakia, Niels H. Damrauer

Abstract: Covalent dimers have been a useful tool for deriving key insights into the mechanism of singlet fission, a photophysical process that could increase solar cell efficiency. Here dimers of TIPS-acetylene substituted tetracene (TIPS-BT1′) and pentacene (TIPS-BP1′) connected by a rigid norbornyl bridge were used to interrogate formation of the biexcitonic 1TT state and its relaxation to the ground state. TIPS-BP1′ showed a complete conversion to the 1TT over 4.4 ps followed by a 100 ns relaxation down to the ground state.[1] TIPS-BT1′ also showed rapid formation of the 1TT with a time constant of 5 ps as an excited-state equilibrium (K ~ 1) with the excited state S1 that decays to the ground state after 36 ns.[1] Marcus theory was used to retrieve diabatic couplings and reorganization energies for both systems. Comparison with the constitutional isomer TIPS-BT1, which shows minimal 1TT formation, suggests that the rate of TT formation is influenced by exchange interactions in the triplet manifold.[2] Asymmetric variants of the tetracene dimer were prepared in order to investigate the influence of orbital symmetry on diabatic coupling.

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Institution: University of Colorado - Boulder

Code: FUNDPhoto_P3

Presenter: Rachel VanOsdol (USA)

Abstract Title: Charge Transfer from Triplet Excitons Subsequent to Singlet Fission

Co-Author(s): Justin Johnson, Garry Rumbles

Abstract: Singlet fission is a process in which a chromophore in a singlet state couples with a neighboring ground-state chromophore and transfers some of its energy to produce two triplet states. Providing that these triplets can produce two charge carrier pairs, singlet fission has the potential to enhance solar cell efficiency by circumventing thermalization losses. This work utilizes ultrafast transient absorption spectroscopy and time-resolved microwave conductivity to investigate the charge transfer dynamics in crystalline thin films of singlet fission materials sensitized with a dilute concentration of acceptor molecules. Through control of molecular and crystal properties, we can investigate the factors that influence charge transfer from triplet and singlet excitons and determine how to selectively dissociate triplet excitons into charge carriers in high yields.

Institution: CU Boulder, NREL

Code: FUNDPhoto_P4

Presenter: Anuja Singh (IND)

Abstract Title: Emergent Cross-Conjugated Enediynyl Fluorophores

Co-Author(s): Avik Kumar Pati and Prof. Ashok Kumar Mishra*

Abstract: Organic fluorophores with π-conjugated scaffolds are important because of their interesting optoelectronical properties. In recent years, our lab has been engaged in understanding the photophysics of small diacetylene bridged fluorophores(1-4) and found the diynes as a promising class of π-conjugated fluorophores(5,6). Building on these understanding, recently we have focused on the photophysics of a less explored class of cross-conjugated Y-shaped enediynes (one double and two triple bonds). Here we present the photophysical properties of such enediynes which show interesting photophysical properties that include dual emissions from locally excited (LE) and intramolecular charge transfer (ICT) states and ring size dependent aggregate fluorescence in non-aqueous media.(7,8) The dyes also show prominent aggregate fluorescence in mixed-aqueous solvents and solid powder form. The enediynes with push-pull electronic substituents/moieties exhibit high contrast fluorescence color switching upon continuous photon illumination and under sunlight.(8) The intriguing photophysical outcomes of the enediynyl fluorophores are judiciously exploited to generate single-component white light emission in binary solvent mixtures and sense polar aprotic vapor in polymer film matrices.(7) The photophysical behavior of the dyes is further successfully utilized to monitor the microenvironment changes of biologically relevant anisotropic media such as bile salts. In summary, the newly introduced cross-conjugated enediynes enrich the toolbox of organic fluorophores and vouch to display versatile applications.

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Institution: Department of Chemistry, IIT Madras, Chennai-600036, India

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Code: FUNDPhoto_P5

Presenter: Henry A. Nkabyo (ZAF)

Abstract Title: Reversible Photo-induced Isomerism as Key to the Isolation of Novel Pd(II) Complexes of N,N-di-substituted Aroylthioureas

Co-Author(s): Klaus R. Koch

Abstract: The N,N-di-substituted acyl(aroyl)thioureas represent a group of neutral bidentate ligands which form predominantly cis-[M(L-S,O)2] type complexes with d8 transition metal ions (M=Pt(II), Pd(II), Cu(II) and Ni(II)), as reflected by only a single-known Pt(II) complex with a trans-[Pt(L-S,O)2] mode of coordination[1]. Photo-induced isomerization after polychromatic light irradiation of the cis-[M(L-S,O)2] complexes produces their trans-[M(L-S,O)2] derivatives in acetonitrile[2]. A unique method for isolating the representative trans-[M(L-S,O)2] isomers from cis-[M(L-S,O)2] is by concomitant vapour diffusion of diethyl ether into the acetonitrile solution under continuous light exposure[3,4]. The isolated cis-trans geometric isomers are distinguished by their differences in NMR resonances, RP-HPLC elution times as well as their differences in melting point as confirmed by thermal analysis. In addition, single-crystal X-ray diffraction studies reveal significant differences in bond distances across the six-membered –N-C–S-Pd-O-C chelates in the cis-trans structures. In the absence of light, the isolated trans-[Pd(L-S,O)2] isomers undergo a spontaneous trans → cis isomerization, with higher relative rates highlighting the importance of acetonitrile as a coordinating solvent compared to lower rates in chloroform. Although the mechanism of both photo-induced cis → trans, and thermal trans → cis isomerization is not yet fully understood, our results reveal that the reversible isomerization induced by light is also a ligand-exchange mediated process.

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Institution: Department of Chemistry and polymer science, University of Stellenbosch, Private Bag X 1, Matieland, South Africa

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Code: FUNDPhoto_P6

Presenter: MENG-CHEN Shih (TWN)

Abstract Title: Does Tetrahydrofuran (THF) Behave like a Solvent or a Reactant in the Photolysis of Thionyl Chloride (Cl2SO) in Cyclohexane?

Co-Author(s): Li-Kang Chu

Abstract: Pulsed photolysis of thionyl chloride (Cl2SO) in cyclohexane (cHex) and in cHex with a small amount of tetrahydrofuran (THF) at 266 nm was monitored with time-resolved step-scan Fourier-transform spectroscopy. The density functional theory (B3LYP), coupled with the conductor-like polarizable continuum model to account for the effects of solvents, was employed to predict the molecular parameters of the relevant [S,O] species. We found that SO2 was the major oxygen-containing end product for the thermal decomposition of Cl2SO. Upon successive irradiation of the Cl2SO/cHex mixture, the major product was S2O with minor SO3, which could be generated from the secondary reactions of the photolytic intermediate ClSO. The majority of the transient vibrational features upon 266 nm irradiation of the Cl2SO/cHex mixture was attributed to ClSO, characterized at 1155 cm-1, coupled with a minor contribution of (ClSO)2 at 1212 and 1173 cm-1. For the mixture of Cl2SO/THF/cHex, the transient population of ClSO was retained, but the amount of (ClSO)2 was slightly reduced. Instead, a new upward feature appeared at 1054 cm-1 that was plausibly attributed to the C-O-C asymmetric stretching mode of THF moiety in ClSO-THF complex. Upon the successive irradiation of the Cl2SO/THF/cHex mixture, the amount of S2O was decreased. The observed complexes of THF with solutes suggested that THF should not be merely treated as a solvent but regarded as a coordination molecule in organic synthesis, in accordance with the alteration in the reaction pathways and the types and populations of the end products.

Institution: Department of Chemistry, National Tsing Hua University

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Code: FUNDPhoto_P7

Presenter: Tatsuhiro Nagasaka (JPN)

Abstract Title: Elucidation of 6π-electrocyclic Reaction Dynamics of a Dithiazolylarylene Derivative

Co-Author(s): Hikaru Sotome, Ryosuke Sei, Tsuyoshi Kawai, Hiroshi Miyasaka

Abstract: 6π-electrocyclic reactions are one of photochemical processes where the formation and cleavage of chemical bonds proceed on a femtosecond-to-picosecond timescale. This process is a crucial initial step driving photoresponses and photofunctions in the field of material science, as represented by photochromic reactions of diarylethene derivatives. According to many reports on electrocyclic reactions, the cyclization and cycloreversion reactions take place on the 2A potential energy surface (PES), and the same conical intersection (CI) mediates the 2A and 1A (ground state) PESs in both the reactions. However, we have discovered that the reaction mechanism of one derivative cannot be explained by the conventional scheme. In the present study, to elucidate the specific reaction mechanism, we have applied transient absorption spectroscopy to a dithiazolylarylene derivative(DTA), which shows the cyclization reaction yield of almost unity [1]. Transient absorption measurements of the open-ring isomer indicate that the open-ring isomer undergoes rapid relaxation in the excited state within 1 ps, followed by the formation of the closed-ring isomer with a time constant of 22 ps. On the other hand, in the cycloreversion dynamics, transient absorption of the closed-ring isomer decayed also with a similar time constant. In addition, shape of the transient spectra is similar to each other in both the reactions. This spectral similarity indicates that both the reactions proceed via the same intermediate species. At the conference site, we discuss the reaction mechanism together with results obtained from fluorescence spectroscopy.

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Institution: Osaka University

Code: FUNDPhoto_P8

Presenter: Nobuaki Oyamada (JPN)

Co-Author(s): Hiro Minamimoto, Kei Murakoshi

Abstract Title: Arbitrary Optical Molecular Condensation at the Confined Plasmonic Field under Electrochemical Potential Control

Abstract: The optical manipulation of the single small molecule in solution would drastically improve the efficiency of the photochemical reactions at the nanoscale region. However, it is still a very difficult challenge because of the molecular fluctuation induced by so-called Brownian motion, especially under the ambient condition. Localized surface plasmon resonance (LSPR) excited under the light illumination onto the metal nanostructures leads to the formation of the electromagnetic field. Up to date, previous theoretical study has expected that the large gradient force formed in the LSPR field could overcome the Brownian motion and change the surface diffusion rate. In this study, we have attempted to achieve the optical molecular manipulation through surface-enhanced Raman scattering (SERS) measurements in the mixed solution of two type structural isomer molecules under electrochemical potential control. It is well known that both the adsorbate and the molecular orientation can be determined at the specific electrochemical potential. Through the bi-analyte SERS measurements, we have successfully observed the different stable adsorption species and the orientation depending on the electrochemical potential. It must be emphasized that SERS intensities corresponding to one or the other molecules became obviously stronger with the increase of the laser illumination time under the specific electrochemical potential control. These experimental results would suggest that the molecular selectively condensation at the certain gap has been realized by both the LSPR field and the electrochemical potential control of the Au bowtie structure.

Institution: Graduate School of Chemical Sciences and Engineering, Hokkaido University

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Code: FUNDPhoto_P9

Presenter: Yi LI (CHN)

Co-Author(s): Yi ZENG, Li LI

Abstract Title: Upconversion Organic Nanocrystals Based on Triplet-triplet Annihilation

Abstract: Harvesting and converting low energy photons into higher ones through upconversion have great potential in solar energy conversion. Triplet-triplet annihilation (TTA) upconversion has prevailed because it can effectively take place upon excitation with noncoherent, low-power light sources close to the solar irradiance. TTA upconversion involves a bimolecular system consisting of sensitizers and acceptors, and its efficiency is affected not only by the TTA processes and fluorescence quantum yield of acceptors, but also by the triplet production of sensitizers and the triplet-triplet energy transfer between sensitizers and acceptors. Efficient TTA upconversion by solid systems remains a challenge, owing to the requirement for diffusion and proximity of photoactive components to guarantee serial Dexter-type energy transfers during conventional TTA upconversion and a concentration-induced emission quenching. In this presentation, our recent results on TTA upconversion organic nanocrystals will be discussed.

Institution: Technical Institute of Physics and Chemistry, Chinese Academy of Sciences

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Code: FUNDPhoto_P10

Presenter: Takahiro Hayashi (JPN)

Co-Author(s): Shunpei Oikawa, Hiro Minamimoto, Kei Murakoshi

Abstract Title: Optical Property of Strong Coupling Regime between Lattice Plasmon Mode and Dye Molecules under Electrochemical Potential

Abstract: It is well known that the strong electromagnetic field forms in the vicinity of the metal nanoparticle by the excitation of the localized surface plasmon resonance. Up to date, various interesting photochemical phenomena caused by the plasmon, such as the strong coupling regime, have been reported. Regarding to the strong coupling regime, the new light-matter hybridized state is formed by the reversible light energy exchange between plasmon and exciton. On the other hand, the two dimensionally arranged metal lattice structure has been receiving much attention. The lattice structure can suppress the radiative damping due to the interaction between the collective electron oscillation and the diffractive light. In this study, we fabricated various Au lattice structures on a conductive substrate and deposited the dye molecular coverage to form the strong coupling between molecules and plasmon. From extinction spectra of the substrate, the formation of the strong coupling regime has been successfully observed as the peak splitting. In addition, we investigated optical properties of strong coupling system under electrochemical potential control. Consequently, we found that coupling strength of system can be actively tuned via electrochemical potential scan. This behavior is attributed to the change of dye molecules involved in strong coupling caused by the redox reaction of the dye molecules on the surface. Through the investigations, we have concluded that the active tuning of the strong coupling on the lattice structure had been realized.

Institution: Graduate School of Chemical Sciences and Engineering, Hokkaido University

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Code: FUNDPhoto_P11

Presenter: Jamuna Kanaram Vaishnav (IND)

Abstract Title: Long-Range Resonance Coupling-Induced Surface Energy Transfer from CdTe Quantum Dot to Plasmonic Nanoparticle

Co-Author(s): Tushar Kanti Mukherjee

Abstract: Fundamental understanding and precise control of complex nonradiative processes in nanoscale system finds significant interest in recent times due to their importance in various nanophotonics applications. Here we have systematically investigated the mechanism behind photoluminescence (PL) quenching of mercapto succinic acid (MSA)-capped CdTe QDs in the near field of gold and silver nanoparticles (Au and Ag NPs) by using steady-state and time-resolved photoluminescence (PL) spectroscopy. Resonance coupling between excitonic emission and localized surface plasmon resonance (LSPR) of Au NPs has been tuned by varying the size of QDs. Herein, three differently sized MSA-capped CdTe QDs have been synthesized namely, 2.15±0.71, 3.13±0.41 and 3.92±0.34 nm with emission in green, yellow and red region of the electromagnetic spectrum, respectively. It has been observed that both the luminescence intensity and lifetime of green QDs quench significantly in the near field of 20 nm sized Au NPs. In contrast, the luminescent intensity and lifetime of yellow and red QDs remain unaltered in the presence of Au NPs. Moreover, it has been observed that ligand exchange at the surface of Au NPs with Poly (ethylene glycol) methyl ether thiol (PEG-SH) decreases the quenching efficiency of green QD-Au NP pair significantly. In addition, the extent of quenching strongly depends on excitation wavelength. The observed quenching is more efficient at the excitation wavelength close to the LSPR of Au NP. These results have been explained on the basis of a modified surface energy transfer (SET) model by incorporating the changes in the complex dielectric function and the absorptivity of the Au NP. On the contrary, irrespective of the sizes of QDs, significant PL quenching has been observed in the presence of 10 nm sized citrate-capped Ag NPs as a consequence of photoinduced electron transfer (PET). The present findings of size and wavelength-dependent long range nonradiative electromagnetic coupling in hybrid QD-metal NP system can be useful to understand and optimize the performance of various nanophotonic devices.

Institution: IIT indore. India

Code: FUNDPhoto_P12

Presenter: Natalie G. K. Wong (GBR)

Abstract Title: Coupling Solution-Phase UV Photolysis Systems with Gas-Phase Laser Dissociation Spectroscopy to Probe Sunscreen Photochemistry

Co-Author(s): Jacob A. Berenbeim and Caroline E. H. Dessent

Abstract: Few studies have explored the fundamental mechanisms that govern how sunscreens function at the molecular level until now.[1-2] Here, we employ a novel fusion of laser dissociation spectroscopy and electrospray ionization mass spectrometry (ESI-MS) to probe the intrinsic absorption properties of sunscreen molecules, addressing how pH affects their photochemical behavior.

In several systems, we observe that protonation state indeed has a dramatic effect on the UV absorption of organic sunscreens. The gaseous spectral profile of deprotonated oxybenzone, for instance, displays a remarkably-modified absorption spectrum, and photogenerates both electrons and free radicals.[2] Likewise, deprotonated 2-phenyl-3H-benzimidazole-5-sulfonic acid yields anionic and neutral free radical species via all photodissociation routes. We report, for the first time, the gaseous photoabsorption and photofragment production spectra of deprotonated forms of FDA-approved sunscreens octisalate and homosalate.

Free radical production is an undesirable property for sunscreen molecules. Using a series of new solution-phase irradiation experiments incorporating both home-built photolytic cells and ESI-MS, we highlight how this behavior transfers into the solution phase and quantitatively probe how concentrations of ionized sunscreen molecules and their photoproducts change as a function of irradiation time.

These findings at the molecular level raise questions about the suitability of existing commercially-available sunscreens and demonstrate the utility of laser-interfaced mass spectrometry for fundamental studies of sunscreen photochemistry.

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Institution: University of York

Code: FUNDPhoto_P13

Presenter: Supattra Panthai (JPN)

Abstract Title: Liquid-Crystalline AIEgens Emitting White-Color Luminescence

Co-Author(s): Maruoka Yui, Sami H. Alijuzayri, Osama Yousin, Kyohei Hisano, Osamu Tsutsumi

Abstract: Highly luminescent materials are of great interest for use in light-emitting devices. However, the luminescence intensity of most organic molecules is abruptly reduced in concentrated solutions or condensed phases owing to concentration quenching or aggregation-caused quenching. Recently, some types of organic molecules have shown strong photoluminescence in the condensed phase, where the aggregation enhanced the photoluminescence through a phenomenon called an aggregation-induced emission (AIE). The structure of their molecular aggregates, as well as their own molecular structure, must strongly affect the luminescence of AIE materials. We have developed liquid-crystalline (LC) luminophores with the AIE property (AIEgen). Some useful characteristics of LCs that lend themselves to efficient aggregate control include their self-assembled nature, fluidity, and responsivity to external stimuli. Since the aggregated structure of luminophores can be easily manipulated in the LC phase, their luminescence behavior can be controlled.

Herein, we have developed three novel LC AIEgens. We found that all molecules emitted blue- color emission with proper quantum yields in a crystalline phase through AIE. Interestingly, 6T-H displayed pure white-color emission in an LC phase. The results indicated that emission color can be tuned by the aggregated structure of AIEgens, and that pure white-color emission can be obtained from the single compound.

Institution: Department of Applied Chemistry, Graduate school of Life Sciences, Ritsumeikan University, Japan

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Code: FUNDPhoto_P14

Presenter: Maria Wächtler (DEU)

Abstract Title: Ultrafast Photoinduced Electron Transfer Dynamics in Ru(II) Bis(terpyridine) Based Molecular Triads

Co-Author(s): Yusen Luo, Benjamin Dietzek

Abstract: In molecular triads containing a Ru(II)bis(terpyridine) photosensitizer, a phenothiazine (PTZ) electron donor and a fullerene (C60) electron acceptor a two-step electron transfer takes place. First upon excitation of Ru(tpy)2 an electron is transferred from PTZ to photoexcited Ru(tpy)2 followed by an electron shifting from reduced Ru(tpy)2 to C60.[1] Temperature dependent fs transient absorption (TA) spectroscopy was employed to gain deeper insight into the mechanisms of the single transfer steps. The first electron transfer step is specifically addressed applying a model system just containing the PTZ donor and a remote tpy ligand with varying substituents. The nature of these remote tpy ligand is found to significantly alter the electronic coupling between PTZ and Ru(tpy)2 despite the same PTZ-Ru(tpy)2 distance, chemical linkage and constant driving force.[2] In a combined analysis of temperature- and distance-dependent electron transfer rates of the second electron transfer step it is revealed that superexchange is operative in short triads while hopping dominates in the longest triad.[3] Interestingly, hopping shows weaker temperature dependence than superexchange. This unexpected result is rationalized by considering the specific geometrical and electronic structure of the Ru(tpy)2 photosensitizer.

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Institution: Leibniz Institute of Photonic Technology, Jena, Germany

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Code: FUNDPhoto_P15

Presenter: Yogita Silori (IND)

Abstract Title: Role of Solvents on the Interplay between Homo- and Hetero-energy Transfers in a Multichromophoric System

Co-Author(s): Arijit K. De

Abstract: The mechanism of excitation energy transfer (EET) in light harvesting systems, which includes absorption of light energy by antenna chromophores followed by the exchange of energy among multiple chromophores and finally funneling of energy toward the reaction center chromophores where it is trapped, has attracted high interest. By taking artificial analogs of such hetero-chromophores, the energy transfer efficiency can be enhanced by controlling surrounding conditions. In past few decades, energy transfer has been studied between fluoresceins or rhodamines or fluorescein to rhodamine 6G (Rh6G) dyes with varying concentration, pH and also on different surfaces like polymers, clays, DNA, etc.

To this end, we have studied EET dynamics by using time-resolved fluorescence anisotropy method to understand the mechanism of energy transfer between fluorescein and Rh6G dyes in different solvents with varying viscosity and concentrations of both dyes. Also, we observe that at very high concentration of dyes, the weak coupling between different chromophores (which are well understood by Forster theory of Resonance Energy Transfer) is dominated by strong coupling between like chromophores (as explained by Generalized Forster theory).

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Institution: PhD student, Indian Institute of Science Education and Research Mohali

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Code: FUNDPhoto_P16

Presenter: Miroslav Dvorak (CZE)

Abstract Title: Up-converted Fluorescence in 1-aminopyrene-based Multichromophores

Co-Author(s): Numan Almonasy, Martin Michl, Shyamal K. K. Prasad, Timothy W. Schmidt

Abstract: Organic multichromophoric compounds are promising materials which often exhibit nonlinear optical properties, e.g. high two-photon absorption cross section. There is an interesting question of localization of excited states and energy migration over the individual chromophores which goes hand in hand with the strength of interaction between the chromophores. We studied a set of molecules containing one, two or three 1-aminopyrene moieties linked via a triazine ring. The comparison of their absorption spectra is indicative of a rather weak interaction between the chromophores. The quantum chemical calculations together with fluorescence anisotropy measurements then suggest that the lowest excited singlet state is localized on a single chromophore.

Solutions of studied multichromophores with concentrations higher than 5x10-6 M were illuminated with 532 nm Q-switched laser pulses, i.e. by photons with energy below the first excited singlet state. This resulted in observation of up-converted fluorescence signal in the 400-500 nm region.. The intensity of the fluorescence signal was found to be quadratically dependent on the intensity of the excitation laser beam. Time resolved luminescence measurements also indicate presence of delayed fluorescence together with the red shifted emission assigned to an excimer. In this type of multichromophores, there is a number of possible mechanisms leading to up-converted emission which involves either processes on a single molecule or bimolecular processes: two-photon absorption, triplet excited state absorption followed by intersystem crossing and intra- or intermolecular triplet-triplet annihilation. In this contribution, we try to elucidate the photophysical mechanisms leading to the observed fluorescence up-conversion.

Institution: Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering, Prague, Czech Republic

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Code: FUNDPhoto_P17

Presenter: Tsung-Wei Shih (TWN)

Abstract Title: Optical Trapping-controlled Asymmetric Photocyclodimerization of 2-anthracenecarboxylic Acid Mediated by γ-cyclodextrin

Co-Author(s): Xueqin Wei, Cheng Yang, Yoshihisa Inoue, Teruki Sugiyama

Abstract: Optical trapping in a target solution with a focused laser beam increases local concentration at the focus, where the crystallization and polymorphism are controlled by manipulating laser power and polarization [1]. The local concentration area produced by optical trapping is regarded as a new chemical photoreaction filed. We here demonstrate the results of the asymmetric [4+4] photocyclodimerization of 2-anthracenecarboxylate (AC) through 2:1 complex with γ-cyclodextrin (CD) under an optical trapping condition.

When a 532 nm-laser used as a trapping light source was focused into an aqueous solution containing AC and CD, four stereoisomeric cyclo¬dimers, i.e., achiral anti-head-to-tail (anti-HT) (1), chiral syn-HT(2), chiral anti-head-to-head (anti-HH) (3), and achiral syn-HH (4), were produced through two-photon excitation. To our surprise, the thermodynamically less stable HH dimers 3 and 4 became dominant, which is in contrast with the results obtained using incoherent light [2]. Furthermore, the enantiomeric excess (ee) of 3 was significantly enhanced from -2% to 40 %, while the ee of 2 decreased from 32% to 15%. Upon irradiation at lower laser power or with circular-polarized laser, the yields of the HH dimers were decreased. Besides, the highest ee value was obtained upon irradiation of linearly polarized light, while the use of right- and left-circularly polarized light led to obviously lower ee's. We suspect that the precursor complexes, in which two ACs are aligned in HH manner responding to the electric field of laser, are preferentially aggregated and two-photon excited at the laser focus to afford the cyclodimers in distinctly different product distribution and enantioselectivity.

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Institution: Department of Applied Chemistry, National Chiao Tung University, Taiwan

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Code: FUNDPhoto_P18

Presenter: R. Marshall Wilson (USA)

Abstract Title: Pyridinium Based Compounds as Photo-induced and Thermal DNA Damaging Agents

Co-Author(s): Nikolai A. Tcyrulnikoc and Anastasiia A. Tikhomirove

Abstract: Herein, we present the design, synthesis, and studies of photochemical properties of masked 9,10-phenanthrenequinone. The research work covers the DNA binding properties of this compound and provides insights into its interaction with DNA duplex investigated by means of a variety of analytical and spectroscopic techniques (UV-vis, CD, Viscometry, Fluorescence Spectroscopy, etc.). The oxidative DNA damage triggered by the photochemical release of the highly reactive ortho-phenanthrene quinone was described and quantified by ΦX 174 plasmid relaxation assays.

In addition, as a part of continuing research devoted to the investigation of thermal DNA damage caused by Reactive Oxygen Species (ROS) formed during aerobic oxidation of the 1,1,2,2-tetrakis(N-methylpyridin- 4-ium)ethane salt,1 we synthesized bis(N-methylpyridin-4-ium)alkane salt. During aerobic oxidation of the latter compound, we discovered an unusual transformation from saturated alkane to gem-diol. The mechanism of the spontaneous non-catalytic aerobic oxidation of bis(N-methylpyridin-4-ium)alkane salt was proposed based on the product and intermediate characterization. Thermal DNA damage induced by the formation of ROS during the aerobic oxidation of ,1,2,2-Tetrakis(N-methylpyridin- 4-ium)ethane and bis(N-methylpyridin-4-ium)alkane and was observed, characterized and their efficiency compared.2 Results of this work present the first example of thermal DNA damage induced by pyridinocyanines generated in situ.

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Institution: Bowling Green State University

Code: FUNDPhoto_P19

Presenter: H. Y. Yoshikawa (JPN)

Abstract Title: Development of Photophysical Methodology for Reconstruction of Ordered, Dynamic Cytoskeletal Networks

Co-Author(s): T. Takeshige, F. Kiryu, C. -S. Wu, Y. -H. Shih, S. Nakabayashi, T. Sugiyama, R. Kawamura

Abstract: Cytoskeleton is a dynamic network of interlinking protein fibers in cells. Since cytoskeleton plays an essential role in various cellular functions such as cell divisions, many studies have been trying to reveal its structure-function relationship via biochemical approaches such as the use of chemical/drugs and gene manipulation. In addition, recent studies have demonstrated in vitro reconstruction of cytoskeletal networks for applications towards artificial cells and micro-machines. However, the production of ordered cytoskeletal networks is still very challenging, whereas it should allow for understanding and regulation of biological machinery. In this work, we have utilized photophysical effects (photon pressure and thermal elevation) with a focused laser beam to reconstruct ordered, dynamic microtubule networks from cytoskeletal protein, tubulin. We found that the focused irradiation with a near-infrared continuous-wave Nd3+: YAG laser (λ = 1064 nm) via an objective lens (NA = 0.90) can induce the aggregation of tubulin in solution. Through the systematic investigation, we succeeded in fabricating the large (> 10 μm) and semi-circular aggregates by focusing the laser beam at a three-phase interface. Observation of the aggregates under a crossed Nicols condition clearly showed birefringence alternately, indicating the fibrous structures are anisotropically aligned by the laser irradiation. Furthermore, the aggregates could be dynamically driven in the presence of motor protein (kinesin) and chemical energy (ATP). We expect that the laser method can offer a new photophysical (not biochemical) means for the production of dynamic cytoskeletal networks with desired structures.

Institution: Saitama University

Code: FUNDPhoto_P20

Presenter: An-Chieh Cheng (TWN)

Abstract Title: Enantioselective Amplification in Chiral Crystallization of Sodium Chlorate by Plasmonic Optical Trapping

Co-Author(s): Shutaro Ishida, Hiromasa Niinomi, Takashige Omatsu, Keiji Sasaki, Teruki Sugiyama

Abstract: Plasmonic optical trapping is achieved by the significantly-enhanced electric field with a steep gradient in a nanometer-sized hotspot beyond the diffraction limit of light. We here demonstrate the control of chirality in chiral crystallization of sodium chlorate (NaClO3) using the plasmonic optical trapping. Triangle trimmer gold nanostructures with the side length of 170-230 nm were fabricated on a glass substrate. After pipetting a droplet of a saturated NaClO3 D2O solution on the plasmonic substrates, continuous-wave linearly-, right- or left-handed circularly-polarized light (LPL, l-CPL, and r-CPL) of 1064 nm at 1.0 MW/cm2 was focused into the single triangle trimmer structure to trigger crystallization through an objective lens in an inverted microscope. After a few seconds of the laser irradiation, the single metastable achiral crystal was firstly generated. Continuous irradiation into the achiral crystal led to the polymorphic transition to a chiral crystal. The handedness of the resulting crystals was in-situ identified by rotating analyzer method under a polarized microscope. Same experiments were repetitively performed for 50 samples under each condition, and the crystal enantiomeric excess (CEE) was estimated. Linearly-polarized light caused no symmetry breaking in the CEE value, while circularly-polarized light gave the highest CEE value of more than 50 %. The detailed dynamics and mechanism of the chirality control are discussed in view of asymmetric light-cluster interactions during plasmonic optical trapping.

Institution: National Chiau Tung University

Code: FUNDPhoto_P21

Presenter: Chiaki Kojima (JPN)

Abstract Title: Synthesis and Spectroscopic Studies of Gold(I) Complexes with Nucleobase Moieties

Co-Author(s): Yasuyuki Tsuboi, Toshiyuki Moriuchi

Abstract: Organogold(I) complexes have attracted much attention because of their luminescent properties such as mechanochromic luminescence and aggregation induced emission. Such interesting luminescence behaviors are exhibited by the control of aurophilic interactions. Especially, self-assembly and self-aggregation of organogold(I) complexes would represent a new strategy to control the aurophilic interactions. For such backgrounds, we have recently succeeded in the synthesis of the dinuclear organogold(I)-uracil complexes with a bridging diphosphine ligand [1]. We found that the uracil moieties played an important role for self-assembly formation of the complexes through the intermolecular hydrogen bonds between the uracil moieties. These findings can give new insights into the control of aurophilic interactions by using bioconjugates like nucleic acids. We herein synthesized the novel gold(I) complexes having nucleobase moieties and characterized spectroscopic properties of them.

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Institution: Graduate school of science, Osaka city university, Japan

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Code: FUNDPhoto_P22

Presenter: Thomas Custer (POL)

Abstract Title: Absolute Intensities and Photolytic Behavior of Methyl Mercaptan (CH3-SH), Ethyl Mercaptan (CH2CH3-SH), and Dimethyl Sulfide

Co-Author(s): Marcin Gronowski, Joanna Zapala

Abstract: The sulfur-containing species ethyl and methyl mercaptan (HS-CH2CH3 and HS-CH3) have both been detected in space. Dimethyl sulphide (CH3-S-CH3), while not yet detected, is another plausible interstellar “complex organic molecule”. Species such as these are thought to have their origin in CO-rich ices. While spectra of all three of these species have been measured in noble gas matrices, no absolute band intensities are available and no UV photolysis studies in either noble gas matrices or CO ices have been reported. We isolated these molecules in solid Ar and CO ices at 6 K and exposed them to UV radiation from an excimer laser (193 nm) and H2 discharge lamp (121 nm) in separate experiments. Photolysis progress was monitored using FTIR spectroscopy in each case. Samples were subsequently annealed and emission monitored using a small CCD spectrometer. Photoproducts consisted of large amounts of CH4, CS, and, with the exception of ethanthiol, CH2=S. Smaller amounts of CxSy species were also detected for each. Ethane (CH3-CH3), ethene (CH2-CH2), and ethyne (HCCH) could also be seen in small amounts for experiments in Ar matrices. H-atom loss products, OCS and H2S can also be detected. Annealing of the ices resulted in emission due to S recombination between 12 and 20 K. Absolute intensities were estimated starting from matrix thicknesses obtained from interference fringes in the IR spectra. These experiments provide a first look into the photochemistry of these species in low temperature ices in pursuit of a better understanding of S astrochemistry.

Institution: Institute of Physical Chemistry, Polish Academy of Sciences

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Code: FUNDPhoto_P23

Presenter: Kevin Felter (NLD)

Abstract Title: Singlet Fission and Photoluminescence in Perylene Diimides

Co-Author(s): Ferdinand Grozema

Abstract: Singlet exciton fission is one of the emerging strategies to optimize and surpass the Schockly-Queisser limit for (organic) single junction photovoltaic cells [1,2]. Singlet exciton fission involves the conversion of a singlet excited state (S1) formed on photoexcitation into two distinct triplet excited states (T1+T1)In this study we have investigated the effect of temperature on rate of the singlet fission in perylene diimides (PDI) and the diffusive properties of the triplet excitons created in this process by time resolved microwave conductivity (TRMC), photoluminescence and femtosecond pump-probe and nanosecond transient absorption measurements.

The solid-state organization of PDIs can be tuned to a large extent by modifications in the substituents. In these experiments we demonstrate a clear effect of the solid state packing on the temperature dependence of exciton diffusion and singlet fission in PDI polycrystalline films. These results show that the formation and diffusion of triplets in PDIs can be tuned to a large extent and thus side-chain engineering is a viable approach to optimize the properties of these materials for device applications.

[1] Hanna, M. and A. Nozik, Journal of Applied Physics, 2006. 100(7): p. 074510.
[2] Smith, M.B. and J. Michl., Chemical reviews, 2010. 110(11): p. 6891-6936.

Institution: Delft University of Technology

Code: FUNDPhoto_P24

Presenter: Sandra P. Gonzalez Lopez (ZAF)

Abstract Title: Triplet-triplet Annihilation Up-conversion Sensitizes Metal Oxide Nanoparticles for Photocatalytic Reactions

Co-Author(s): Julien Gorenflot, Patrick Murton, Maximilian Moser, Capucine Tong, Iain McCulloch, and Frédéric Laquai

Abstract: Many metal oxide semiconductors, such as TiO2, ZrO2, and CeO2, require UV excitation in order to drive photocatalytic reactions. However, UV photons account for only 3-5% of the solar spectrum and thus strategies to extend the range of harvested photons into the visible wavelength range are required. One potential way is to use triplet-triplet annihilation photon up-conversion (TTA-UC). TTA-UC systems generate higher energy photons from lower energy, low intensity, and non-coherent excitation. In this work, we synthesized several 9,10-diphenylanthracene derivatives and attached them to different wide-bandgap metal oxide nanoparticles, which were then dispersed in solutions containing triplet sensitizers. Triplet energy transfer leading to triplet-triplet annihilation photon up-conversion and charge generation were probed through steady-state and transient spectroscopy techniques such as photo-induced absorption, time-resolved photoluminescence, and transient absorption spectroscopy. As a proof of concept, we apply these TTA-UC systems in photocatalytic processes.

Institution: King Abdullah University of Science and Technology (KAUST), Division of Physical Science and Engineering, KAUST Solar Center

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Code: FUNDPhoto_P25

Presenter: Yuichi Hirai (FRA)

Abstract Title: Photophysical Investigation on Mechanofluorochromic Pyrene–Derived Aminophosphonates

Co-Author(s): Anna Wrona-Piotrowicz, Janusz Zakrzewski, Rémi Métivier, Clémence Allain

Abstract: Mechanofluorochromism (MFC) refers to the solid-state emission color change upon mechanical stimuli, and has attracted increasing attention in recent years.1 In general, the molecular arrangements or intermolecular interactions are forced to be altered by anisotropic mechanical stress, and crystal-to-amorphous or crystal-to-crystal phase change is induced. The solid-state phase change also brings emission color change through excimer formation and metal-metal distance change.2 Growing numbers of molecules have been developed and investigated; however, study on MFC is still in the early stage in terms of systematic molecular design and mechanical/photophysical point of view.

In this study, we focused on pyrene-based compounds to develop a library of organic solid-state emitters with MFC properties. In order to control the solid-state steric structures, the pyrene-derivatives with aminophosphonates groups were prepared.3 The obtained compounds showed monomer-to-excimer like spectral change with bathochromic shift upon grinding the pristine sample powders. The hypsochromic shift in ground samples at room temperature also indicated that the molecular rearrangements can occur in solid state. Photophysical parameters including emission spectra, quantum yields and lifetimes were evaluated before/after grinding, and structure-property relationships were discussed including the thermal back reaction.

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Institution: ENS Paris-Saclay

Code: FUNDPhoto_P26

Presenter: Natalie Pace (USA)

Abstract Title: Triplets Generated by Singlet Fission Dissociate Less Efficiently than Triplets Generated by Intersystem Crossing

Co-Author(s): Tyler T. Clikeman, Steven H. Struass, Olga V. Boltalina, Justin C. Johnson, Garry Rumbles, Obadiah G. Reid

Abstract: We compare triplet dissociation in sensitized pentacene films using two different triplet generation mechanisms: singlet fission (SF) and intersystem crossing (ISC). In both cases, the same substituted PDI molecule is used as an electron acceptor to ensure that the driving force for charge transfer from the pentacene triplet state is held constant. In order to produce triplets via SF, we excite the pentacene film directly. In order to produce triplets via ISC, we incorporate a second molecule into the pentacene film, which undergoes intersystem crossing and transfers its triplets to pentacene. We selectively excite this lead phthalocyanine sensitizer at an energy below the pentacene band edge, which eliminates the possibility of singlet energy transfer to pentacene. We use time-resolved microwave conductivity (TRMC) to compare the charge generation yield after SF to the charge yield after ISC. The SF and ISC triplet population sizes are determined via transient absorption (TA). Taken together, these measurements indicate that the relative charge yield per triplet is at least nine times higher for ISC triplets than for SF triplets. Since the driving force for charge transfer is held constant, the lower SF triplet dissociation efficiency is attributed to some aspect of the SF process itself.

Institution: National Renewable Energy Laboratory, University of Colorado at Boulder

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Code: FUNDPhoto_P27

Presenter: Hrishikesh Somayaji (USA)

Abstract Title: Optimizing Long-range Resonant Energy Transfer using Waveguide Environments

Co-Author(s): Gregory Scholes

Abstract: Resonant energy transfer (RET) between donor and acceptor molecules as a phenomenon has been examined since the early part of the 20th century, most notably by Förster who developed his theory of RET (FRET) that allowed for prediction of RET rates using experimentally-retrievable properties (1). In the 60s and 70s, quantum electrodynamics was used to develop a ground-up picture of RET, and an expression for the matrix element that described RET in 3D was derived (2). The rate derived from this approach, which accounts for relativity, predicts more efficient long-range RET than does the FRET-derived rate, and reveals the presence of a virtual photon that mediates the energy transfer. Following this lead, the matrix element for RET in two spatial dimensions is derived, and revealed to yield greater long-range energy transfer character both in its distance dependence and the degree to which the virtual photon obeys “real” photon character. RET in a 2D waveguide environment is approximated and the matrix element derived, and showed to have still greater long-range efficacy and interesting orientational dependence with respect to the transition dipole moments of the donor and acceptor. This theoretical study opens the door to further study and development of devices and environments that optimize RET over distances that far exceed the traditionally understood distance “limit” as imposed by FRET.

1. Förster, T. Disc. Faraday Soc. 27, 7-17 (1959).
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Institution: Princeton University

Code: FUNDPhoto_P28

Presenter: Alexei Cravcenco (SWE)

Abstract Title: Triplet to Singlet Energy Transfer in Composite Molecules

Co-Author(s): M. Hertzog, C. Ye, M. N. Iqbal, U. Mueller, L. Eriksson, K. Börjesson.

Abstract: The ability to convert between molecular spin states is of utmost importance in materials chemistry. For instance, charge recombination in commercial organic light emitting diodes (OLED) leads to a statistical mixture of excited states being 25% singlets and 75% being triplets (1). Typically, the singlet state emits light much faster than the triplet states, and therefore a singlet emitting state is preferred. Thus, efficient methods to convert excited triplet states to an excited singlet state are of importance. Förster-type energy transfer is based on dipole–dipole interactions (2) and can therefore theoretically be used to convert between molecular spin states.

Here, a molecular dyad that is capable of transferring energy from an excited triplet state to an excited singlet state is presented. The rate of conversion between these states was shown to be 36 times faster than the rate of emission from the isolated triplet state. This dyad provides the first solid proof that intramolecular Förster-type triplet-to-singlet energy transfer is possible, revealing a general method to increase the rate of light extraction from excited triplet states.

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2. Förster, "Zwischenmolekulare Energiewanderung und Fluoreszenz", Annalen Der Physik, 1948, 2, 55-75.

Institution: Department of Chemistry and Molecular Biology, University of Gothenburg, SE-412 96 Gothenburg, Sweden.

Code: FUNDPhoto_P29

Presenter: J. Curtis Beimborn II (USA)

Abstract Title: New Intermediate State Found in Orthorhombic Rubrene Crystals Using Photoluminescence Upconversion Spectroscopy

Co-Author(s): Wyatt Zagorec-Marks, J. Mathias Weber

Abstract: Rubrene crystals are a model system for studying the optical properties of polycyclic aromatic hydrocarbons. It has only recently been reported that rubrene crystals can undergo photoluminescence upconversion without the presence of a sensitizer; however, the properties of the intermediate state have so far been elusive. Using a tunable near infrared (NIR) nanosecond pulsed laser system we recorded upconversion photoluminescence excitation spectra of rubrene powder under different conditions. We found evidence of an intermediate state centered around 12,500 cm-1 (805 nm) for orthorhombic rubrene crystals. This state has not been previously reported, and may explain the origin of upconversion photoluminescence.

Institution: JILA and the University of Colorado

Code: FUNDPhoto_P30

Presenter: Manuel Hertzog (SWE)

Abstract Title: Strong Light-matter Interaction Enhancement through Molecular Dipole Alignment

Co-Author(s): P. Rudquist, J. A. Hutchison, J George, T. W. Ebbesen, K. Börjesson

Abstract: Strong light-matter coupling with organic molecules has recently attracted interest [1] due to the possibility of controlling chemical dynamics, such as triplet harvesting [2] or chemical reactions [3]. In this work, we present a fine control over the coupling strength of light–matter hybrid states by controlling the orientation of a nematic liquid crystal. The microcavity was made from ITO-Gold electrode/mirrors on IR-transparent CaF_2 substrates. Through an external voltage, the liquid crystal is seamlessly switched between two orthogonal directions. The C – N vibration on the liquid crystal molecule is coupled to a cavity mode, and FT-IR is used to probe the formed vibro–polaritonic states. Using these features, we demonstrate electrical switching and increased Rabi splitting through transition dipole moment alignment compared to an isotropic phase. Moreover, the scalar product used in the modelisation of light–matter interaction is verified [3].

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Institution: Department of Chemistry and Molecular Biology, University of Gothenburg, Kemigården 4, 412 96 Gothenburg, Sweden

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Code: FUNDPhoto_P31

Presenter: Haacke, Stefan (FRA)

Abstract Title: Fluorescence Spectroscopy of Short-lived 3MLCT States in Metallo-organic Complexes

Co-Author(s): Li Liu1, D. Agathangelou1, E. Domenichini1, K. Magra3, M. Darari2, O. Crégut1, T. Duchanois2, M. Beley2, J. Léonard1, C. Cébrián

Abstract: Since very recently, metallo-organic Fe(II) complexes with N-heterocyclic carbene (NHC) ligands are designed with an increased ligand field splitting leading to the suppression of ultrafast spin crossover (SCO) [1-4]. This opens the way for Fe-based photo-sensitizers with, e.g. up to 2 ns excited state lifetimes for a 6-carbene coordinated Fe(III) [5]. For Fe(II) complexes, it was shown by femtosecond transient absorption (TA) spectroscopy that the excited 1MLCT (metal-to-ligand charge transfer) state relaxes within less than 100 fs into a triplet state, which, depending on the ligands, display lifetimes of up to 530 ps [3]. However, the exact nature of this state, a 3MLCT or a metal-centred triplet state (3MC), is still controversial. Since triplet stimulated emission is quasi spin-forbidden and therefore too weak to be detected in TA, it would be extremely valuable to detect the luminescence directly in a background-free experiment in order to determine its energy shift and its radiative rate with respect to the bright fluorescence from the 1MLCT state. We implemented a broadband, high-sensitivity fluorescence up-conversion set-up, capable of detecting the luminescence of a triplet state in a metalorganic complex. For the 4-carbene coordinated Fe(II) complexes reported in [2,3], with 20-30 ps lifetime, the triplet emission is characterized by a 350 meV red-shift, and a 500-1000 times weaker radiative rate than the 1MLCT transition. This allows us to assign this long-lived state to the 3MLCT transition rather than to 3MC, since emission from the latter is double forbidden due to spin and symmetry selection rules.

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[4] P. Chábera, et al., J. Phys. Chem. Lett., 9, 459−463 (2018).
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Institution: University of Strasbourg & CNRS, IPCMS, F-67034 Strasbourg Cedex

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Code: FUNDPhoto_P32

Presenter: Xihan Chen (USA)

Abstract Title: Ultrafast Probe at the Interfaces of Solar Energy Conversion Materials

Co-Author(s): Xihan Chen, Kang Wang, Yaxin Zhai, Haipeng Lu, Matthew C. Beard

Abstract: Ultrafast carrier dynamics at interfaces plays a major role in governing solar energy conversion efficiency in solar conversion materials, especially in solar cells and photoelectrochemical devices. Some recent ultrafast spectroscopic probes have been developed to understand the dynamics at interfaces. Transient reflectance enables monitoring of the surface carriers that are within ~ 10 nm of the surface or interface of interest. Cruicial parameters such as surface recombination and carrier diffusion can be determined. When a strong surface or interfacial field is present the reflectance spectrum will exhibit Franz-Kelydesh oscillations. Monitoring the transient formation or decay of such oscillations informs upon the interfacial field. Such fields are helpful in designing systems in order to move carriers away from surfaces where photocorrision can occur and towards catalytic surfaces. Finally, transient infrared attenuate total reflection can be used to probe the ultrafast reaction intermediates in a photo-driven chemical reaction.

Institution: National Renewable Energy Lab

Code: FUNDPhoto_P33

Presenter: Mr. Arnab Ghosh (IND)

Abstract Title: Ultrafast Photo-Induced Processes in Polymer-Based Nanostructures

Co-Author(s): Prof. Amitava Patra

Abstract: Ultrafast Photo-Induced Processes in Polymer-Based Nanostructures
Arnab Ghosh, Amitava Patra*

The recent emergence of the conjugated polymer-based nanostructured materials has stimulated a lot of interest in developing light-harvesting systems because of their engrossing photo-induced properties. Upon photoexcitation, several ultrafast photo-induced processes can occur parallelly inside polymer nanoaprticles along with the relaxation of the optically populated excited state. This involves both intra/ intermolecular modes and takes place on very short timescales. We have probed the formation of nanoparticles and their collapsing mechanism from extended form was understood. Ultrafast spectroscopic analysis and time resolved anisotropy indicate fast depolarization process arises due to interchain energy transfer in collapsed state. We will also present a brief overview of crucial ultrafast photoinduced processes, namely excition diffusion and sensitization of singlet fission, and illustrate their mode of function in polymer based nanostructures. After obtaining knowledge about fundamental photophysics of conjugated polymer nanoparticles, we designed hybrid light-harvesting systems based on polymer naoparticles. They showed promising light-harvesting nature such as photocatalysis, photovoltaics; where significant charge separation occurs due to photoinduced electron transfer. Ultrafast femtosecond up-conversion and transient absorption spectroscopy unequivocally confirms the energy-funneling followed by electron transfer from excited state polymeric donor to acceptor of nanocomposite. The fundamental understanding of the charge transfer dynamics open up new possibilities to design efficient light-harvesting system based on inorganic-organic hybrid system.
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Institution: Indian Association for the Cultivation of Science, Kolkata, India

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Code: FUNDPhoto_P34

Presenter: Michelle Chen (USA)

Abstract Title: State Mixing Determines the Fate of the Multiexciton State in Singlet Fission

Co-Author(s): Michael R. Wasielewski, Aritra Mandal, Matthew D. Krzyaniak, Ryan M. Young, Youn Jue Bae, Eileen D. Foszcz, et al.

Abstract: Singlet fission (SF) is a photophysical process in organic systems in which a singlet exciton, 1(S1S0), down-converts into two triplet excitons via a multiexciton correlated triplet pair state, 1(T1T1). The formation of the 1(T1T1) state is complex and can involve additional states. Using 2D electronic spectroscopy (2DES), we studied a covalently linked, slip-stacked terrylene-3,4:11,12-bis (dicarboximide) dimer (ss-TDI2) to elucidate the role of the charge transfer (CT) state and vibronic coupling. ss-TDI2 undergoes rapid SF in non-polar 1,4-dioxane. According to 2DES, the spectral features in 1,4-dioxane have pump wavelength dependencies, which suggests that the multiexciton state is a mixed state with variable 1(S1S0), 1(T1T1), and CT contributions that evolve over time. 2DES of ss-TDI2 in CH2Cl2 reveals the presence of a state having predominantly 1(T1T1) character during symmetry-breaking charge separation. Furthermore, we studied a linear TDI dimer (lin-TDI2) in which the two TDIs are directly linked at their imides. According to femtosecond transient absorption spectroscopy, lin-TDI2 undergoes ultrafast SF to form the (T1T1) state. The (T1T1) state's spin dynamics were studied in lin-TDI2 aligned in 4-cyano-4’-pentylbiphenyl (5CB), a nematic liquid, at room temperature. Time-resolved electron paramagnetic resonance revealed that the (T1T1) state has mixed 5(T1T1) and 3(T1T1) character; this spin mixing is magnetic field dependent with a maximum triplet yield at ~200 mT. Mixing with the 3(T1T1) state promotes a triplet-triplet annihilation pathway that produces a single uncorrelated triplet. These results emphasize that understanding the electronic and spin character of the multiexciton state is critical to ensure high-yielding SF.

Institution: Northwestern University

Code: FUNDPhoto_P35

Presenter: Dr. Shambhavi Tannir (USA)

Abstract Title: Mallory Photocylizations: Using Temperature as a Tool to Enhance Helicene Formation

Co-Author(s): Prof. Edward L. Clennan

Abstract: The photochemical dehydrogenation, referred to as the Mallory photocyclization, is a pioneer reaction for formation of helicenes and other polyaromatic hydrocarbons. Four bis-Mallory photocylization substrates have been examined from both experimental and computational (B3LYP/6-311+G(2d,p)) perspectives. Only one of the substrates showed the formation of all the three possible regioisomers at room temperature. The other three substrates only produced the two C2-symmetric products and not the C1 product. For these three reactions it was found that a low photocylization temperature (< 0oC) resulted in the exclusive formation of the helicene regioisomer despite the fact that the other potential isomers that could form are 11.0, 10.7, and 12.2 kcal/mol more stable. This is due to three factors: (1) the DHP (dihydrophenanthrene) precursors of these two sets of regioisomers are closer in energy (<5 kcal/mol) than the helicene products; (2) the extinction coefficients of the DHP precursors to the helicenes are smaller than that of the DHP precursors of their competitively formed regioisomers by a factor of 4.8-9.2: (3) thermal decomposition of intermediates are suppressed at low temperatures. These factors taken together allow the formation of a photostationary state dominated by the helicene DHP precursor. We have also conducted calculations at the B97D/cc-pVDZ computational level for a helicene with an extended acene appendage to further explore the scope of photostationary state driven helicene formation.

(1) J. Org. Chem. 2019, 84, 2, 817-830.

Institution: University of Wyoming

Code: FUNDPhoto_P36

Presenter: Chavdar Slavov (DEU)

Abstract Title: En route to new functional nanostructures – properties of multiazobenzene systems

Co-Author(s): C. Slavov, C. Yang, C. Boumrifak, L. Schweighauser, A. H. Heindl, S. Bellotto, T. Stauch, H. A. Wegner, A. Dreuw, J. Wachtveitl

Abstract: Azobenzene derivatives are extensively utilized as photoswitches for precise and non-invasive control of nanostructures and chemical reactions.[1] The popularity of azobenzenes is due to the large spectral and geometrical changes that the molecule undergoes after E ↔ Z photoisomerization.[1] While the photochromic properties and the dynamics of single azobenzenes is studied in detail[1], the behavior of connected azobenzenes is not well understood yet[2].
We combine ultrafast spectroscopy and quantum chemical calculations to investigate the properties of linear and cyclic bis- and tris-azobenzenes.[3-7] Our studies show that the spectral characteristics, the ultrafast photochemistry and the isomerization quantum yields of these systems are strongly altered. We reveal that the arrangement and the interaction between the individual photoswitching units give rise to new and versatile effects like intramolecular excitonic coupling, extended π-delocalization, molecular strain, etc. Furthermore, we develop a concept for a single-molecule triple photoswitch, with selectively addressable units that can be utilized in functional nanomaterials as a hub integrating the response to different signals. In the light of the wide spread construction and utilization of photoresponsive compounds, our studies bring important molecular insights.

Funding: DFG (WA 1850/4-2, WE 5601/6-1)
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Institution: Institute of Physical and Theoretical Chemistry, Goethe University, Frankfurt, Germany

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Code: FUNDPhoto_P37

Presenter: Joshua Scott Brown (USA)

Abstract Title: Fragment Basis Tight Binding Model

Co-Author(s): Bjoern Baumeier, Jens Whener, Sean Shaheen

Abstract: Polymeric semiconductor materials defy easy electronic structure characterization due to the inherent disorder in their molecular conformations. Here, a divide-and-conquer computational approach is realized for calculating the electronic structure of large systems with linear scaling. The approach is effective for reducing the performance cost of both DFT and Hartree-Fock (HF) methods that are known to scale as N2-N3 and N3-N4, respectively. The method is designed specifically for pi-conjugated molecules of rigid, aromatic rings connected by single carbon-carbon bonds along the backbone. The polymer chains are separated at their single carbon-carbon bonds into two categories of fragments: the first consisting of individual aromatic rings, and the second consisting of aromatic rings and their nearest-neighbors. After running ground state self-consistent calculations on both categories of fragments, the tight binding coupling elements may be determined by projecting the smaller fragments onto the larger ones. Using tight binding theory on a fragment level, it is then possible to calculate all of the molecular energies of the full molecule. Preliminary results using P3HT (8 monomers in length) show less than 1% error in the HOMO and LUMO energies and minimal error in the charge probability distributions along the backbone when used with low-level STO-3G or 3-21 basis sets. Though promising, the approach is susceptible to all the limitations of the tight binding approximation albeit on a fragment level.

Institution: CU Boulder

Code: FUNDPhoto_P38

Presenter: Fumika Kiryu (JPN)

Abstract Title: Study of Structure-Motion Relationship of Cytoskeletons by Using Laser-Fabricated Dynamic Microtubule Networks

Co-Author(s): T. Takeshige, K. Takano, C. -S. Wu, Y. -H. Shih, S. Nakabayashi, T. Sugiyama, R. Kawamura, H. Y. Yoshikawa

Abstract: Microtubule which consists of tubulin, a hetero dimeric protein, is one of the major cytoskeletons that exist in the cytoplasm of cells. It is well-known that collective motions of microtubule networks play significant roles for various dynamic functions of cells such as cell division and flagella movement. So far, to understand its structure-motion relationship, self-organization methods have been widely used to reconstruct microtubule networks in vitro. However, such spontaneous process cannot allow for the spatiotemporal control of reconstruction of highly ordered microtubule networks. In this work, we have studied structure-motion relationship of microtubule networks that were reconstructed harnessing a focused laser beam. We found that various network structures of microtubules (e.g., radially, linearly, or randomly oriented) could be prepared by the photophysical effects (photon pressure and temperature elevation) via the focused irradiation with a near-infrared continuous-wave Nd3+: YAG laser (λ = 1064 nm) through an objective lens (NA = 0.90). Interestingly, the laser-fabricated microtubule networks showed active movements depending on their structures in the presence of motor proteins (kinesins) and chemical energy (ATP), indicating that the microtubules obtained by the laser irradiation were biochemically intact. In particular, ordered microtubule networks made from intermolecularly crosslinked tubulin dimers by chemical reaction showed flagellum-like rotational motions that were not observed for those without the crosslinking. We expect the laser method enables us to study the critical structures in the cytoskeletal networks that can regulate various dynamic cell functions.

Institution: Saitama University

The 29th International Conference on Photochemistry

Boulder, Colorado
July 21 – 26, 2019

DEVICE-INSPIRED PHOTOCHEMISTRY AND PHOTOPHYSICS (DEVInsp) ABSTRACTS

INVITED TALKS

Code: DEVInsp_I1

Presenter: Carlos Silva (USA)

Abstract Title: Optical Dephasing by Exciton-exciton Scattering in Two-dimensional Metal-halide Hybrid Perovskites

Co-Author(s): F. Thouin, D. Cortecchia, A. Petrozza, A. R. Srimath Kandada

Abstract: Quantum-well like derivatives of organic-inorganic perovskites are emerging material systems where strongly bound two-dimensional excitons are being exploited in efficient light-emitting technologies. Given that such devices operate at relatively high excitation densities, it is crucial to comprehend exciton-exciton interactions for further material optimization. Here, we identify and quantify the photophysical factors that govern the multi-body interactions in (PEA)2PbI4 (PEA = phenylethylammonium), a prototypical 2D perovskite. Employing high-sensitivity coherent non-linear spectroscopy, we measure the homogenous linewidth of multiple excitonic transitions. By following the evolution of the linewidths with temperature and excitation density, we obtain pertinent insights into the exciton-phonon and exciton-exciton interactions. Importantly, we observe that the probability of exciton-exciton scattering is an order of magnitude smaller than 2D single layers of transition metal dichalchogenides in spite of equivalent exciton binding energies.

Institution: School of Chemistry and Biochemistry, Georgia Institute of Technology

Code: DEVInsp_I2

Presenter: Andrew Monkman (GBR)

Abstract Title: Vibrational Coupling Thermally Activated Delayed Fluorescence Boasted by Multiple Resonant Energy States

Co-Author(s): Marc Etherington, Daniel de Sa Pereira, Paloma Lays dos Santos

Abstract: Electroluminescence light generation in the best OLEDs has ~100% internal charge to photon conversion efficiency. This requires quantitative triplet to singlet excited state harvesting and has been the strict preserve of electrophosphorescent heavy metal complex emitters, until now. However, recently it has found that organic donor-acceptor (DA) charge transfer molecules can also yield such efficient triplet harvesting and OLEDS with 100% internal efficiency fabricated. Here the process of triplet harvesting is by thermally activated delayed fluorescence, 'TADF', i.e. E-type delayed fluorescence. From detailed photophysical measurements of intramolecular charge transfer (ICT) states especially temperature dependent time resolved delayed emission and photoinduced absorption the energy levels involved in the reversed intersystem crossing mechanism were elucidated 1, and through dynamic quantum chemical modelling, TADF modelled. Vibronic coupling second order spin orbit interactions dominate both ISC and reverse ISC (rISC) and we have shown how both D-A-D molecule structure and conformation control TADF 2, leading on to the demonstration of deep blue OLEDs having 22.4% EQE 3. Here I will explain these intriguing photophysical processes 4 and describe our latest TADF emitters that seem to break the laws of physics in having a PLQY ~1 and rISC rate > 10-7 s-1, i.e. faster triplet harvesting than an Ir complex!

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[4] Dias, F. B. et al. Advanced Science 3, 1600080 (2016).

Institution: Durham University

Code: DEVInsp_I3

Presenter: Maria Antonietta Loi (NLD)

Abstract Title: Cooling, Scattering and Recombination: The Role of the Material Quality for the Physics of Tin Halide Perovskites

Co-Author(s): Shuyan Shao, Simon Kahmann

Abstract: Tin-based perovskites have long remained a side topic in current perovskite opto-electronic research. With the recent efficiency improvement in thin film solar cells [1] and the observation of a long hot carrier cooling time in formamidinium tin iodide (FASnI3) [2], a thorough understanding of the material's photophysics becomes a pressing matter. Since pronounced background doping can easily obscure the actual material properties, it is of paramount importance to understand how different processing conditions affect the observed behavior.
Using photoluminescence spectroscopy, we therefore investigated thin films of FASnI3 fabricated through different protocols. We show that hot carrier relaxation occurs much faster in highly p-doped films due to carrier-carrier scattering. From high quality thin films, we extract the longitudinal optical phonon energy and the electron-phonon coupling constant, which are fundamental to understand carrier cooling. Importantly, high quality films allow for the observation of a previously unreported state of microsecond lifetime at lower energy in FASnI3, that has important consequences for the discussion of long lived emission features in the field of metal halide perovskites.

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Institution: University of Groningen, The Netherlands

Code: DEVInsp_I4

Presenter: Anunay Samanta (IND)

Abstract Title: Charge Carrier Dynamics and Single-Particle Photoluminescence of Caesium Lead Halide ($CsPbX_3$) Perovskite Nanocrystals

Co-Author(s): Navendu Mondal, Sudipta Seth, Apurba De, Tasnim Ahmed

Abstract: Great attention is being paid in recent years to both hybrid (organic-inorganic) and all-inorganic lead halide perovskite nanocrystals because of their potential in photovoltaic and photonic applications.1,2 However, despite growing interests in these substances, our understanding of the various channels of relaxation and dynamics of the photo-generated charge carriers that is key to exploitation of these materials in different applications, is still very limited. In this talk, we plan to highlight some of our recent work on this topic highlighting how femtosecond pump-probe and single-particle fluorescence based techniques can be effectively employed to obtain valuable information on the identity and energy states of the photogenerated species, pathways and dynamics of relaxation of the charge carriers (including their recombination), location and nature of the trap states and their role in fluctuation of the photoluminescence of caesium lead halide ($CsPbX_3$) perovskite nanocrystals.3-6

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6. Mondal, N; De, A.; Samanta, A. J. Phys. Chem. Lett. 2018, 9, 3673

Institution: School of Chemistry, University of Hyderabad

Code: DEVInsp_I5

Presenter: Xiaoyang Zhu (USA)

Abstract Title: Ferroelectric Polarons in Lead Halide Perovskites

Co-Author(s): K. Miyata, S. F. Maehrlein, P. P. Joshi

Abstract: Lead halide perovskites have been demonstrated as high performance materials in solar cells and light-emitting devices. These materials are characterized by coherent band transport expected from crystalline semiconductors, but dielectric responses and phonon dynamics typical of liquids. Here we explain the essential physics in this class of materials based on their dielectric functions and dynamic symmetry breaking on nano scales. We show that the dielectric function in the THz region may lead to dynamic and local ordering of polar nano domains by an extra electron or hole, resulting a quasiparticle which we call a ferroelectric large polaron, a concept similar to solvation in chemistry. Compared to a conventional large polaron, the collective nature of polarization in a ferroelectric large polaron may give rise to order(s)-of-magnitude larger reduction in the Coulomb potential. Using two-dimensional optical Kerr effect spectroscopy, we directly probe the energetics and local phonon responses of ferroelectric polarons. The ferroelectric polaron may explain the defect tolerance and low recombination rates of charge carriers in lead halide perovskites and the slow cooling of hot carriers, as well as providing a design principle of the “perfect” semiconductor for optoelectronics.

Institution: Columbia University

CONTRIBUTED TALKS

Code: DEVInsp_T1

Presenter: Kyle T. Munson (USA)

Abstract Title: Using Time-Resolved Infrared Spectroscopy to Investigate the Structural Origins of Slow Recombination in Halide Perovskites

Co-Author(s): John B. Asbury

Abstract: Solution-processed photovoltaics based on lead-halide perovskites have emerged as leading candidates to replace existing photovoltaic technologies because of their high photovoltaic performance (~23 %), and potential for low-cost, high-throughput production. The record efficiencies of perovskite photovoltaics are mainly because of the 1 µm carrier diffusion lengths (LD) and ~102 ns carrier lifetimes exhibited in this class of material. However, despite the rapid progress made in lead-halide photovoltaics, a comprehensive understanding of the material’s photophysics and the corresponding role of structural dynamics is still lacking. Such knowledge is critical for the development of design rules about how the electronic properties of perovskites depend on their composition and structure. Using time-resolved mid-infrared (TRIR) spectroscopy, we investigate the structural origins of slow recombination in lead-halide perovskites by probing the vibrational dynamics of the perovskite lattice’s $CH_3NH_3^+$ ions following optical excitation.1-2 We also use TRIR spectroscopy to characterize large polaronic states that form within the perovskite lattice by examining their spectral signatures in the mid-IR. Our work provides a new framework to understand how fluctuations of the perovskite lattice affect large polaron formation and recombination in this class of material. These findings also suggest that substitution of differently sized ions in halide perovskites can be used to tune the structural flexibility and therefore the self-tapping of charge carriers into large polarons.

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2.Munson et al., J. Phys. Chem. C. (2019), DOI: 10.1021/acs.jpcc.9b00555

Institution: Penn State

Code: DEVInsp_T2

Presenter: Tom Hopper (GBR)

Co-Author(s): Andrei Gorodetsky, Jarvist M. Frost, Robert Lovrincic, Maksym V. Kovalenko, Artem A. Bakulin

Abstract Title: Hot-carrier Dynamics in Lead-halide Perovskites: Role of Carrier Density, Nanoconfinement, and Surface Ligands

Abstract: The major efficiency limit in conventional solar cells is imposed by the rapid relaxation of above-bandgap “hot” carriers via electron-phonon coupling. Lead-halide perovskites (LHPs) currently hold the efficiency record for solution-processable solar cells, and previous observations of slow hot-carrier cooling in these materials have piqued a deeper interest into their application in disruptive next-generation photovoltaics. Here we implement an ultrafast “pump-push-probe” technique to study the sub-ps cooling dynamics in LHP thin films and nanocrystals (NCs). We demonstrate that cooling in the all-inorganic CsPbBr3 is slower than its hybrid counterparts (e.g. FAPbBr3) in the high hot-carrier density regime, owing to the relative abundance of optical phonon modes associated with the organic cation. We scrutinise the thermal equilibration between cold and hot states in the single- and multiple-exciton-per-NC cases, and remark on the effect of surface ligands on the cooling dynamics.

Hopper et al., ACS Energy Lett., 2018, 3 (9), pp 2199–2205

Institution: Imperial College London

Code: DEVInsp_T3

Presenter: Woon Yong Sohn (JPN)

Co-Author(s): Yuhei Taga, Kenji Katayama

Abstract Title: Time-Resolved Spectroscopic Study of Photo-Excited Charge Carrier Dynamics in Hematite: Effect of Re-Growth Treatment

Abstract: Hematite (alpha-Fe2O3), one of mineral forms of iron oxide, has been regarded as one of the best photo-anode materials for water splitting due to its high earth abundance, high photo-stability and low price. However, it is imperative that its low photoelectrochemical (PEC) performance, caused by multiple limiting factors such as poor conductivity, short electron-hole lifetime and poor charge carrier transfer/transport efficiency among others, must be improved for its implementation.

In order to make up for the weak points of hematite, various treatments have been tried such as surface coating with an overlayer, adding a dopant, heterojunction with other semiconductor material and so on. Among them, in 2015, Wang group in Boston college developed a fabrication method of a hematite film, in which surface disorders were reduced by a facile re-growth strategy. Using this method, they succeeded in obtaining both significantly low turn-on voltage (0.45 V) and high current density (1.2 mA cm-2). (Nature Communication, 2015, 6, 7447) Even though the performance improvement has been attributed to the reduction of the disorder in the previous study, the effect of this treatment on the charge carrier dynamics, playing crucial roles in the activity, has not been investigated yet so far. Therefore, in this study, we conducted a comparative study of the photo-excited charge carrier dynamics of bare and re-growth treated hematite films to obtain the direct evidence of the reduction of the surface disorders and a determining cause of the performance improvement, originating from the photo-generated charge carriers.

Institution: Chuo University

Code: DEVInsp_T4

Presenter: Kenneth P. Ghiggino (AUS)

Co-Author(s): Bolong Zhang, Wallace W.H. Wong

Abstract Title: Developing Large Area Luminescence Concentrator Devices

Abstract: Luminescent solar concentrators (LSCs) consist of highly fluorescent dyes embedded in, or coated on, transparent waveguide substrates. Light absorption by fluorophores over the large surface area of the LSC leads to luminescence that is concentrated by total internal reflection to the thin edge of the substrate where photovoltaic (PV) cells are located. Efficient large area LSCs require high emission yield dyes, low luminescence re-absorption effects and high light transmissive substrates. In addition, the PV cells should be well matched to the emissive properties of the LSC. We describe here how each of these requirements can be addressed to provide high performance LSCs. A series of sterically insulated perylene diimide dyes have been synthesized that resist concentration quenching and remain highly emissive in polymer substrates.[1] Combinations of different dyes can be formulated to provide energy transfer donor-emitter pairs that result in a large Stokes Shift while maintaining a high emission quantum yield thus minimizing luminescence reabsorption. LSCs are prepared by doctor-blade coating of dye-PMMA solvent mixtures onto PMMA substrates. Finally, PV cells matched to the emissive properties of the dyes are coupled to the LSC edges. We will describe details of a large area LSC device (400 cm2 area, geometric gain = 50) with a flux gain >7 and PCE > 2.5% under one sun irradiation that is amongst the best performance reported.

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Institution: University of Melbourne

Code: DEVInsp_T5

Presenter: Makoto Ebihara (JPN)

Abstract Title: Lifetime Mapping of Photo-excited Charge Carriers on TiO2 by Transient Grating Imaging

Co-Author(s): Woon Yong Sohn, Kenji Katayama

Abstract: Titanium dioxide (TiO2) is one of the most well-known photocatalyst due to its chemical stability and nontoxicity. Time-resolved techniques such as the transient absorption have been applied to study the charge carrier dynamics. Although most of photocatalytic substrates are made of nanoparticles and include many defects, it has been difficult to obtain the structure-dependent charge carrier dynamics, owing to the lack of the spatial resolution of the time-resolved techniques. In this study, we developed a new time-resolved imaging method called transient grating (TG) imaging, where the spatio-temporal refractive index change due to the photo-excited carriers can be visualized.

A sample was a nanoparticulate TiO2 film in contact with acetonitrile. In the TG imaging, a pulsed UV light with a stripe pattern was illuminated onto a sample and the refractive index change was imaged by a phase contrast imaging. We could observe the refractive index change due to the photo-excitation gradually increased for 1µs and decreased for 100 µs, corresponding to the decay of the surface trapped electrons and the thermal diffusion in TiO2/acetonitrile, respectively.1 In the TG imaging data, the local responses of the refractive index change at each pixel were analyzed with multi-exponential fitting and the lifetimes of the photo-excited carriers were mapped out. We successfully confirmed that the lifetimes of the carriers significantly depended on the position. We believe that this technique will pave a way to investigate local charge carrier behavior for the improvement of photocatalytic activity.

1) S. Kuwahara, Phys. Chem. Chem. Phys. 2016, 18, 25271.

Institution: Chuo University

Code: DEVInsp_T6

Presenter: Christopher J Collison (USA)

Abstract Title: Exciton Diffusion for Monomeric and H-aggregated Squaraines and the Impact on Efficiency in their Small-Molecule Photovoltaic De

Co-Author(s): Chenyu Zheng, Michael Mark, Tyler Wiegand, Jeremy Cody, Frank C. Spano, David McCamant

Abstract: Electronic aggregation and intermolecular charge transfer interactions strongly influence the excited state properties for organic solids, which dictate the effectiveness of these materials in optoelectronic devices.

We will first describe how excitonic coupling via long-range coulombic interaction in quadrupolar Squaraines diverges from established Frenkel exciton models when the intermolecular pi-stacking distance is small (~3-5 Å). We will further present the results of subpicosecond transient absorption spectroscopy, which probes the excited state photophysics of an anilino-squaraine, known for its successful use in the active layer of organic photovoltaic devices. Our samples are designed with a continuum of intermolecular separation from monomers in solution, through solid solution thin films, to the fully condensed phase, demonstrating the increasing contribution of short-range quadrupolar interactions. We measure excited state kinetics that confirm species assignments. The experimental results are in excellent agreement with our theoretical modeling. In conclusion we will combine theory and excited state characterization with our measured efficiencies in relevant small molecule organic photovoltaic devices.

The comprehensive explanation of device efficiencies and time-resolved excited state absorption spectroscopy with our excited state modeling leads us to recognize a far-reaching mechanistic bottleneck for molecular and polymeric bulk heterojunction devices.

Institution: Rochester Institute of Technology

Code: DEVInsp_T7

Presenter: Kyra Schwarz (USA)

Abstract Title: Capacitor-like Field Buildup in an Organic Solar Cell Inhibits Charge Recombination

Co-Author(s): PB Geraghty, VD Mitchell, SU Khan, B Kudisch, BP Rand, TA Smith, DJ Jones, KP Ghiggino, GD Scholes

Abstract: One of the greatest challenges for light harvesting technologies is the successful collection of mutually attracted photogenerated charges. In contrast to photosynthetic complexes where nanoscale structural sophistication aids in successful charge separation, organic bulk heterojunctions are dominated by complexity and disorder that are generally viewed as challenges to be overcome. Here, we report an unexpected sub-nanosecond build-up of electric field within an organic photovoltaic active layer following light absorption, which manifests as an intrinsic Stark effect, revealed with transient absorption spectroscopy. Local nanoscale morphology appears to cause the pooling of charges in pure crystalline domains—away from the donor-acceptor interface—and is resistant to recombination. These observations suggest that a particular bulk heterojunction morphology can cause the heterojunction to act as a capacitor, allowing charges to separate into electron and hole domains, while suppressing recombination and allowing charges to survive on relevant timescales. We relate this charge-pooling on the sub-nanosecond timescale to the prevention of loss pathways, improvement in device performance, and discuss its relevance as a broader design principle in heterojunction devices.

Institution: Princeton University

Code: DEVInsp_T8

Presenter: Dario M. Bassani (FRA)

Abstract Title: Evidencing Light-Induced Diffusion in Hybrid Organic Inorganic Perovskites and the Effect of Surface Passivation

Co-Author(s): Subha Sadhu, Thierry Buffeteau, Lionel Hirsc

Abstract: We pioneer the use of a surface-specific IR spectroscopy technique to probe how molecules deposit on the surface and diffuse into hybrid organic-inorganic perovskites.[1] Although surface passivation can considerably improve their performance, there is as yet little understanding on how molecules interact with the ionic crystal due to the lack of suitable experimental techniques. We show that PM-IRRAS can be adapted to work on perovskites to provide information on the density and orientation of molecules on the surface as well as the chemical nature of the molecules, much the same way as IR spectroscopy can be used to identify molecules in solution or in the solid.[2] Thanks to this technique, we are also able to follow the diffusion of protons from ambient humidity into the active layer and show that this is affected by surface passivation. Surprisingly, we find that the diffusion and/or exchange process is dependent on the incident irradiation intensity.

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Institution: University of Bordeaux

Code: DEVInsp_T9

Presenter: Navendu Mondal (USA)

Abstract Title: Revealing Ultrafast Exciton Dynamics of Two-Dimensional Single-Crystal Perovskites

Co-Author(s): Yuri Gartstein and Anton Malko

Abstract: Two dimensional (2D) perovskites offer unique optical and electronic properties owing to the complex interplay between inorganic layers comprising of lead halide octahedra and the organic layers that mostly consist of large ammonium cations. Unlike 3D counterparts, 2D-hybrid perovskites open up a large space to tune their optoelectronic properties by the wide variety of organic cations, whose influence in modulating these properties presents an ongoing research interest. Herein, with the aid of ultrafast spectroscopy, we explore the exciton dynamics of a new millimeter size 2D perovskite crystals, MA(en)PbBr4, where the organic cation is the derivative of methyl ammonium.

At low excitation density, band-edge excitonic bleach ~ 518 nm is described by a single-exponential decay with a time constant of >1.5 ns. While at moderate exciton density, a non-exponential decay component emerges and the decay dynamics vary quadratically with the exciton density. At higher exciton density, three-body Auger recombination prevails in the decay dynamics. In addition to the excitonic bleach signal, we also observe an instantaneous appearance of a broad long-lived (>10 ns) photoinduced absorption signal in the transient absorption measurements. In addition to the band-edge excitonic PL (~ 520 nm), we also observed an appearance of a wide PL band that is Stokes shifted to 615 nm. We found PL dynamics to be wavelength dependent (average lifetime at 520 and 615 nm is 2.3 and 13.6 ns, respectively), which is consistent with the formation of trapped exciton in this class of perovskites. The detailed knowledge on exciton dynamics and exciton many-body interactions will be useful in realization of high performance light-emitting devices based on 2D perovskite compounds.

Institution: UT Dallas

Code: DEVInsp_T10

Presenter: Christopher Hall (AUS)

Abstract Title: Imaging and Spectroscopy of Phase Segregation in Mixed-Halide Perovskite Single Crystals

Co-Author(s): Wenxin Mao, Anthony S. R. Chesman, Craig Forsyth, Yi-Bing Cheng, Noel W. Duffy, Trevor A. Smith, and Udo Bach

Abstract: Mixed halide perovskites (MHPs), such as CH3NH3Pb(BrxI1−x)3, represent an important class of materials with immense potential for use in photovoltaic and light emitting devices. However, it has been shown that Br/I based MHPs undergo phase segregation when exposed to light, yielding localized I-rich domains with reduced bandgap.[1] Recent work suggests phase segregated domains are localized to grain boundaries, motivating investigations into the role of boundary states and structure, as well as the development of methods for growing larger grains with reduced relative surface area.[2,3] We have recently developed a method for growing large (30×30×1 μm) monocrystalline MAPb(BrxI1−x)3 single crystals. In these we directly visualize the growth of I-rich domains throughout the entire crystal, revealing grain boundaries are not required for phase segregation.[4] With narrowband widefield fluorescence imaging and time-resolved spectroscopy we provide new insight into the nature of phase segregated domains and the collective impact on optoelectronic properties.

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Institution: School of Chemistry, University of Melbourne, Australia

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Code: DEVInsp_T11

Presenter: Marius Jakoby (DEU)

Abstract Title: Investigations of Singlet and Triplet Diffusion in Thermally-Activated Delayed-Fluorescence Emitters

Co-Author(s): Bryce S. Richards, Uli Lemmer and Ian A. Howard

Abstract: An interesting class of molecules under significant investigation for the harvest of triplet excitons in an organic light emitting diode is those displaying thermally activated-delayed fluorescence (TADF). In TADF molecules, the local triplet and singlet states are coupled by a spin orbit coupling charge transfer mechanism leading to an intermixing of both states. This property leads also to particular intriguing exciton transport, as it is defined by multiple cycles through singlet and triplet spin-configurations that have significantly different transport properties. Herein, we use Monte Carlo simulations to investigate how the singlet and triplet diffusion lengths can be experimentally established for this unique class of molecules. First, we show that if the triplet diffusion length is equal or longer than the singlet diffusion length both values can be accurately determined by a Stern-Volmer analysis based on charge-transfer type acceptors (i.e. fullerene derivatives). Second, we demonstrate if the triplet diffusion length is smaller than its singlet counterpart that triplet-only quenchers are favorable. Here, the Stern-Volmer analysis enables an accurate estimation of the triplet diffusion length in case the ‘static’ quenching occurring after inter-system crossing of singlet excitons is carefully corrected. Finally, and of interest to molecular design for devices, our studies show that poor triplet transport between the TADF molecules can ensure efficient transfer to a singlet emitter – so called hyperfluorescence, even when the fluorescent dopant is not sterically protected against triplet transfer. Thus, the design of TADF molecules with reduced triplet transfer is of interest, and should be experimentally possible.

Institution: Institute of Microstructure Technology,
Karlsruhe Institute of Technology,
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Code: DEVInsp_T12

Presenter: Nikolaos Droseros (CHE)

Abstract Title: What Determines the Open Circuit Voltage of Perovskite Solar Cells?

Co-Author(s): B. Dänekamp, D. Tsokkou, V. Brehm, P. P. Boix, M. Sessolo, H. J. Bolink, N. Banerji

Abstract: Despite the rapid increase in the efficiency (PCE) of perovskite solar cells, their open circuit voltage (Voc) limits their commercialization. Contradictory results exist in the literature concerning the dependence of the Voc on the ionization energy (IE) of the hole transporting layer (HTM) while different timescales have been reported concerning the injection of photogenerated holes from CH3NH3PbI3 even towards the same HTM. Here, we present a series of fully evaporated devices employing HTMs with different IEs. The Voc of the devices along with the processes of hole injection and trapping are studied in terms of ideality factors and fs-transient absorption (TA) spectroscopy. We prove that the Voc is mainly determined by the bulk and surface recombination rather than by the energetic offset between the valence band (VB) of the perovskite and the IE of the HTM. Furthermore, we find that hole injection competes with carrier thermalization and takes place from hot states in the VB independently of the IE of the HTMs. Finally, the observed difference in the timescale between hole injection and interfacial trapping is found to contribute to the high efficiency of the studied HTMs when employed in solar cell devices. Our results provide an understanding of the origin of the Voc and point to other crucial factors that should be considered when searching for novel HTMs rather than their IE.

References:

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Institution: Femtomat, Department of Chemistry and Biochemistry, University of Bern

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Code: DEVInsp_T13

Presenter: Linda Peteanu (USA)

Abstract Title: Electronic Coupling and Exciton Dynamics in Conjugated Polymer Aggregates

Co-Author(s): Stephanie Kramer, Jasper Brown, Anthony J. Varni, Kevin J. T. Noonan, Tomasz Kowalewski, David J. Yaron

Abstract: Fluorescent conjugated polymers to produce low-cost and lightweight organic electronics are of continued fundamental interest due to their unique photo-physical properties. These depend sensitively on the structure and packing of the polymer chains through this connection is challenging to control or predict. As the emission wavelengths and quantum yields of these materials are highly sensitive to their solid-state interactions, pre-aggregation in solution can assist in comparing properties through the transition between solution and solid state. Here we explore the impact of aggregation on the photo-physical properties of a variety of both well-known and novel organic semi-conducting polymers using bulk and single-molecule fluorescence-based methods.

In the case of the well-studied polymer, poly(3-hexylthiophene) or P3HT, addition of a highly-polar solvents to induce aggregation strongly quenches emission in solution though without a change in the lifetime. However, in the solid state the aggregates exhibit strong emission intensity combined with shorter lifetimes as demonstrated by fluorescence lifetime imaging microscopy (FLIM). To better understand the differences of the aggregate properties in the solution and solid state, fluorescence anti-bunching was used to probe the degree of electronic coupling of the polymer chains. These measurements revealed the highly collective nature of the P3HT aggregate emission, which likely accounts for its strong intensity in the solid state. This work is being extended to novel furan-based polymers that self-aggregate into helices. The goal is a better understanding of the aggregate properties to achieve better control and higher performance of organic semiconductors in device applications.

Institution: Carnegie Mellon University

Code: DEVInsp_T14

Presenter: Obadiah G Reid (USA)

Co-Author(s): N. A. Pace, J. E. Anthony, J.C. Johnson, G. Rumbles

Abstract Title: Slow Charge Transfer From Singlet Fission Triplets at the Marcus Optimum

Abstract: Singlet fission (SF) has the potential to significantly enhance solar cell performance if charges can be efficiently generated from the resulting triplet states. Here, we study charge separation from triplet excitons in polycrystalline pentacene using an electrochemical series of twelve different guest electron-acceptor molecules with varied reduction potentials, and we follow the SF and charge transfer dynamics using a combination of transient absorption spectroscopy and time-resolved microwave conductivity. We observe separate optima in the charge yield as a function of driving force for singlet and triplet excitons, including inverted regimes for the dissociation of both states. Molecular acceptors can thus provide a strategic advantage to SF solar cells by suppressing singlet dissociation at optimal driving forces for triplet dissociation. However, even at the optimal driving force, the rate constant for charge transfer from the triplet state is surprisingly small, ≤ 2 x 10^8 s^(-1), presenting a previously unidentified obstacle to the design of efficient SF solar cells.

Institution: University of Colorado Boulder

Code: DEVInsp_T15

Presenter: Sean T. Roberts (USA)

Co-Author(s): Emily K. Raulerson, Jon A. Bender, Brittany Pollok

Abstract Title: Designing Functional Interfaces for Triplet Energy Transfer

Abstract: Molecules that undergo singlet fission (SF) have garnered interest due to their ability to offset losses in photovoltaic and photocatalytic systems that stem from carrier thermalization, which account for ~50% of the energy lost by these technologies. Likewise, compounds that undergo SF’s inverse, triplet fusion (TF), can be paired with infrared absorbers to create structures that upconvert infrared into visible light. However, designing functional applications based on either process requires organic:inorganic junctions that readily transfer energy from one material to the other. In this presentation, I will describe our group’s efforts to produce organic:inorganic junctions that transmit excitons in a particular spin state. Specifically, I will describe work examining perylenediimide (PDI) films grown on Si(111). Photoexcitation of the PDI layer produces a spin-singlet exciton that undergoes SF over a few hundred picoseconds to yield a triplet exciton pair. Transient reflectivity measurements indicate these triplets are quenched at the Si(111) interface, suggesting triplet energy transfer from PDI to Si. I will also describe work on Si nanocrystals functionalized with acene triplet transmitting molecules. When placed in solution with appropriate TF materials, Si nanocrystal excitation drives photon upconversion of red to blue light with 7% efficiency. Importantly, we find triplet transfer from Si nanocrystals to molecules at their surface occurs via a single Dexter transfer step over 15 ns with an efficiency that can be pushed to >90%.

Institution: University of Texas at Austin

Code: DEVInsp_T16

Presenter: Koichi Yamashita (JPN)

Co-Author(s): Eisuke Kawashima, Mikiya Fujii

Abstract Title: Entropy Promotes Charge Separation in Bulk Heterojunction Organic Photovoltaics

Abstract: Charge separation is one of the crucial processes in the photoelectric conversion of organic photovoltaics. It is considered that organic photovoltaics have low performances because of strong Coulomb attraction. In this work, an entropy driven charge separation mechanism was elucidated using a graph algorithm and dynamic Monte Carlo simulations. Helmholtz energies were decreased by entropies, and had a barrier (240 meV–270 meV) at an electron–hole distance of 6 nm, Separation efficiencies at interfaces of large donor:small acceptor domains were lower than those at large donor:large acceptor domains, which can be attributed to their higher barrier—separation was promoted by a decreased barrier.

Institution: The University of Tokyo

Code: DEVInsp_T17

Presenter: David Jones (AUS)

Co-Author(s): Saghar Masoomi-Godarzi, Maning Liu, Yasuhiro Tachibana, Valerie D. Mitchell, Lars Goerigk, Kenneth P. Ghiggino, Trevor A. Smith

Abstract Title: Non-traditional Singlet Fission Materials

Abstract: Multiple exciton generation (MEG) through singlet fission (SF) is a spin allowed process whereby a singlet excited state is split into two triplet excitons. Inclusion of MEG chromophores into solar cells raises the maximum theoretical efficiency of a solar cell from the Schockly-Queisser Limit of 33% to around 45% by effectively harvesting the energy from high energy photons. In our efforts to produce high efficiency printed organic solar cells we had the desire to incorporate solution processible SF materials, however most of the reported SF materials are highly crystalline and either do not promote SF in the solid state, or controlling crystallisation is difficult. We aim to remove the local order constraint in high efficiency solid-state SF materials by, i) designing intra-molecular SF materials, and ii) using secondary self-association to pre-organise chromophores. Here we report our recent studies of new solid-state singlet fission materials using liquid crystallinity to promote the required self-assembly and to pre-organise triplet host chromophores. We have used the pi-pi stacking in a hexabenzocoronene (HBC) core Donor in an A-D-A intra-molecular SF materials to promote self-association, removing a requirement for local order in the triplet host chromophores (A = thienyl-diketopyrrolopyrrole (TDPP)). Thin films of the discotic liquid crystalline FHBC(TDPP)2 material form hexagonally packed columns and demonstrate a triplet yield of 150% in amorphous thin films, increasing to 170% in thermally annealed films.[1]

[1] Masoomi-Godarzi et al. (Submitted)

Institution: University of Melbourne

Code: DEVInsp_T18

Presenter: Magnus Borgar Fridriksson (NLD)

Abstract Title: The Relationship between Organic Cation Motion and the Low Temperature Phase Transitions in Hybrid Organic-inorganic Perovskites

Co-Author(s): Sudeep Maheshwari and Ferdinand Grozema

Abstract: Hybrid organic-inorganic perovskites are currently among the most promising materials for photovoltaic devices, but are also of interest for other applications, for instance in light-emitting diodes. They consist of an inorganic metal-halide (most commonly lead-iodide) cage structure in which the cavities in the structure are occupied by organic cations. The organic cations are usually freely rotating at room temperature but as the material undergoes a phase transition at low temperatures their rotational motion becomes severely restricted, leading to fixed orientations. Previously it has been shown that the orientations of the organic cation in the hybrid organic-inorganic perovskites can affect the electronic structure of the perovskite through its dipole. In this work we have used both molecular dynamics and Monte Carlo simulations to establish how the organic cations rotate and align at different temperatures, both above and below the phase transition temperature. Simulations have been performed for perovskites containing both methylammonium and formamidinium cations, which differ in the magnitude of their dipole. Furthermore, we shine a light on the cause-effect relationship between the lack of motion of the organic cation at low temperature and the phase transition, concluding that even without the phase transition the motion of the organic cations is severely hampered at low temperatures.

Institution: Delft University of Technology

POSTERS

Code: DEVInsp_P1

Presenter: Cristina Martin (BEL)

Abstract Title: New Hybrid Materials for Lighting Applications

Co-Author(s): Koen Kennes, Min Tu, Alex Cruz, Flip de Jong, Rob Ameloot, , Mark Van der Auweraer, Johan Hofkens

Abstract: The search for new smart-materials in solid-state light-emitting applications, like hybrid organic–inorganic light-emitting devices (OLEDs), has seen an intense growth in the recent years. Among all the possibilities, new composites materials like luminescent zeolites or metal-organic frameworks (MOFs) have been pointed out as one of the best candidates because their properties could be modulated by modifying the building blocks of their structure [1,2].

On this regard, in our research group, we explored the potential use of different nanostructured materials as light-emitting materials in the OLED architecture. Then, a profound spectroscopic characterization using different time-resolved spectroscopic tools were used to decipher their photo- and electrical behaviour. In this way, it was possible to unravel the dynamics of the materials and use this obtained information for a rational optimization in the OLED construction. For example, we found that the presence of different type of clusters or molecules inside of zeolites or MOFs could increase the charge carrier mobility as well as to tune the optoelectronic properties of the framework [3,4,5].

The obtained results will provide new insights into promising materials and will help to pave the way to a new type of easy, tuneable, hybrid, and cost-effective MOF-LEDs.

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2. I. Stassen et al., Chem. Soc. 2017, 46, 3185
3. K. Kennes et al., Adv. Funct. Mater. 2017, 27, 1606411
4. M. Gutiérrez et al., Adv. Opt. Mater. 2018, 6, 1701060
5. K. Kennes et al., ACS Appl. Mater. Interfaces. 2019, 11, 12179

Institution: Leuven Chem & Tech, Molecular Imaging and Photonics, KU Leuven, 3001 Heverlee, Belgium

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Code: DEVInsp_P2

Presenter: Muazzam Idris (USA)

Abstract Title: Phenanthro[9,10-d]imidazole as Hosts and Fluorescent Emitters for Hybrid White Organic Light-emitting Diode Application

Co-Author(s): Chan Ho So, Moon Chul Jung, Abegail Tadle, Karim Elroz, Peter I. Djurovich, Stephen R. Forrest and Mark E. Thompson

Abstract: In this work, we report hybrid fluorescent/phosphorescent WOLEDs employing blue fluorescent and green and red phosphorescent emitters doped into a host matrix. The fluorescent dopant harnesses all electrically generated high energy singlet excitons for blue emission, and the phosphorescent dopants harvest the remainder of lower-energy triplet excitons for green and red emission. This design requires the singlet state (S1) of the host to be higher than the S1 of the fluorescent dopant so that the singlet excitons generated on the host are transferred to the fluorescent dopant. Furthermore, the triplet state (T1) of the host matrix should be lower than the T1 of the fluorescent dopant so the triplet excitons generated on the fluorescent dopant can be transferred to the host matrix which will then be transferred to the green and red phosphors. To develop a host material that can serve this purpose, we tune the electronic properties of phenanthro[9,10-d]imidazole by incorporating phenyl and/or pyridyl moieties at the N1 and C2 positions of phenanthro[9,10-d]imidazole. This substitution resulted in a variety of host materials with different singlet/triplet energies, quantum efficiency, and redox values. The resulting phenanthro[9,10-d]imidazoles are employed as host materials for fluorescent and phosphorescent dopants and as neat fluorescent emitters. Monochromatic devices with a fluorescent emitter and the phenanthro[9,10-d]imidazoles as host materials or as neat fluorescent emitter achieved near theoretical maximum efficiency. Finally, efficient three-color hybrid WOLEDs were fabricated using the phenanthro[9,10-d]imidazoles as hosts for a fluorescent dopant or as neat fluorescent emitters and host for green and red phosphors.

Institution: Department of Chemistry, University of Southern California

Code: DEVInsp_P3

Presenter: Federica Ricci (USA)

Co-Author(s): Taesu Kim, and Theodore Goodson, III

Abstract Title: Coherent Energy and Charge Transport Processes in Oligothiophene Dendrimers Probed in Solution and in the Solid State

Abstract: Dendritic molecules demonstrate a broad variety of transfer processes under different geometric and coupling regimes, which can be utilized in photovoltaic applications. Conjugated dendritic systems have shown several advantages for organic photovoltaic applications compared to conjugated polymer and small organic molecules due to the extended π-conjugation chain.

In this work, coherent energy and charge transfer processes were investigated in different oligothiophene dendritic systems functionalized with diketopyrrolopyrrole (DPP) groups. Time-resolved spectroscopy in solution and two-photon interferometric near-field microscopy in the solid-phase have allowed us to compare coherent transport properties in solution and in organic films with high time (~50 fs) and space resolution (~40 nm).

For the first time, these methods have been compared in order to investigate ultrafast coherent dynamics in semiconducting organic materials. Investigation of coherent dynamics in photovoltaic organic materials is important as related to longer exciton diffusion length and to power conversion efficiency. Differences in the excited state coherent dynamics have been found in films compared to the solution phase. Interestingly, the dendron structure has shown higher charge delocalization in the solid-phase due to stronger intra- and inter-molecular couplings contribution compared to the dendrimer system.

Varnavski, O.; Kim, T.; Cai, Z.; Yu, L.; and Goodson, T. III Inhomogeneity of the Ultrafast Excited State Dynamics in Organic Photovoltaic Materials Measured at Nanoscale. J. Phys. Chem. C 2018, 122, 38

Carlotti, C.; Cai, Z.; Kim, H.; Sharapov, V.; Madu, I. K.; Zhao, D.; Chen, W.; Zimmerman, P.; Yu, L.; and Goodson, T. III Chem. Mater., 2018, 30 (13)

Institution: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

Code: DEVInsp_P4

Presenter: Fei Zheng (AUS)

Co-Author(s): Trevor A. Smith, Kenneth P. Ghiggino

Abstract Title: Investigating Photophysics and Structure in Layered Perovskite Films

Abstract: Layered perovskites composed of two-dimensional (2D) perovskite with a few layers (n) of metal halide octahedrons confined by long-alkyl-chain ammonium cation ligands, such as butylammonium (BA), have received growing attention due to their improved stability compared to conventional three dimensional (3D) perovskites when applied to photovoltaics. Due to the insulating nature of organic ligands, 2D perovskite layers are required to be vertically aligned to the substrate in perovskite solar cell devices to ensure high power conversion efficiency (PCE). However, the crystallization mechanism of layered perovskite when hot-cast from precursors with respect to the preferential spatial distribution of ammonium ligands remains controversial.[1, 2] A knowledge of this distribution profile is important to enable the optimization of layered perovskite solar cell device design protocol. In this work we have applied several experimental techniques that can provide information on the photophysics and structure information within hot-cast layered perovskite films nominally composed of (BA)2(MA)3Pb4I13. The techniques used include steady-state and time-resolved fluorescence, fluorescence anisotropy and evanescent wave spectroscopy that is powerful in the optical characterization of interfaces.[3] We will report our progress in revealing the energy harvesting mechanism involving exciton funneling and carrier diffusion as well as the distribution profile of the 2D perovskite layers present in these layered perovskite films for achieving long-term stable perovskite solar cells.

References:
[1]. A. Z. Chen, et al., Nature Communications, (2018) 9:1336.
[2]. Y. Lin, et al., Nature Communications, (2019) 10:1008.
[3]. T. A. Smith, et al., Reviews in Fluorescence, Springer: New York, 2005; pp245-270.

Institution: ARC Centre of Excellence in Exciton Science, School of Chemistry, The University of Melbourne, Australia

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Code: DEVInsp_P5

Presenter: Taylor Allen (USA)

Abstract Title: Photoinduced Electron Transfer Investigation in Molecular Organic Photovoltaic Systems

Co-Author(s): Joshua Carr, Bryon Larson, Obadiah Reid, Garry Rumbles

Abstract: Achieving high-performing, excitonic, organic photovoltaic (OPV) systems requires the careful selection of electron donating and accepting compounds whose electronic and optical properties maximize photoinduced electron transfer (PET). Previous work from our group showed that this can be accomplished by pairing high bandgap polyfluorene hosts with known ionization potentials (IP) and low bandgap fullerenes whose electronic affinities (EA) and exciton binding energies (Eex) are judiciously tuned to optimize the driving force (ΔG=IP-EA-Eex) for PET as described my Marcus theory in films with dilute acceptor. [1] While similar observations have been reported for other systems in the dilute regime [2], investigations at device-relevant concentrations where aggregation is probable are lacking in the literature. Poor insight regarding the influence of aggregation on PET presents a barrier to fundamentally understanding OPV systems that further precludes the intelligent design of systems and devices. In this study, we investigate a series of molecular systems whose aggregation can potentially be controlled to afford this information. IP and EA for this series are estimated by cyclic voltammetry with which accurate calculations of PET driving force (ΔG) are made. The rate of PET is measured via the yield mobility product obtained by time-resolved microwave conductivity in the solid state. Analysis is provided into the range of driving forces achievable by these systems and the outlook for their utility for OPV aggregation studies. References: 1) Coffey, D. C. et al. J. Phys. Chem. C. 2012, 116, 8916-8923, 2) Ihly, R. et al. Nat. Chem. 2016, 8, 603-609

Institution: National Renewable Energy Laboratory, Chemistry and Nanoscience Center

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Code: DEVInsp_P6

Presenter: Angela Muthike (USA)

Abstract Title: Using Ultrafast Spectroscopy to Investigating the Effect of Donor Conjugation Length and Acceptor Strength on the Photophysical

Co-Author(s): Keller, B., Cai, Z., Muthike, A. K., Sahu, P. K., Kim, H., Eshun, A., Zimmerman, P.M., Zhang, D., Goodson III, T.

Abstract: The most common organic light harvesting materials are designed by alternating different types of electron rich (donor) and electron poor (acceptor) moieties. In this way, researchers have found ways to control the HOMO and LUMO orbitals, which have an impact in their overall optoelectric performances. It has been suggested that the HOMO and LUMO energy levels of the polymers are mostly determined by the nature of the donor moiety and acceptor moiety, respectively. However, little is known on their impact on their excited state dynamics. In this study, we used time-resolved spectroscopy and nonlinear optical methods to investigate the influence of both, extending the conjugation length of the donor and changing the acceptor strength on the excited state dynamics of light harvesting polymers. The polymers were based on thiophene additions to s-Indacene donors with diketopyrroloryrrole, Isoindigo, and Thienothiophene as acceptors. The steady state absorption showed a bigger range of absorption in the visible spectrum for the polymers with extended conjugation length. The extinction coefficient was higher when the polymer possess a stronger acceptor subunit. The fluorescence up-conversion experiments revealed that the donor conjugation length increased the fluorescence lifetimes of the systems. The Two-Photon Absorption (TPA) experiments showed a higher TPA cross-section for the polymers with stronger acceptors moieties, which is consistent to polymers with higher charge transfer nature. The fs/ns time-resolved absorption studies revealed longer transient species recovery time for the systems with extended donor conjugation length, with no significant effect by the acceptor strength on the transient species.

Reference

Keller, B., Cai, Z., Muthike, A. K., Sahu, P. K., Kim, H., Eshun, A., Zimmerman, P.M., Zhang, D., Goodson III, T. Investigating the Optical Properties of Thiophene Additions to s-Indacene Donors with Diketopyrrolopyrrole, Isoindigo, and Thienothiophene Acceptors. The Journal of Physical Chemistry C, 2018. 122(48), 27713-27733.

Institution: The University of Michigan

Code: DEVInsp_P7

Presenter: Hwan Kyu Kim (KOR)

Abstract Title: Over 14% Efficiency Dye-Sensitized Solar Cells by Co-sensitizing Thieno[3,2-b]indole-Based Organic Dyes with a Promising Porphyr

Co-Author(s): Jung Min Ji

Abstract: Four 4-hexyl-4H-thieno[3,2-b]indole (HxTI) based organic sensitizers have been developed by donor structural engineering with different fluorenyl moieties. In comparison to a reference dye SGT-137 based on a biphenyl-based donor, the effects of the donating ability and bulkiness of the fluorenyl based donor in D–π–A-structured organic sensitizers on molecular properties and photovoltaic performance were investigated. The incorporation of fluorenyl donors into HxTI-based organic chromophores exhibited a bathochromic shift of the absorption band and an upshift of the highest occupied molecular orbital (HOMO) energy level along with the donating ability order of donor groups. The photovoltaic performances of dye-sensitized solar cells (DSSCs) were improved along with the trend in bulkiness of the donor groups. As a result, the DSSCs based on HxTI-based organic sensitizer with hexyloxy-phenyl substituted fluorenyl moiety (SGT-149) showed high power conversion efficiencies (PCEs) of 11.71% and 10.02% with a [Co(bpy)3]2+/3+ and an I-/I3- redox electrolyte, respectively. This result indicated that the substitution of hexyloxy-phenyl group onto fluorene could be a more effective design strategy to improve photovoltaic performance. Notably, the co-sensitization of SGT-149 with a porphyrin dye, by utilizing a simple “cocktail” method, showed state-of-the-art PCEs of 14.19% and 11.65% with a [Co(bpy)3]2+/3+ and an I-/I3- redox electrolyte, respectively.

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2. S. H. Kang and H. K. Kim, et.al., Adv. Energy Mater., 2017, 7, 1602117.
3. J. M. Ji and H. K. Kim, et.al., J. Mater. Chem. A, 2018, 6, 14518.

Institution: Korea University

Code: DEVInsp_P8

Presenter: Pavel A. Panchenko (RUS)

Co-Author(s): Anna S. Polyakova, Yuri V. Fedorov, Olga A. Fedorova

Institution: A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, 119991, Vavilova str. 28, Moscow, Russia

Abstract Title: Chemoselective Detection of Ag+ in Purely Aqueous Solution using Fluorescence «turn-on» Probe based on Crown-containing 4-methox

Abstract:

Determination of transition and heavy metals in aqueous media is of significant importance due to their hazardous effects on the environment and humans[1,2]. In the present work, a novel derivative of 4-methoxy-1,8-naphthalimide (MNI) bearing N-phenylaza-15-crown-5 ether receptor as N-aryl substituent attached to the N-imide nitrogen of the naphthalimide ring was evaluated as fluorescent probe for the detection of silver (I) ions in aqueous solutions at neutral pH [3].
The probe was configured as fluorophore–space–receptor system in which binding with metal cation triggers the fluorescence between «OFF» and «ON» states due to inhibition of the photoinduced electron transfer process (PET) in the excited state. Upon addition of Ag+ to the solution of MNI, the fluorescence intensity increases in a linear fashion covering the range from 0.5 μM to 3.5 μM; the detection limit is 3.8·10–7 M. Based on the fluorometric titration data, the calculated stability constant (lgK) of (MNI)·Ag+ complex is found to be 6.39 ± 0.07. Competition studies have shown that the other metal ions including Cu2+, Ca2+, Pb2+, Mg2+, Zn2+, Ni2+, Cd2+ don’t interfere the emission of silver (I) complex, however Hg2+ and Fe2+ have a little effect. Thus, the proposed sensor MNI can be applied to selective detection of Ag+ in purely aqueous media.

References:

[1] Velmurugan, K. et al., J. Photochem. Photobiol. A. 2017, 333, 130.
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[3] Panchenko, P. A. et al., Mendeleev Commun. 2019, 29, 155.

The 29th International Conference on Photochemistry

Boulder, Colorado

July 21 – 26, 2019

PHOTOCHEMISTRY USING NANOSTRUCTURES WITH ENHANCED OPTOELECTRONIC PROPERTIES (NANOpto)

ABSTRACTS

INVITED TALKS

Code: NANOpto_I1

Presenter: Uri Banin (ISR)

Co-Author(s): NONE

Abstract Title: Hybrid Semiconductor-metal Nanoparticles as Photocatalysts

Abstract: Semiconductor-metal hybrid nanoparticles (HNPs) combine disparate materials onto a single nanosystem thus providing a powerful approach for bottom-up design of novel architectures. Beyond the fundamental development in synthesis, the interest in HNPs arises from their combined and often synergistic properties exceeding the functionality of the individual components. These ideas are well demonstrated in the light-induced charge separation in HNPs, allowing photocatalytic activity which can promote light induced surface chemistry redox reactions. The latest chemical and physical aspects of HNPs as photocatalysts are the focus of this talk.

We will introduce a reductionist approach for studying the influence of various parameters of the photocatalytic HNPs on hydrogen generation from water. The effects of the surface coating, the co-catalyst metal size, and the light intensity into the regime of multiexcitons on the photocatalytic function of metal tipped semiconductor nanorods will be presented. Some aspects of the synthesis of a new generation of photocatalytic nanoparticles based on Zn-chalcogenides will be presented. An additional area of interest is in use of the HNPs for light-induced generation of radicals opening options for light-induced on-demand radicals formation with relevance for chemical, environmental and biomedical applications. The design and functionality of HNPs for this task and its potential applications will also be highlighted.

Institution: Institute of Chemistry & the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem

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Code: NANOpto_I2

Presenter: Gordana Dukovic (USA)

Co-Author(s): TBD

Abstract Title: Elucidating How Photoexcited Semiconductor Nanocrystals Drive Redox Enzyme Catalysis

Abstract: This presentation will focus on the coupling of semiconductor nanocrystals as light absorbers with redox catalysts for multi-electron transfer reactions to drive solar photochemistry. Reactions of interest include H2 generation, CO2 reduction, N2 fixation, and water oxidation. We have demonstrated that nanocrystal excited state behavior, charge transfer dynamics, and surface chemistry play a governing role in the overall photochemistry. This presentation will describe our most recent findings about how the reactions of interest can be driven and controlled through manipulation of nanocrystal excited state dynamics.

Institution: University of Colorado Boulder

Code: NANOpto_I3

Presenter: Sohee Jeong (KOR)

Co-Author(s): Hyekyoung Choi, Youngsik Kim, Jung Hoon Song

Abstract Title: III-V Colloidal Nanocrystals: Understanding the Surface for Enhanced Optoelectronic Properties

Abstract: Wet chemistry synthesis and shape/size control of III-V (InP, InAs) colloidal quantum dots (CQDs) has been challenging, compared to well-established synthetic solution chemistry for II-VI (CdSe, CdS) and IV-VI (PbS, PbSe) CQDs. The difficulty stems from the limited choices of precursors suitable for solution chemistry of the III-V materials. At more fundamental level, the difficulty lies in the inherent covalency of the III-V materials, which does not allow an easy solution chemistry to control their surfaces. Therefore, the key is how to control the surface chemistry of rather covalent III-V materials. Based on our previous experience on the atomic control of surface chemistry for IV-VI rock-salt materials, our recent understanding on the surface of III-V colloidal nanocrystal will be presented. Further attempts on designing the surface for enhanced optoelectronic properties of III-V nanocrystals will be discussed.

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Institution: Sungkyunkwan University

Code: NANOpto_I4

Presenter: Tim Lian (USA)

Abstract Title: Toward Unity Quantum Efficiency for Plasmon Induced Hot Electron Transfer at Metal/Semiconductor Junctions

Co-Author(s): none

Abstract: Excitation of plasmons in metal nanostructures can lead to the injection of hot electrons or holes into semiconductors or adsorbed molecules to drive plasmonic hot carrier photocatalysis. The efficiency of such processes are often low because of unfavorable initial hot electron distribution and the competing ultrafast hot electron relaxation processes within the metallic domain. In this talk, we discuss two approaches to enhance the efficiency of plasmon induced hot electron transfer. In the first approach, we explore the possibility of enhancing hot electron distribution by decreasing the size of plasmonic Au particles. Using CdS/Au nanorod heterostuctures, we show that the hot electron injection efficiency increases at smaller Au particle size. We attribute this size dependence to increasing contribution of surface assisted plasmon damping, which generates more hot electrons compared to damping by interband transition. In the second approach, we demonstrate that in CdSe/Au hetersostructures with strong metal/semiconductor coupling, the plasmon decays by direct excitation of an electron from the metal to semiconductor, i.e. plasmon induced interfacial charge transfer transition (PICTT) and hot electron transfer quantum efficiency of > 24% has been reported. We will discuss preliminary findings of highly efficient (quantum efficiency > 50%) plasmon induced hot electron transfer at plasmonic metal/oxide semiconductor interfaces and the generality of PICTT mechanism.

Institution: Emory University

Code: NANOpto_I5

Presenter: Emily Weiss (USA)

Abstract Title: Regio- and Diastereoselective Intermolecular [2+2] Cycloadditions Photocatalyzed by Qu

Co-Author(s): Yishu Jiang, Chen Wang, Cameron Rogers, Mohamad Kodaimati

Abstract: Tetrasubstituted cyclobutyl structures are precursors to, or core components of, many important bioactive molecules, including prospective drugs. Light-driven [2+2] cycloaddition is the most direct strategy for construction of these structures. [2+2] photocycloadditions that proceed through the triplet excited state are advantageous because (i) their scope is not limited by the electrochemical potentials of the substrate, (ii) triplets have long enough lifetimes to mediate intermolecular cycloadditions, and (iii) triplets can be accessed using visible light through excitation of a triplet sensitizer followed by triplet-triplet energy transfer (TT EnT). Synthetic applications of [2 + 2] photocycloadditions however also demand high selectivity, not only for specific coupling products, but also for particular stereo- and regioisomers of those products. Achieving selectivities for (i) a particular regioisomer of the coupled product, (ii) a particular diastereomer of the coupled product, and (iii) homo- vs. hetero-coupling within a mixture of reactive olefins still remains a challenge. Here, we discuss the use of colloidal CdSe quantum dots (QDs) as visible light absorbers, triplet exciton donors, and scaffolds to drive homo- and hetero-intermolecular [2+2] photocycloadditions of 4-vinylbenzoic acid derivatives, with (i) perfect and switchable regioselectivity and (ii) 97-98% diastereoselectivity for the previously minor syn-head-to-head (HH) or syn-head-to-tail (HT) configurations of the adducts. The diasteromeric ratios (d.r.) we achieve are a factor of 5 - 10 higher than those reported with all other triplet sensitizers. Furthermore, the size-tunable triplet energy of the QD enables regioselective hetero-intermolecular couplings through selective sensitization of only one of the reagent olefins.

Institution: Northwestern University

CONTRIBUTED TALKS

Code: NANOpto_T1

Presenter: Li-Kang Chu (TWN)

Abstract Title: Radiative Cooling of Surface-Modified Gold Nanostructures upon Photoexcitation

Co-Author(s): Jia-Ling Liu, Shao-Syuan Guo

Abstract: A step-scan time-resolved Fourier-transform infrared spectrometer was employed to record the photothermal infrared emissions of gold nanoparticles (AuNPs) and nanorods (AuNRs) upon irradiation. The photoexcitation of the surface plasmonic resonance bands of the AuNPs capped with different agents (AuNP@X, X = citrate, CTAB, and mPEG) with a 532-nm nanosecond pulsed laser leads to a transient infrared emission within 1 µs. Compared with the blackbody radiations, the near nascent temperature of the AuNP@mPEG reached ca. 400 degree Celsius in 90–120 ns. Unchanged morphology and size distribution of AuNP@mPEG suggested that the surface modification via covalent bonding helped retaining the morphology of the nanostructures after laser heating [1]. In addition, transient IR emissions of AuNR@X (X = CTAB, PSS, mPEG, and silica) upon ca. 70-µs pulsed 1064-nm excitation of their longitudinal surface plasmonic bands were recorded [2]. The emission contours included the blackbody radiation and additional emission intensities at 1300-1000 wavenumbers that were attributed to the vibrational modes of capping materials. Moreover, the IR emission of AuNR@silica was more prolonged (1 ms) than those of the other three (300 µs). We proposed that the photothermal energy can be efficiently randomized to the internal degrees of freedom of the soft molecular capping materials but can be stored by the rigid ones, e. g., silica, followed by extended radiative cooling.

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[2]Guo, S.-S.; Chu, L.-K.* J. Phys. Chem. Lett. 2018, 9, 5110-5115.

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Code: NANOpto_T2

Presenter: Jino George (IND)

Abstract Title: Cavity Catalysis: Controlling Chemical Reactions by Coupling to Vacuum Field

Co-Author(s): Jyoti Lather, Pooja Bhatt, Anoop Thomas, Thomas W. Ebbesen

Abstract: Coherence chemistry was introduced to control a chemical reaction very preciously by targeting a vibrational state. However, this process is less efficient due to intramolecular vibrational relaxation (IVR) processes in the system. Here we introduce an efficient way of controlling a chemical reaction by coupling to vacuum field (zero-point-energy).[1] A Fabry-Perot cavity tuned to a fundamental vibrational mode of the reactant or the solvent molecules by vibrational strong coupling (VSC), result in the opening of Morse potential envelope, that modify the bond dissociation energy. This process is called as cavity catalysis.[2] Here, we explain our first observation of cavity catalysis of a simple ester hydrolysis process by collective VSC of selective vibrational bands that involved in the bond making/breaking process.[3] Such catalysis is highly sensitive to cavity tuning and exponentially varies with collective coupling strength. This different way of controlling chemical reaction has immediate impact on chemistry.

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[2] ChemRxiv 2018, https://doi.org/10.26434/chemrxiv.7234721.v3
[3] ChemRxiv 2018, https://doi.org/10.26434/chemrxiv.7531544.v1

Institution: Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Punjab-140306, INDIA

Code: NANOpto_T3

Presenter: Tomohiro Fukushima (JPN)

Abstract Title: Plasmonic Metal Nanostructure Enables Photo-Modulation of Proton Transport

Co-Author(s): Motohiro Sai, Kei Murakoshi

Abstract: Control of dynamic motion of ions and molecules is challenging. Faster mobility of ion species is useful for ion conductor, which is useful for electrochemical application such as fuel cell or electrolyzer. On the other hand, stimuli-responsive ion conductivity is still limited due to the thermal diffusion nature. Here we utilize plasmonic metal nanostructure enabling the controlled proton conductivity. Metal nanoparticles in Nafion membrane were prepared by ion exchange and chemical reduction. Metal nanoparticle incorporated Nafion are denoted as M-Nafion. The existence of metal nanoparticles were confirmed from the extinction spectra. Temperature dependent measurements were investigated and M-Nafion shows smaller activation energy barrier, which can be assigned to the tunneling mechanism of protons. In order to investigate the structural origin of the proton conductivity, nuclear magnetic resonance (NMR) spectroscopy was conducted. We found that Ag nanoparticle influenced on the relaxation time of water molecules, and water molecules were segregated to the mobile and frozen phase in Nafion. On the other hand, Ni-Nafion showed very broad signal under downfield in chemical shift, strong interaction between electron spin and nuclear spin. We further investigated photo-irradiation effect of proton conductivity of water molecules in Nafion. Interestingly we investigated that proton conductivity is actually dependent on light intensity under even weak white light irradiation (~3 mW cm-2). Photo-induced switching of conductivity and energy-dependence will be discussed based on the metal nanostructure. The observed results clearly suggest that plasmonic metal nanostructure can be utilized for the stimuli-responsive modulation of proton conduction.

Institution: Department of Chemistry, Faculty of Science, Hokkaido University

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Code: NANOpto_T4

Presenter: Hui Fang (USA)

Abstract Title: Photoexcited Electron Dynamics in Ag Nanoplatelets Adsorbed on TiO2 Nanorods

Co-Author(s): Yi Rao, Jianqiang Ma, Danielle L. Kuhn, Zander Zachary, Brendan G. DeLacy, and Hai-Lung Dai

Abstract: Ultrafast dynamics of photoexcited electrons in Ag nanoplatelets adsorbed on TiO2 nanorods, a nanocomposite that may have potential for photosensitized voltaic applications is studied using femtosecond transient infrared (IR) absorption spectroscopy. Hot electrons are generated in Ag nanoplatelets through plasmonic excitation by a femtosecond light pulse at 400 nm. Injection of the photoexcited electrons and the following dynamics processes in TiO2 nanorods, in the conduction band, are probed by the absorption of femtosecond pulses in the mid-IR range with varying time delay. The observed transient absorption response is analyzed by a model that includes hot electron injection, hot electron relaxation, band edge electron annihilation, electron diffusion from the surface to bulk, and electron back diffusion from bulk to surface. The corresponding time constants are extracted to be around 13 fs, 0.8 ps, 6 ps, 14 ps, and 70 ps, respectively. It is significant to note that the electron injection from the Ag platelets is occurring at a rate much faster than that from Au to TiO2, which is one order of magnitude faster than that from dye molecules to the semiconductor. The characterization of the electron dynamics is useful for mechanistic understanding and designing of efficient photovoltaic and photocatalysis devices.

Institution: Temple University

Code: NANOpto_T5

Presenter: Jao van de Lagemaat (USA)

Abstract Title: Electrochemically and Plasmonically Modifying the Interfacial Thermodynamics, Excitonic and Charge Transfer Kinetics of 2D Trans

Co-Author(s): G. Michael Carroll, Jeremy Dunklin, Aaron Rose, Hanyu Zhang, Elisa M. Miller, and Nathan R. Neale

Abstract: In this study, we investigate the modulation of (photo)catalytic fuel forming reactions in nanoscale two-dimensional transition metal dichalcogenide (TMDC) systems using electrical, optical, and plasmonic modulation of excitonic and electronic states. Few-layer MoS2 and WS2 were studied in conditions relevant to their use in photoelectrochemistry. The applied electric field under these conditions causes uniaxial tensile strain indicating strong structural changes of the (photo)electrocatalyst. We also show that electron injection into the conduction band is coupled with a red-shift of the exciton resonance and that band gap reduction and modification of electron injection rates occur under photoelectrochemical hydrogen evolution conditions. These observations do not follow the classical description of the free-energy of charge transfer at the semiconductor interface pioneered by Marcus and Gerischer and have strong implications for the scientific understanding of (photo)catalytic fuel forming reactions using two-dimensional systems.
Concurrently, we study the photoexcited dynamics of TMDCs and how coupling to plasmonic systems can generate active polariton states that modify the energetics and dynamics of photo(electro)chemical reactions on the TMDCs; this potentially enables overall water splitting from systems that normally can’t energetically. The coupling to plasmons is enabled both from directly growing plasmonic nanoparticles on the TMDCs or by depositing TMDCs directly on metal substrates. We show this coupling permits both manipulation of the energy levels and dynamic changes related to hot carrier generation and transfer. Use of these effects in water splitting systems is investigated.

Institution: National Renewable Energy Laboratory

Code: NANOpto_T6

Presenter: Susumu Kuwabata (JPN)

Abstract Title: Photoluminescence Property of Band-edge Emission from AgInS2/Ga2S3 Core/shell Quantum Dots

Co-Author(s): Taro Uematsu, Tatsuo Kameyama, and Tsukasa Torimoto

Abstract: I–III–VI semiconductor nanoparticles are promising candidates for non-toxic quantum dots[1,2]. It has, however, not been achieved yet to remove defect levels responsible for their broad-band emission. In the present study, coating of core AgInS2 nanoparticles possessing a bandgap in the visible region with III–VI group semiconductors has been attempted. The prepared AgInS2/InSx and AgInS2/GaSx (x = 0.8–1.5) core/shell structures generate intense narrow-band photoluminescence originating from a band-edge transition at a wavelength shorter than that of the original defect emission. Microscopic analyses reveal that the GaSx shell has an amorphous morphology, which is quite different from the typical shell materials such as crystalline lattice-matching ZnS. Single particle spectroscopy shows that the average linewidth of the band-edge photoluminescence is as small as 80.0 meV, which is comparable with that of industry-standard II–VI semiconductor quantum dots. In terms of photoluminescence quantum yield, a value of 56% with nearly single-band emission has been achieved as a result of several modifications to the reaction conditions and post-treatment to the core/shell nanoparticles. These results indicate the increasing potential of AgInS2 nanoparticles for use as practical cadmium-free quantum dots [3].

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[2] T. Torimoto, et al., J. Phys. Chem. Lett., 2014, 5, 336.
[3] T. Uematsu, et al., NPG Asia Materials, 2018, 10, 713.

Institution: Graduate School of Engineering, Osaka University

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Code: NANOpto_T7

Presenter: María C. Gélvez-Rueda (NLD)

Abstract Title: Efficient Photo-generation of Mobile Free Charge Carriers in 2D Hybrid Perylene Diimide-perovskite Nanoplatelets

Co-Author(s): Magnus B. Fridriksson, Ward van der Stam, Rajeev K. Dubey, Wolter F. Jager and Ferdinand C. Grozema

Abstract: Two-dimensional perovskites are an emerging new class of materials with potential application in a broad range of opto-electronic devices. These materials are formed by layers of inorganic metal-halide octahedrals separated by large organic cations. The organic cations improve the stability and give a large freedom to tune the opto-electronic properties. However, the organic cations used so far act only as a dielectrical non-conductive layer that contributes to the large exciton binding energy of these materials. This large binding energy limits their application in opto-electronic devices in which efficient charge carrier separation is required (such as solar cells, photo-detectors and photo-catalists). In order to achieve charge separation, we have replaced non-functional organic cations by a strongly electron accepting moiety: perylene diimide (PDI) in 2D CsPbBr3 nanoplatelets. We show by ultrafast transient absorption and fluorescence that photoexcitation of these perovskite nanoplatelet:PDI conjugates leads to fast quenching of the fluorescence, fast decay of the bleach of the nanoplatelets and the appearance of a photoinduced absorption feature specific for the the PDI anion. This latter feature unequivocally shows that the fluorescence quenching is due to electron transfer to the PDI molecules. Finally, we show by time-resolved microwave conductivity (TRMC) measurements that this charge transfer leads to long-lived hole conduction (tens of microseconds) in the two-dimensional perovskite nanoplatelets. This opens up a new approach, where the properties of two-dimensional perovskites can be tuned for specific device applications by introduction of strong functional dyes in the organic component of the material.

Institution: Delft University of Technology

Code: NANOpto_T8

Presenter: Cansel Temiz (NLD)

Abstract Title: Effect of Substitution Pattern on the Self Assembly of Hexa-peri-Hexabenzocoronene Derivatives in Solution and Solid State

Co-Author(s): Elena Galan, Rienk Eelkema, Ferdinand C. Grozema

Abstract: This study aims to achieve control over charge and excited state dynamics in hexa-benzocoronenes (HBC) by engineering the way they organize in the solid state. Due to the steric hindrance of the side chains, neighboring HBC molecules in the pi-stack are typically rotated by 30 degrees with respect to each other. Interestingly, DFT calculations of the charge transfer integral between neighboring molecules have shown that this is the least favorable conformation for charge and exciton transport.1 Despite the interest in varying the side chains attached to self-assembling HBC molecules, knowledge on the effect of substitution location of these side chains is almost completely absent. Therefore, in this work, we propose novel meta-position substitution in comparison with well-known para-position substitution on HBC molecules. We have examined the effect of the substitution position the self-assembly properties of HBC molecules in solution and in the solid state. Concentration and temperature dependent UV-vis, PL and NMR measurements show that both para- and meta-HBC derivatives starts aggregating at very low concentrations, in common solvents. In the solid state, XRD measurements show that the position of the side chains have a distinct effect on the assembly in the solid state. We have analyzed the solid-state charge transport properties by using unique PR-TRMC technique, yielding high values for the mobility, 0.135 cm2/Vs and 0.062 cm2/Vs for para-HBC and meta-HBC respectively.

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Code: NANOpto_T9

Presenter: Tomoya Oshikiri (JPN)

Abstract Title: Exploring the Mechanism of Near-field Chirality Generation on an Achiral Plasmonic Structure

Co-Author(s): Tomoya Oshikiri, Hiroki, Yamada, Quan Sun, Kosei Ueno, Hiroaki Misawa

Abstract: The optical properties of localized surface plasmon resonances that occur on metallic nanostructures have been the subject of intense study for the past few decades. In particular, the chirality of the optical near-field has gained substantial interest. Recently, it was reported that a local chirality in the electric near field could be produced by the interaction of circularly polarized (CP) light even with an achiral gold (Au) nanostructure [1]. In this study, we observed photoemission electron images of the achiral rectangular structure under the irradiation of left and right CP (LCP and RCP) light using photoemission electron microscopy.

Au nanostructures were fabricated on the ITO-coated glass substrate using electron beam lithography. Near-field properties of Au rectangular structures with different aspect ratios, such as mapping and spectra, were investigated using photoemission electron microscope to explore the mechanism of near-field chirality generation. For example, an Au rectangular structure with the size of 160 × 240 nm showed two near-field peaks derived from T- and L- modes and the near-field circular dichroism (CD) calculated by the difference of the near-field spectra in the local region of LCP and RCP excitation also showed two peaks. However, the peaks of near-field CD slightly differed from those of the near-field spectrum and matched with cross points of phase angles of two modes. We concluded that the origin of the near-field chirality can be traced to an interaction between T- and L-modes which is maximized when their phase angles are harmonized.

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Institution: Research Institute for Electronic Science, Hokkaido University

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Code: NANOpto_T10

Presenter: Yasuyuki Tsuboi (JPN)

Abstract Title: Non-plasmonic Nanostructured-semiconductor-assisted (NASSCA) Optical Tweezers

Co-Author(s): Yuki Uenobo, Sawa Komoto, Tatsuya Nagai, Sayaua Hashimoto, Shuhei Ogita, Kentra Ushiro, Tatsuya Shoji

Abstract: We propose an new approach using a nano-structured material that can enhance the optical force and be applied to optical tweezer. The material is metal-free black silicon (MFBS), the plasma etched nano-textured Si. We demonstrate that MFBS-based optical tweezers can efficiently manipulate small particles with characteristic features. The advantages of MFBS-based optical tweezers are: 1) simple fabrication with high uniformity over wafer-sized areas, 2) free from thermal effects detrimental for trapping, 3) switchable trapping between one and two - dimensions, 4) tight trapping because of no detrimental thermal forces, and so on.

We call this technique NASSCA optical tweezers (Nano-Structured SemiConductor Assisted optical tweezers). The concept of NASSCA optical tweezer is illustrated in Fig. 1. This is the NON-PLASMONIC NOVEL optical tweezer. It is MFBS-assisted optical trapping, and has several advantages as compared with plasmonic optical trapping (POT). Moreover, although MFBS-assisted trapping has a weaker optical force as compared to POT, MFBS-assisted trapping can perform tighter trapping than POT because it is free from the detrimental thermal effects. By optimizing the surface nanostructure, it should be possible to realize stiffer traps optimized for specific wavelengths. MFBS-assisted optical trapping mean that it can potentially be developed and applied to the manipulation of a variety of nanomaterials.

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Institution: Osaka City University

Code: NANOpto_T11

Presenter: Hiroaki Misawa (JPN)

Co-Author(s): Xu Shi, Kosei Ueno, Tomoya Oshikiri, Quan Sun, and Keiji Sasaki

Abstract Title: Insight into Modal Strong Coupling and its Application to Photochemical Reactions

Abstract: Plasmon-induced hot electron transfer has attracted much attention as a novel strategy for the solar energy conversions. However, the solar energy conversion efficiency is limited by the insufficient absorption on monolayer of metallic nanoparticles. To solve this problem, in the present study, we apply the principle of strong coupling to plasmonic water splitting induced by the plasmon-excited electron transferring into wide-bandgap semiconductor on a Au nanoparticle (Au-NP)/TiO2 thin-film/Au-film (ATA) photoanode.
Strong coupling between the Fabry–Pérot nanocavity mode of the TiO2 thin-film/Au-film and the localized surface plasmon mode of the Au-NPs is induced when their resonant frequencies overlap. To increase the coupling strength in this strong coupling regime, a key feature is partially inlaying of Au-NPs into the TiO2 nanocavity by several nanometers. Under a three-electrode system measurement with a saturated calomel electrode (SCE) as a reference electrode, a Pt wire as a counter electrode and an electrolyte of KOH (0.1 mol/dm3), we demonstrated that the action spectrum of incident photon to current conversion efficiency (IPCE) exhibited two bands, which almost corresponds to the absorption spectrum of ATA. The IPCE of ATA is extraordinarily enhanced as compared to that of Au-NPs/TiO2 photoanode. Most importantly, under the strong coupling regime, the internal quantum efficiency (IQE) of the photocurrent generation is also enhanced at the strong coupling wavelengths. The increase in IQE implies the possibility of increasing the generation of hot electrons due to the strong coupling. The plasmon-induced water splitting using a two-electrode system is also discussed.

Institution: Research Institute for Electronic Science, Hokkaido University

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Code: NANOpto_T12

Presenter: Maria Wächtler (DEU)

Co-Author(s): Bei Liu, Kaituo Dong, Yifat Nakibli, Mathias Micheel, Lilac Amirav

Abstract Title: Charge-separation in Ni-tipped CdSe@CdS Nanorods for Hydrogen Evolution

Abstract: Colloidal nanostructured semiconductor materials, e.g. dot-in-rod heteronanostructures, gained a lot of interest over the past decade as sensitizers for the light-driven water-reduction half reaction by coupling such nanostructures with potential catalysts, e.g. metal nanoparticles. The electronic and optical properties of these nanostructures, which are tunable via their dimensions, render them perfect model systems to study fundamental aspects of their function spectroscopically.
Recently, one of the essential steps in the photocatalytic scheme, the charge separation at the semiconductor/catalyst interface, was studied for a series of CdSe@CdS nanorods tipped with Ni nanoparticles by applying time-resolved transient absorption and photoluminescence spectroscopy. The results indicate that the efficiency of this step depends sensitively on the size of the metal tip, which can be explained based on a model comprising two opposing trends: a size dependent Coulomb blockade and Schottky barrier. [1,2] Further, indications for the need to put charge-carrier transport between the spot of exciton generation and the separating interface into consideration, especially for anisotropic nanostructures with one dimension in the 10s of nm, are currently under closer investigation.

Financial support is acknowledged by the Fonds der Chemischen Industrie (FCI), the COST Action CM1202 PERSPECT-H2O, and the German Research Foundation (DFG) - project number 364549901 - TRR234 [CataLight, B4)].

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Institution: Leibniz Institute of Photonic Technology, Jena, Germany

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Code: NANOpto_T13

Presenter: Tsung-Han Liu (JPN)

Co-Author(s): Ken-ichi Yuyama, Takato Hiramatsu, Naoki Yamamoto, Eri Chatani, Hiroshi Miyasaka, Teruki Sugiyama, and Hiroshi Masuhara

Abstract Title: Promotion of Amyloid Fibrillation by Femtosecond Laser Irradiation

Abstract: Femtosecond (fs)-laser-induced crystallization pioneering in light-induced crystallization from supersaturated solutions was proposed for the first time by our group. Under fs laser irradiation, ablation of water accompanying with cavitation bubbling can be induced. As deformation of bubbles occurs repeatedly and vigorously, nucleation is likely to be triggered near bubble surfaces, so time required for crystallization from a supersaturated solution can be efficiently shortened. Besides, without losing crystal quality, it is reported that growth rate of protein crystals can be sophisticatedly enhanced by fs laser irradiation. Accordingly, we further extended our investigation from protein crystallization to amyloid fibrillation of proteins, which is also known as a nucleation-dependence process. Here we demonstrate that necessary time for amyloid fibrillation can be significantly shortened by fs laser irradiation, leading to favorable enhancement. The enhancement was confirmed by both spectral measurements and direct observations of amyloid fibrils. The thioflavin T fluorescence intensity of laser-irradiated solution increased earlier than that of the control solution, and such a difference was simultaneously revealed by ellipticity changes. At the same time before intensity saturation in fluorescence, the number of amyloid fibrils obtained under laser irradiation was generally more than that in the control solution. In addition, such an enhancement is correlated to the laser power threshold of cavitation bubbling. Possible mechanisms are proposed by referring to fs-laser-induced crystallization and ultrasonication-induced amyloid fibrillation.

Institution: Kwansei Gakuin University

Code: NANOpto_T14

Presenter: Amedeo Agosti (ITA) **Abstract Title:** Predicting and Upgrading Photocatalytic H2 Production via Fluorescence Quenching Method

Co-Author(s): Yifat Nakibli, Mirko Natali, Lilac Amirav, Giacomo Bergamini

Abstract: The framework of photocatalytic solar-to-chemical energy conversion is mapped by a plethora of materials, reactions and experimental conditions that can be explored and optimised. However, while current high-throughput screening tools accurately classify materials according to intrinsic properties, descriptors that can discriminate suitable catalyst for the expanding chemical reactions investigation space are still lacking. Here, we propose fluorescence quenching as a key descriptor to bridge optoelectronic materials properties to redox activity towards combined light-driven chemical reactions. Using this approach with metal-chalcogenide core-shell hybrid nanorods we demonstrate hydrogen production with quantum efficiencies up to 45%, while simultaneously oxidising electron-donor moieties with different functional groups, using visible light and mild conditions. Spectroscopic analysis further shows robust photo-chemical stability over 18 hours, while product selectivity is evidenced in oxidising molecules carrying amino- and alcohol-groups. As such, the method stands as one of the general benchmarks to reliably and rapidly forecast and characterise in-operando solar-fuel generation performance within the dispersive chemical-transformations exploration.

Institution: University of Bologna

Code: NANOpto_T15

Presenter: Aaron H. Rose (USA) **Abstract Title:** Exciton-plasmon and Plasmon-mediated Exciton-exciton Strong Coupling in Few-layer Molybdenum Disulfide

Co-Author(s): Jeremy R. Dunklin, Hanyu Zhang, Sanjini U. Nanayakkara, Elisa M. Miller, Juan M. Merlo, Michael J. Naughton, Jao van de Lagemaat

Abstract: Controlling chemical reaction pathways is one of the grand challenges in photocatalysis. One way to tailor the electronic band structure of semiconducting catalysts is through strong exciton-polariton coupling where mode hybridization leads to band splitting. Such rearrangement of the bands implies new photochemical behavior and indeed strong coupling has been used to modify decay pathways of excited carriers in organic dye and photochromic molecules [1,2].

Two-dimensional transition metal dichalcogenides (2D TMDCs) show promise as photocatalysts for solar fuels and are well suited for strong coupling studies with plasmon polaritons due to their sharp excitonic transitions and ultrathin nature.

The work herein shows strong exciton-plasmon polariton coupling in CVD-grown few-layer MoS2 films on 40 nm silver thin films in the Kretschmann configuration. Rabi splitting of ~70 meV is observed in experimental dispersion relations at both the A and B exciton energies. Furthermore, the A and B excitons exhibit hybridization, mediated by the plasmon. Ultrafast transient reflection spectroscopy results show increased carrier lifetimes under strong coupling. Finally, these effects are investigated in water.

The analysis is extended to other TMDCs using a transfer matrix model and the theoretical results show strong coupling for every (and has been experimentally verified for some) metal-TMDC combination of the metals Au, Al, Ag, and Cu and the 2D TMDCs MoS2, MoSe2, WS2, and WSe2.

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Institution: National Renewable Energy Laboratory, Golden, CO

Code: NANOpto_T16

Presenter: David Steinebrunner (DEU) **Abstract Title:** Synergistic Effect in ZnPc - npAu Hybrid Materials Leading to Enhanced Photocatalytic Singlet Oxygen Formation

Co-Author(s): Guenter Schnurpfeil, Dieter Wehrle and Arne Wittstock

Abstract: Recently a new photocatalytically active hybrid material has been reported which consists of a zinc phthalocyanine (ZnPc) immobilized on a nanoporous gold support (npAu).[1] This system showed significantly higher singlet oxygen yield compared to the same amount of phthalocyanine in solution. A possible explanation for this observation is the higher stability of the phthalocyanine against decomposition when immobilized on a support as well as a synergistic effect between the phthalocyanine and the plasmonic states of the nanoporous gold support. [2,3]

In our present work a series of hybrid systems on different types of nanoporous gold was synthesized and compared regarding their structural differences and their activity for singlet oxygen formation. The composition of the self-assembled monolayer was also optimized during this study. For the investigation of the synergistic effect and the interactions between the photosensitizer and the surface plasmon resonance of npAu, the catalysts were studied in the photooxidation of 1,3-diphenylisobenzofuran (DPBF) as selective quencher of singlet oxygen using different optical filters to achieve selective irradiation and excitation of only the phthalocyanine, the plasmon resonance of the npAu support or both absorption sites simultaneously.

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Institution: University of Bremen, Germany

Code: NANOpto_T17

Presenter: Jordan P. Hooker (AUS)

Abstract Title: With Polymer Photoclicks to Fluorescent Microspheres

Co-Author(s): Laura Delafresnaye, Leonie Barner, Christopher Barner-Kowollik

Abstract: The application of photochemistry to the synthesis of increasingly advanced molecular materials continues to aid the development of a broad variety of fields. Microspheres are one such class of materials with important and ubiquitous application, but their synthesis has generally not extended to the utilisation of modern photochemical reactions. This work presents a new class of functional, fluorescent polymer microspheres using a highly efficient, additive-free photochemical ligation technique.

Underpinned by the utilisation of pre-functionalised polymers for the first time – which provide control over the cross-linking functionality – microspheres are prepared in one step from pre-polymers via a precipitation technique. Importantly, preparation of a polystyrene-based random copolymer containing chloromethyl-styrene via nitroxide-mediated polymerisation (NMP) provides control over size and percentage of functional monomer, which may then be post-functionalised with cross-linkable groups. Highlighting the power of this technique, functionalisation with tetrazole and acrylates facilitates the use of the efficient nitrile-imine mediated tetrazole-ene cycloaddition (NITEC) reaction to prepare highly fluorescent, narrow-disperse microspheres (0.25 - 0.75 µm) in 1-2 hours under ambient conditions.

Utilising the NITEC reaction as a cross-linker in particle synthesis is an important step forward, removing the need for photo-initiators or photo-bases in photochemical microsphere synthesis, and enables a simplified reaction mixture consisting of only polymers in solution. Most importantly, this new paradigm in particle synthesis provides a broad platform for utilising the plethora of chemical reactions yet to be explored as cross-linking chemistries in particle synthesis.

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Institution: Queensland University of Technology (QUT)

POSTERS

Code: NANOpto_P1

Presenter: Katya Marinova Simeonova (BGR)

Abstract Title: Computational Modeling of Nanoscale Materials (CNTs, Nanocomposites, nanoparticles)' Magnetic and Optical Properties

Co-Author(s): Mrs Ganka Marinova Milanova

Abstract: Nanoscale materials (carbon nanotubes, nanocomposites, nanoparticles, NanoDots, nanowires, etc.) possess exceptional physic mechanical properties, [1]. Moreover these nanomaterials have small nanosizes and very wide applications in nanotechnology, nanochemistry, Quantum optics, nanophotonics, [2]. The aim of the work, presented a computational model (designed by authors), for study of magnetic, electronic and optical properties of these nanomaterials. Numerical algorithms and numerical FORTRAN programs for numerical experiments, based on classical mechanics, and novel computational models has been developed, too[3]. By numerical simulations have been studied magnetic, electronic and optical properties of nanoscale materials defined above.
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[3]. Katya Simeonova, XXV Intern. Summer School, "Nicola Cabrera", Miraflores de la Sierra, Madrid, Spain, Sept. 9-14, 2018, poster presentation, (Grant)

Institution: Institute of Mechanics, Bulgarian Academy of Sciences

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Code: NANOpto_P2

Presenter: Yuchun WANG (JPN)

Abstract Title: In-situ Surface Enhanced Raman Scattering Observations of Water Oxidation Reactions Enhanced by the Modal Strong Coupling

Co-Author(s): Jinjiang Zhang, Hiro Minamimoto, Xu Shi, Kosei Ueno, Hiroaki Misawa, and Kei Murakoshi

Abstract: The plasmonic photoconversion system is the combination of the wide-gap semiconductor electrode and the plasmonic metal nano-structure. When the localized surface plasmon resonance (LSPR) is excited on the metal nano-structure, this system shows photo response character in the visible or near-infrared region. Very recently, our research groups have found that the TiO2 electrode sandwiched by Au film and Au nano-particles can enhance the light harvesting efficiency. This is because that the interaction between the Fabry–Pérot nanocavity modes of the TiO2/Au film and LSPR of the Au nano-particles can improve the light absorption across a broad range of wavelength. This interaction is called as the modal strong coupling and can drastically enhance the water oxidation efficiency. However, at the present stage, the detail information about the molecular process of the water oxidation reaction (OER) on this system is still unclear. In this study, we have performed the electrochemical surface enhance Raman scattering (SERS) measurements to understand the catalytic properties of this electrode. Through various attempts, we have observed the appearance of the Raman band at 580 cm−1 at the positive polarized surface. This band can be assigned to Au2O3 which is the intermediate specie of OER. It should be noted that the appearance of this intermediate specie indicates the OER proceeds on the high catalytic surface. In addition, we introduced graphene into the system as the probe of the Fermi level. Through these attempts, the unique characteristic of the reaction process induced by the modal strong coupling has been revealed.

Institution: Graduate School of Chemical Sciences and Engineering, Hokkaido University

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Code: NANOpto_P3

Presenter: Kristina Vrouwenvelder (USA)

Abstract Title: Light-driven H2 Production in Sulfide-capped Nanocrystals Without Co-catalyst

Co-Author(s): Tais Labrador, Gordana Dukovic

Abstract: Using semiconductor nanocrystals (NCs) to drive the hydrogen evolution reaction is an emerging strategy for solar fuel generation. In most previously-studied systems, the NC transfers photogenerated electrons to a co-catalyst, which serves as the site for hydrogen evolution. However, to our knowledge the effect of the surface-capping ligand on charge transfer in photocatalytic systems without a co-catalyst has not been explored. We find that cadmium sulfide (CdS) NCs capped with ultrashort sulfide (S2–) ligands can generate hydrogen when photoexcited without an additional co-catalyst. The efficiency of this process is significant when compared with CdS NCs paired with known co-catalysts for hydrogen production. Using ultrafast transient absorption and steady-state photoluminescence (PL) spectroscopies, we find evidence that electron traps enable this hydrogen production. We hypothesize that these electron traps are introduced by the post-synthetic removal of surface-capping S2– ligand, exposing unpassivated cadmium surface sites where hydrogen generation could occur. Moreover, we show using time-resolved PL measurements that the rate of hole transfer to a hole acceptor, often a rate-limiting step in photochemical systems, is two orders of magnitude faster for S2–-capped NCs than for MPA-capped NCs. Thus, we conclude that hydrogen evolution by S2–-capped CdS NCs without a co-catalyst is significant and is controlled by the amount of electron trapping in the nanocrystal, demonstrating that the surface-capping ligand has a fundamental role in NC photochemistry.

Institution: University of Colorado Boulder

Code: NANOpto_P4

Presenter: Katya Marinova Simeonova (BGR)

Abstract Title: Nanostructures: Preparation, Modeling and Applications. Computational Study of Nanotubes' Electronic and Optical Properties

Co-Author(s): Mrs Ganka Marinova Milanova

Abstract: Nanostructures (nanotubes, nanocomposites, nanoparticles, Nano Dots etc.) possess extraordinary physic-mechanical, electrical, chemical, conductivity, electronic, magnetic, optical properties, [1]. These nanomaterials find applications in chemistry, engineering, technique, electronic, optics, environments, nano quantum optics, [2]. Its interesting and actual novel applications of these nanomaterials, could be connected with nanotechnology, based on nanoparticles (nanoshells, nanorods, Nano Dots) for cancer research. The aim of the work, presented could be formulated as follows: to discuss characterization, modeling and applications of these nanostructures. Also to develop author's computational model for study of Carbon Nanotubes' Electronic, Optical, Magnetic and so on properties. Analysis of nanochemistry' applications of nanostructures, have been described as well. Chirality effects of nanoscale materials has been modeled also. The author's models, have been based on classical mechanics and mathematics theories, and nanomechanics. Numerical mathematical authors algorithm's have been presented. By numerical FORTRAN Programs, designed by authors has been conducted numerical experiments and have been obtained graphics by numerical experiments. Comparison of these theoretical (computational) models by literature's experiments shows a very good agreement.

[1]. Katya M. Simeonova, Ganka M. Milanova, ISCOM2007, 24-30 September 2007, Peniscola, Spain, Book of Abstract, poster, P123, Grant

[2]. Katya M. Simeonova, Annual Meeting of ES1205 2014, June 2014, Pula, Croatia, Oral presentation

Institution: Institute of Mechanics, Bulgarian Academy of Sciences

Code: NANOpto_P5

Presenter: Xing Yee Gan (USA)

Abstract Title: Plasmon-Driven Chemical Conversion Using Copper Selenide Nanoparticles

Co-Author(s): Lauren Marbella, Derrick Kaseman, Scott Crawford, Jill Millstone

Abstract: The phenomena of localized surface plasmon resonances (LSPRs) has been broadly studied and is a property of nanomaterials that can be used to enhance or enable a wide variety of technologies including cancer treatment, light-driven catalysis, and ultrasensitive detection. While most widely observed and studied in noble metal nanomaterials, degenerately doped colloidal semiconductor nanoparticles have been identified as one such class of alternative plasmonic nanomaterials. As new plasmonic materials come online, it is important to assess their ability to generate comparable plasmonic properties to their noble metal counterparts. Here, we first track and quantify carrier density in a well-studied non-noble metal plasmonic system, copper selenide (Cu2-xSe), using 77Se solid state NMR spin lattice relaxation measurements as a function of particle oxidation. We find that NMR can be used as a powerful tool to observe presence of degenerate carriers in samples that do not have optically discernible plasmonic properties. Additionally, we demonstrate plasmon-driven chemistry on Cu2-xSe for the first time. Specifically, we observed hot-electron driven dimerization of nitrobenzenethiols on Cu2-xSe nanoparticle surfaces with yields comparable to those observed from noble metal nanoparticles. Importantly, our results indicate that degenerately-doped semiconductor nanoparticles are promising for light-driven chemistry applications.

Institution: University of Pittsburgh

Code: NANOpto_P6

Presenter: Sayaka Hashimoto (JPN)

Abstract Title: Selective Optical Trapping of Polystyrene Nanospheres using Nano-structured Semiconductor-Assisted (NASSCA) Optical Tweezers

Co-Author(s): Sawa Komoto, Tsuya Shoji, Yasuyuki Tsuboi

Abstract: An optical manipulation technique based on optical force is expected to be applied to separation and sorting of nanomaterials. Recently, we have developed a novel optical trapping method using nanostructured silicon surfaces (black silicon) [1]; nanostructured-semiconductor-assisted optical tweezers (NASSCA-OT) [2], [3]. This method allows us to trap numerous nanoparticles in a wide area, being capable of optically separating and aligning them on the basis of chemical composition, shape and size of nanoparticles. Here, we demonstrate such selective trapping of nanospheres according to their size on a black silicon.

The trapping targets were fluorescent polystyrene nanoshperes with diameter of 500 and 1000 nm. These nanospheres were dispersed in water. We used near-infrared (NIR) laser (wavelength 808 nm) as trapping light source. Upon NIR laser irradiation, larger nanospheres were preferentially trapped than smaller nanospheres on a black silicon. Finally, a larger nanosphere was trapped at the center of the focal spot, while smaller nanospheres were trapped with surrounding the larger nanosphere. We succeeded in size selective trapping of polystyrene nanospheres. Optical selective trapping with NASSCA-OT has potential an application technique to separate and trap nanospheres according to size and shape.

[1] Gediminas, G., Saulius, J., et al., Ann. Phys, 525 (2013) 907-914
[2] M. Toshimitsu, Y. Tsuboi et al, J. Phys. Chem. C, 116 (2012) 14610
[3] T. Shoji, Y.Tsuboi et al, Sci. Rep., 7 (2017) 12298

Institution: Osaka City University

Code: NANOpto_P7

Presenter: Ryota Takao (JPN)

Abstract Title: Non-plasmonic Optical Trapping of DNA using Nano-structured Semiconductor-assisted (NASSCA) Optical Tweezers

Co-Author(s): Tatsuya Shoji, Yasuyuki Tsuboi

Abstract: Optical trapping of biomolecules is important in bioscience. However, it is much difficult because of their small polarizabilities. Recently, we have developed nano-structure semiconductor-assisted (NASSCA) optical tweezers using a nano-structured silicon (B-Si) to trap nanoparticles with great efficiency (1). In this study, we demonstrate NASSCA optical trapping of DNA.

We used λ-DNA stained with fluorescence dye (YOYO-1) in aqueous solution. B-Si was fabricated by reactive ion etching. We used near-infrared laser light (λ = 1064 nm) for NASSCA optical trapping and visible laser light (λ = 473 nm) for fluorescence excitation. These laser beams were coaxially introduced into an inverted microscope, and focused on a surface of the B-Si. We observed trapping behavior by means of fluorescence microspectroscopy.

Upon trapping laser irradiation, a dramatic increase in fluorescence of DNA was observed in the irradiation area. Upon further irradiation, the fluorescence intensity gradually increased. Turning off the irradiation, the trapped DNA were released from the irradiation area. In this process, we observed numerous DNA were trapped to form a DNA micro-assembly on the B-Si. The trapping behavior was monitored also by fluorescence spectroscopy. These behaviors clearly indicated that NASSCA optical tweezers performed the efficient trapping of DNA. NASSCA optical tweezers will be a promising technique for a biomolecular manipulation.

(1) Y. Tsuboi et al., Sci. Rep., 2017, 7, 12298.

Institution: Osaka City University

Code: NANOpto_P8

Presenter: Tatsuya Nagai (JPN)

Abstract Title: Optical Trapping of Poly(N-isopropylacrylamide) Using a Nanostructured Silicon Crystal: A Confocal Microspectroscopic Study

Co-Author(s): Tatsuya Shoji, Yuriko Matsumura, Yasuyuki Tsuboi

Abstract: Optical trapping of nanomaterials potentially holds a great promise for applications in various research fields. We have demonstrated optical trapping of soft nanomaterials by a plasmon-enhanced optical force [1, 2]. However, such plasmonic optical trapping frequently suffers from photothermal effects, which block stable trapping. Recently, we developed a non-plasmonic and non-thermal optical trapping method using a silicon crystal with a nanostructured surface (black silicon); Nano-structured Semi-Conductor-Assisted (NASSCA) optical tweezers [3]. In the present study, we demonstrate NASSCA optical trapping of polymer chains in water.

As trapping targets, we synthesized poly(N-isopropylacrylamide) labeled with a polarity-responsive fluorescence molecular probe. As trapping light source, we used near-infrared (NIR) laser. Upon NIR laser irradiation to the black silicon surface, we observed a bright fluorescence spot in an irradiated area. This result indicate an increase in the local polymer concentration by optical trapping. It disappeared immediately after the stop of NIR laser irradiation. We believe that NASSCA optical tweezers will become trapping and manipulation technique for nanomaterials.

[1] Y. Tsuboi et al., J. Phys. Chem. C, 116 (2012) 14610.
[2] Y. Tsuboi et al., J. Am. Chem. Soc., 135 (2013) 6643
[3] Y. Tsuboi et al., Sci. Rep., 7 (2017) 12298

Institution: Osaka City University

Code: NANOpto_P9

Presenter: Yen-En Liu (JPN)

Abstract Title: Manipulation of Modal Strong Coupling between Localized Surface Plasmon and Fabry–Pérot Nanocavity Modes

Co-Author(s): Xu Shi, Quan Sun, Tomoya Oshikiri, Kosei Ueno, Hiroaki Misawa

Abstract: Modal strong coupling between localized surface plasmon and Fabry–Pérot nanocavity modes can induce a strong light absorption in a wide visible range. We have successfully applied the modal strong coupling to efficient light harvesting for light energy conversion such as plasmon-induced water splitting. In the present study, we fabricate a well-defined gold nanodisks (Au-NDs) on thin-film TiO2 nanocavity by using electron beam lithography and lift-off method and elucidate the optical as well as photoelectrochemical (PEC) properties of the modal strong coupling systems in visible and near-infrared wavelength ranges.

We explored the optical properties of the modal strong coupling system with various Au-ND densities and observed the splitting energy of modal strong coupling is proportional to the square root of the density of Au-ND. This relationship between strong coupling strength and the density of active elements is the same as the ensemble light-matter strong coupling between molecules and optical cavity resonance.

Applying this strong coupling system as a photo-anode, we further studied its PEC characterizations using a three-electrode system. The 0. 1 M KClO4 was used as supporting electrolyte and 1.0 vol% of TEOA was added to accelerate the electrochemical reactions. From the PEC measurement, a higher IPCE and IQE value were observed on a stronger coupling system with a higher density of Au-ND, which might be attributed to the strong coupling enhanced hot-carriers release. To further understand the contribution of strong coupling on the hot-carriers generation, we will also discuss the near-field distribution and the dephasing time on the strong coupling systems.

Institution: Research Institute for Electronic Science, Hokkaido University, Japan

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Code: NANOpto_P10

Presenter: Sawa Komoto (JPN)

Abstract Title: Assembly Formation of Polystyrene Nanoparticles using Novel Optical Tweezers Assisted by Black Silicon and Black Titanium

Co-Author(s): Tatsuya Shoji, Yuki Uenobo, Saulius Juodkazis, Yasuyuki Tsuboi

Abstract: Optical manipulation techniques for nanoparticles are indispensable for developments of nanoscience and nanotechnology. Recently, we have demonstrated a novel non-plasmonic and non-thermal optical manipulation technique with nanostructured silicon substrate (black silicon); nano-structured semi-conductor-assisted (NASSCA) optical tweezers[1]. Such nanostructured surface would play an important role for the enhanced optical forces. In the present study, we investigated optical trapping behaviors using nanostructured silicon and titanium substrates (black titanium). The trapping targets were fluorescent polystyrene nanoparticles dispersed in water. We used a near-infrared laser as a trapping light source. Using black silicon, the trapped polystyrene nanoparticles formed a 2-dimensional assembly in the irradiation area. Furthermore, numerous polystyrene nanoparticles were simultaneously trapped, resulting in 3-dimensional assembly over the irradiation area during the intense irradiation. Using a black titanium substrate, we found that polystyrene nanoparticles were trapped at the outside of the irradiation area. Such intriguing trapping behavior would be due to the thermophoresis induced by the photothermal effects of black titanium and an enhanced optical force caused by propagating light around the irradiation area. We believe that optical tweezers using a black silicon and a black titanium substrate will become powerful tools for molecular assembly formation.
[1] T. Shoji, Y. Tsuboi, et al. Sci. Rep. 7 (2017), 12298.

Institution: Graduate School of Science, Osaka City University, Japan

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Code: NANOpto_P11

Presenter: Jeremy R. Dunklin (USA)

Abstract Title: Carrier Dynamics in Plasmonic Nanoparticle-decorated Transition Metal Dichalcogenides Photocatalysts

Co-Author(s): Aaron H. Rose, Hanyu Zhang, Jun Liu, Jao van de Lagemaat

Abstract: Layered, semiconducting transition metal dichalcogenides (TMDs) are an emerging source of two-dimensional (2D) nanostructures with intriguing catalytic and optoelectronic properties. Gold nanoparticles (AuNPs), supporting localized surface plasmon resonances, can complement TMDs, allowing their optoelectronic properties to be tuned for photo(electro)chemical applications. Plasmonic AuNPs offer an extraordinary ability to concentrate electromagnetic fields and confine light to sub-wavelength dimensions. Mechanisms of plasmonic enhancements in catalysis include local heating, light scattering, field confinement, energy transfer, and interfacial charge transfer. However, these underlying physical mechanisms are poorly understood in situ, and most devices exhibit modest performance improvement.

This work utilizes transient absorption spectroscopy, with pump tunability and broadband visible-NIR probing, to monitor carrier dynamics in AuNP-decorated TMDs. Fabricated AuNP-decorated molybdenum diselenide (MoSe2) nanosheets exhibit a long-lived, photo-induced absorption feature when excited at the plasmon resonance. The underlying mechanism of this long-lived feature and its implications in photo(electro)chemistry is explored. This development could represent an important advance in harnessing plasmonic dissipation pathways for the generation of long-lived carriers across a broad spectral range well-suited for solar fuel generation.

Institution: National Renewable Energy Laboratory

Code: NANOpto_P12

Presenter: Shuhei Ogita (JPN)

Abstract Title: Development of Optical Tweezers using a Nanostructured Dielectric Substrate for the Manipulation of Nanomaterials

Co-Author(s): Tatsuya Shoji, Keiko Tawa, Junji Nishii, Yasuyuki Tsuboi

Abstract: Manipulating nanomaterials using optical tweezers is of great interests. Several researchers demonstrated that nanomaterials were efficiently trapped on nanostructured surfaces such as plasmonic optical tweezers.[1] However, the POT have frequently suffered from photothermal effects. Recently, we developed non-thermal and non-plasmonic optical tweezers; nanostructured semiconductor-assisted optical tweezers (NASSCA-OT).[2] NASSCA-OT use a silicon nanoneedle surface (black silicon; B-Si). We proposed that a nanoneedle structure played an important role for enhancing optical forces. In the present study, we investigated optical trapping using a nanostructured dielectric substrate instead of B-Si.
A nanostructured dielectric substrate was fabricated by nanoimprint lithography. As a trapping target, we used polystyrene nanospheres (PSs) dispersed in water. We used a cw near-infrared laser for trapping (λ = 1064 nm). During the laser irradiation, several PSs were assembled on the substrate. We evaluated trapping efficiency of this method in terms of trapping stiffness in comparison with NASSCA-OT and POT.

[1] T. Shoji, Y. Tsuboi., J. Phys. Chem. Lett., 2014, 5, 2957.
[2] T. Shoji, Y. Tsuboi et al., Sci. Rep., 2017, 7, 12298.

Institution: Graduate School of Science, Osaka City University

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Code: NANOpto_P13

Presenter: Yoshiki Suganami (JPN)

Abstract Title: Optical Properties of Plasmonic Nanoparticles Composed of Au/Ag Nanocomposite Coupled with Fabry-Pérot Nanocavity

Co-Author(s): Tomoya Oshikiri, Xu Shi, Quan Sun, Kosei Ueno, Hiroaki Misawa

Abstract: The extension of light-energy conversion to longer wavelengths, especially to the visible and near-infrared regions is important to utilize solar energy efficiently. Previously, we have elucidated a modal strong coupling between localized surface plasmon resonance (LSPR) and Fabry–Pérot nanocavity modes which shows a strong light absorption in a wide wavelength range of visible light.[1] In this study, we employed nanoparticles composed of gold/silver nanocomposite (Ag/Au-NCNPs) as plasmonic resonators, which show tunable and broad absorption.

Herein, we report the properties of coupling condition between LSPR of Ag/Au-NCNPs and nanocavity. Ag/Au-NCNPs were loaded by annealing the stacked film of Ag and Au on the nanocavity composed of TiO2 thin-film on Au-film reflector. The absorption spectrum of Ag/Au-NCNPs on TiO2 without nanocavity showed a single broad peak. On the other hand, three peaks were observed in the absorption spectrum of Ag/Au-NCNPs on the nanocavity. Two of them appeared in a shorter wavelength than that without nanocavity, and the other one was observed as a broad peak in longer wavelength. This result suggests that Ag and Au are phase-separated in the Ag/Au-NCNP and are individually coupled with the nanocavity.

To understand the properties of the coupling condition between Ag/Au-NCNPs and nanocavity, we will investigate the near-field properties of this system.

[1] X. Shi, K. Ueno, T. Oshikiri, Q. Sun, K. Sasaki, H. Misawa, Nat. Nanotechnol. 13, 953-958 (2018)

Institution: Research Institute for Electronic Science,Hokkaido University

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Code: NANOpto_P14

Presenter: Azusa Onishi (JPN)

Abstract Title: Emission Properties of Fluorescent Molecules Under the Condition of Modal Strong Coupling between Localized Surface Plasmon and

Co-Author(s): Shuai Zu, Xu Shi, Quan Sun, Tomoya Oshikiri, Kosei Ueno, Hiroaki Misawa

Abstract: We have elucidated a modal strong coupling between localized surface plasmon resonance (LSPR) and Fabry–Pérot nanocavity modes which shows a strong light absorption and large electromagnetic field enhancement effects in a wide wavelength range of visible light.[1] The modal strong coupling is also expected to be applied to highly efficient chemical sensors utilizing surface-enhanced Raman scattering and fluorescence enhancements. In this study, we investigated the emission properties of fluorescent molecules under the modal strong coupling conditions.

We fabricated the Au-NPs/TiO2/Au-film which shows modal strong coupling. A 100 nm-thick Au film was deposited by sputtering on a quartz substrate, and subsequently a TiO2 thin film with a thickness of 30 nm was deposited by atomic layer deposition (ALD). Au-NPs were fabricated by depositing an Au thin film (3 nm) and annealed at 300°C. To fabricate the partially inlaid Au-NPs, a thin layer of TiO2 was additionally deposited on the Au-NP/TiO2/Au-film by ALD. Finally, 2 nm of Al2O3 was deposited on the substrate by ALD to prevent energy transfer from a fluorescent molecule to Au-NP, and subsequently rhodamine 6G molecules were placed on it.

The fluorescence spectra of rhodamine 6G adsorbed on the fabricated nanostructures were measured. As a result, the fluorescence intensity on the Au-NPs/TiO2/Au-film was dramatically enhanced when compared with the Au-NPs on the TiO2 substrate due to the strong absorption and electromagnetic field enhancement with a wide spectrum range. We discuss about the modulation of fluorescence spectral shape under modal strong coupling conditions.

[1] X. Shi, K. Ueno, T. Oshikiri, Q. Sun, K. Sasaki, H. Misawa, Nat. Nanotechnol., 13, 953-958 (2018).

Institution: RIES, Hokkaido University

Code: NANOpto_P15

Presenter: Abdoulaye Djire (USA)

Abstract Title: Electrocatalytic and Optoelectronic Characteristics of Exfoliated Two-Dimensional Titanium Nitride Ti4N3Tx MXene

Co-Author(s): Hanyu Zhang, Jun Liu, Elisa Miller, Nathan Neale*

Abstract: A relatively new class of two-dimensional (2D) materials called MXenes have garnered tremendous interest in the field of energy storage and conversion. Thus far nearly all MXenes reported experimentally have been described as metals, with a lone report of a mixed-metal carbide phase exhibiting semiconducting character. Here, we report the optical, electrocatalytic and electrical properties of the 2D Ti4N3Tx MXene (Tx = basal plane surface terminating groups) and show this material exhbits both metallic and semiconducting behavior. We provide complete structural characterization of exfoliated Ti4N3Tx MXene and assign Tx = O and/or OH and find that this material is susceptible to surface oxidation. Optical experiments indicate that the exfoliated Ti4N3Tx MXene forms a hybrid with a thin surface oxide layer resulting in visible light absorbtion at energies greater than ~2.0 eV and an excitation wavelength-dependent defect-state emission over a broad range centered at ~2.9 eV. As an electrocatalyst for the hydrogen evolution reaction, the exfoliated Ti4N3Tx shows an overpotential of ~300 mV at –10 mA cm–2 and a Tafel slope of ~190 mV/decade. Finally, we observe a clear semiconductor-to-metal transition at ~90 K from temperature-dependent transport measurements under 5 T magnetic field likely resulting from the thin oxide layer. These results unveil the intriguing optical, electrocatalytic, and electrical properties of this 2D Ti4N3Tx MXene that expands the potential of these new 2D materials into electrocatalysis and (opto)electronic applications.

Institution: National Renewable Energy Laboratory

Code: NANOpto_P16

Presenter: Hyungcheoul Shim (KOR)

Abstract Title: High Efficiency PbS Quantum Dot Solar Cell with Reduced Hysteresis using Transfer Printing

Co-Author(s): Jung Hoon Song, Sohee Jeong

Institution: Korea Institute of Machinery and Materials (KIMM)

Abstract:

We fabricated a hole transport layer (HTL) using transfer printing to fabricate high efficiency PbS quantum dot solar cell with minimized hysteresis.

We applied PbS-EDT(1,2-ethanedithiol) as an HTL and controlled the adhesive properties between the donor substrate and the HTL through the UVO process in order to effectively transfer the HTL to the PbS layer, which enabled multilayer transfer printing as a result.

During the transfer printing process, a gradient solid-solution layer was created at the interface with the existing PbS layer to reduce the hysteresis phenomenon, and to improve the power conversion efficiency to about 10% according to the HTL thickness optimization.

In addition, the use of the EDT solvent can be remarkably reduced by using the transfer printing when forming the PbS-EDT layer. This can reduce the amount of organic solvent consumed in the process and improve the potential of environmentally friendly processes.

The 29th International Conference on Photochemistry

Boulder, Colorado
July 21 – 26, 2019

PHOTOCHEMICAL AND PHOTOREDOX PROCESSES (CHEMRedox)
ABSTRACTS

INVITED TALKS

Code: CHEMRedox_I1

Presenter: Eun Jin Cho (KOR)

Abstract Title: Visible-Light-Induced Synthesis of Heterocycles

Co-Author(s): Vineet Soni, Youngmin You

Abstract: Development of practical and selective routes to important building units is a main goal in synthetic chemistry, thus eventually enabling facile access to even complex functional molecules. Since halogens are the most widely used precursors in organic reactions, the development of building blocks containing halogens, especially those with two different halogens in a single step (hitherto unprecedented), will be highly beneficial. We synthesized a new class of heterocyclic building blocks, 4-bromo-2-fluoroquinolines, utilizing halogen bond complex formation under visible light irradiation. The utility of the new di-halogenated building blocks was demonstrated in several applications, including the synthesis of an anti-cancer drug candidate, by exploiting the differential reactivity of the –F and –Br groups in the coupling reaction.

In addition, we demonstrated an unprecedented approach for the generation of iminyl radicals via a photocatalytic energy transfer process from readily available heterocyclic precursors. This method is distinctive to the previous photoinduced electron transfer approaches to N-centered radicals. In combination with singlet oxygen, the in situ generated nitrogen radical undergoes a selective ipso-addition to arenes to furnish remotely double functionalized spiro-azalactam products. The scope of substrates was explored with the mechanistic elucidation to include the computational studies.

Institution: Chung-Ang University

Code: CHEMRedox_I2

Presenter: Steve Marsden (GBR)

Abstract Title: Photochemically-Mediated Direct Aromatic C-H Amination: A Tool for Molecular Innovation

Co-Author(s): Professor John Plane, Dr Sebastian Cosgrove, Dr Tanya Bykova

Abstract: Aromatic amines are key components of a range of effect chemicals both natural and man-made, and methods for their construction are therefore in high demand: ca. 5% of all reactions carried out in the pharmaceutical industry are aimed at this motif. Existing synthetic approaches are typically multi-step and/or involve the use of expensive precious-metal catalysts and pre-functionalised starting materials. An attractive alternative would be involve direct functionalisation of aromatic C-H bonds to introduce the amine group in a single transformation. We have investigated the direct amination of aromatic C-H bonds using photochemically-generated amininium radicals, and further developed conditions whereby direct 'one-pot' conversion of secondary amines to their arylated derivatives is achieved by in situ activation [1]. The reactions can be carried out in batch or continuous flow mode, the latter facilitating simple gram-scale production [2]. Mechanistic studies, supported by DFT calculations, shed light upon the pathways involved in the amination reactions. The highly reactive aminium radicals allow access to unusual highly three-dimensional scaffolds which have properties suitable for fragment-based drug discovery and screening programmes as well as target synthesis. In this presentation we will describe our advances in these areas.

[1] Chemical Science, 2018, 9, 6647-6652; [2] ChemPhotoChem, 2018, 2, 851-854.

Institution: School of Chemistry, University of Leeds

Code: CHEMRedox_I3

Presenter: Daniele Leonori (GBR)

Abstract Title: Use of Nitrogen Radicals in Remote Functionalizations

Co-Author(s): n/a

Abstract: The selective functionalization of unactivated sp3 carbons streamlines access to molecules that can be difficult to prepare using classical disconnections. Radical strategies are powerful platforms to achieve this goal owing to the ability of odd-electron species to undergo fast transposition reactions.
Nitrogen-radicals are versatile synthetic intermediates to achieve this goal. However, the difficulties associated with their generation have somewhat thwarted their use in synthetic chemistry.[1]

We have developed a class of easy-to-make oximes and hyroxy-amides that upon photoredox oxidation enable access to iminyl and amidyl radicals.[2,3] These species have been used in radical transposition reactions thus enabling the site-selective functionalization of unactivated sp3-carbons. In particular, we have harnessed the ability of cyclic iminyl radicals to undergo ring-opening reactions. Following radical functionalization has enabled the preparation of remotely-functionalized nitriles. In the case of the amidyl radicals, we have exploited their ability to undergo efficient 1,5-HAT in order to target the gamma-functionalization of amides and the delta-functionalization of protected amines. These strategies have been applied to the deconstruction–functionalization of complex steroids and to the preparation of unnatural aminoacids.

[1] S. Z. Zard, Chem. Soc. Rev. 2008, 37, 1603.
[2] Chem. Eur. J. 2018, 24, 12154.
[3] Angew. Chem. Int. Ed. 2017, 56, 13361.
[4] Angew. Chem. Int. Ed. 2018, 57, 744.
[5] Angew. Chem. Int. Ed. 2018, 57, 12495.

Institution: School of Chemistry, University of Manchester

Code: CHEMRedox_I4

Presenter: Tanja Cuk (USA)

Abstract Title: Resolving Chemical Bond Dynamics at an Electrode Surface

Co-Author(s): Daniel Aschaffenburg and Xihan Chen

Abstract: Catalytic mechanisms at electrode surfaces guide the development of electrochemically-controlled energy storing reactions and chemical synthesis. The intermediate steps of these mechanisms are challenging to identify in real time, but are critical to understanding the speed, stability, and selectivity of product evolution. In my group, we employ photo-triggered vibrational and electronic spectroscopy to time-resolve the catalytic cycle at a surface, identifying meta-stable intermediates and critical transition states which connect one to another. The talk will focus on the highly selective water oxidation reaction at the semiconductor (SrTiO3)-aqueous interface, triggered by an ultrafast light pulse in an electrochemical cell. Here, I will describe the dynamics from the birth of the initial intermediates that trap charge (Ti-O• and Ti-O•-Ti) through the next event, suggested to be the formation of the first O-O bond of O2 evolution. The dynamics of charge screening at the interface, a hallmark of electrochemically controlled reactions, will be addressed in both aqueous and non-aqueous (battery) electrolytes. While many open questions remain, these experiments provide and benchmark the opportunity to quantify intermediates at an electrode surface and their associated dynamics.

Institution: University of Colorado, Boulder and RASEI

Code: CHEMRedox_I5

Presenter: Scott C. Warren (USA)

Abstract Title: Quantum-confined Superlattices of 2D Materials for Photochemistry

Co-Author(s): Tyler Farnsworth, Adam Woomer

Abstract: Two-dimensional semiconductors offer many useful properties, but these properties are often lost when the 2D materials are restacked into electrically conductive 3D solids. Here we show that 2D semiconductors self-assemble with small molecules to yield 3D superlattices in which the desirable optical, electronic, and vibrational characteristics of the 2D semiconductor are preserved. Structural analysis reveals that the 2D semiconductor is separated by monolayers of small molecules. This separation is just large enough to induce quantum-confined properties within each 2D semiconductor, but just small enough to facilitate tunneling between 2D semiconductors. As a result, the 3D superlattices have high electrical conductivity, reaching over 1 mS/cm. Our simulations illustrate the principles that underly self-assembly and reveal how these materials generalize to many unique compositions that facilitate explorations of novel photoredox chemistry.

Institution: University of North Carolina at Chapel Hill

CONTRIBUTED TALKS

Code: CHEMRedox_T1

Presenter: Max Kudisch (USA)

Abstract Title: The Role of Speciation and Photoexcitation of Ni-amine Complexes in Light-driven C-N Cross Coupling Reactions

Co-Author(s): Chern-Hooi Lim, Garret M. Miyake

Abstract: C–N cross coupling reactions between aryl halides and amines are vital to produce substituted anilines which are important motifs in bioactive compounds. Heat-driven Pd catalysis represents the most developed method to date for constructing C–N bonds and commonly proceeds through a Pd(0)/Pd(II) mechanistic cycle. Recently, Ni catalysis has emerged as a sustainable alternative to Pd that can more readily proceed via radical mechanisms to access a different scope of products. Under light irradiation, dual catalytic Ni/photoredox catalyst (PC) systems have enabled C–N cross coupling with a wide substrate scope under mild conditions. We have recently reported (JACS, 2018, 140 (24), 7667–7673) a Ni-catalyzed C-N cross-coupling methodology in which the Ni-amine complex operates without requiring an added PC. We have employed this process for the synthesis of diverse C-N coupled products (40 examples, including the drug flibanserin) by irradiating a solution containing an amine, an aryl halide, and a catalytic amount of NiBr2•3H2O with a 365 nm LED at room temperature. Excess amine substrate serves as ligand and base. Density functional theory calculations support a mechanistic cycle in which direct photoexcitation of the Ni-amine complex leads to photoinduced electron transfer, forming an amino radical that reacts with the Ni complex or aryl halide to furnish the product. Additional mechanistic studies have revealed that different amine coupling partners form Ni-amine complexes in situ with varying geometry that are the light absorbing species responsible for C–N coupling reactivity.

Institution: Colorado State University

Code: CHEMRedox_T2

Presenter: Ajay Sudhir Pisat (USA)

Abstract Title: The Facet Structure and Photochemical Reactivity of Arbitrarily-oriented SrTiO3 Crystals

Co-Author(s): Dr. Gregory S Rohrer and Dr. Paul A Salvador

Abstract: Differences in electrochemical potential due to material features such as Facets and Surface Chemical Terminations can reduce charge recombination, by driving electrons and holes to different areas on the surface. In this work, we demonstrate spatial selectivity of photoreactions arising from these two factors on the surface of polished polycrystalline SrTiO3. Annealing samples at 1250 °C resulted in the formation of {100} and {110} facets on the surface. The Miller indices of the facets were obtained by using grain orientation data and topographic information. Using photochemical marker reactions, {100} and {110} oriented facets were seen to promote photoreduction and photo-oxidation reactions respectively. Both families of facets were uniformly photocathodic/photoanodic. However, further annealing in a Sr-rich environment resulted in the {110} facets having a combination of photocathodic and photoanodic areas. Hence, our results show that both, facets and chemical terminations, affect the photocathodic to photoanodic area ratio on the sample surface, thus influencing the overall reaction rate. Additionally, these results demonstrate that oxidation/reduction rates can be tailored in polycrystalline SrTiO3 by using thermal treatments to create low index facets and to control the chemical terminations on these facets.

Institution: Carnegie Mellon University

Code: CHEMRedox_T3

Presenter: Chern-Hooi Lim (USA)

Abstract Title: Strongly Reducing Organic Photoredox Catalysts for Visible Light-driven Synthesis of Polymers and Small Molecules

Co-Author(s): Garret Miyake

Abstract: Visible light photoredox catalysis has emerged as a power synthetic method for small molecule transformations and material synthesis. It accesses non-classical chemistry that target compounds can be synthesized in reduced synthetic steps under mild conditions. Despite these benefits, the required use of precious metal photoredox catalysts (PCs) such as Ir(ppy)3 or Ru(bpy)32+, can impede its industrial use. Through combined computational and experimental approach, we have developed strongly reducing dihydrophenazine and phenoxazine organic PCs as alternatives to these precious metals. Guided by DFT calculations, dihydrophenazine and phenoxazine organic PCs were designed to exhibit strongly reducing excited state, long-lived and high triplet quantum yield, charge transfer excited state, and redox reversibility. These traits are important for high performance PCs in oxidative quenchings. In particular, we have successfully applied these organic PCs for the synthesis of polymer via atom transfer radical polymerization (ATRP) and small molecules via trifluoromethylation and dual nickel/photoredox catalyzed C-N and C-S cross-couplings.

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Institution: Colorado State University, New Iridium LLC

Code: CHEMRedox_T4

Presenter: Christoph Kerzig (CHE)

Abstract Title: Novel Two-photon Processes in Water and Their Photoredox Applications

Co-Author(s): Oliver S. Wenger

Abstract: Very strong reductants are essential for many chemical reactions, in which inert substrates are activated via one-electron reductions. However, photocatalytic mechanisms driven by a single visible photon can only provide limited reducing power for thermodynamic reasons. To avoid safety and selectivity problems associated with high-energy UV excitation, sophisticated visible-light driven multi-photon processes have been developed.[1] Owing to the dual applicability of strong photoreductants in water, both for wastewater treatment and "green" syntheses, we focused on aqueous two-photon mechanisms.
In an initial study on green-to-blue upconversion through sensitized triplet-triplet annihilation, we succeeded in providing -2.1 V vs. NHE of reducing power for driving chemical transformations in pure water.[2] This investigation initiated our quest for even more strongly reducing species accessible with visible light. In contrast to the long-standing opinion that expensive pulsed lasers are required for the consecutive absorption of two photons with an excited state as intermediate,[3] we have recently developed a catalytic system able to release the strongest aqueous reductant – the hydrated electron (-2.9 V) – through that mechanism upon irradiation with a cheap continuous wave laser (447 nm).[4]
Detailed mechanistic studies including two-pulse laser flash photolysis experiments and novel applications of our hydrated electron source will be presented.

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Code: CHEMRedox_T5

Presenter: Kyle F. Biegasiewicz (USA)

Abstract Title: Photoexcitation of Flavoenzymes for Selective Chemical Synthesis

Co-Author(s): Simon J. Cooper, Xin Gao, Michael J. Black, Andrew Mechan, Jihye Kim, Braddock Sandoval, Daniel G. Oblinsky, Bryan Kudisch

Abstract: Despite the remarkable advancements over the past several decades for conducting synthetic organic transformations in a catalytic sense, enzymes still provide the most efficient and selective platform for catalysis to date. However, enzyme catalysis is largely limited to reactions found in nature. Here we describe a novel approach to radical-mediated carbon-carbon (C-C) bond formation accomplished by irradiation of the flavin-dependent ‘ene’-reductase family of enzymes with light. This presentation will feature the design, development, and application of reductive and redox neutral radical cyclizations to pharmaceutically prevalent nitrogen heterocycles. The discussion will also feature a series of mechanistic studies to elucidate the photochemical aspects of these systems highlight their implications for future reaction design.

Institution: Princeton University

Code: CHEMRedox_T6

Presenter: Ulrich Lennert (DEU)

Abstract Title: Direct Catalytic Transformation of White Phosphorus into Aryl Phosphines and Phosphonium Salts

Co-Author(s): Ulrich Lennert, Percia Beatrice Arockiam, Verena Streitferdt, Daniel J. Scott, Christian Rödl, Ruth M. Gschwind, Robert Wolf

Abstract: Tertiary phosphines R3P are widely used both in organic chemistry[1,2] and as ligands for homogeneous metal complexes.[3] Meanwhile, salts incorporating quaternary phosphonium cations (R4P+) can operate as ion-pair extractants,[4] and as additives in Heck reactions.[5] In almost all cases these compounds are prepared via hazardous and wasteful multistep procedures involving oxidation of P4 to phosphorus chlorides (PCl3, PCl5, POCl3) using Cl2 gas, and subsequent displacement of chloride.[6] Far superior would be efficient catalytic methods to form P–C bonds directly from P4; however such reactions are all but unknown.
Herein, we describe a catalytic method for the preparation of valuable triarylphosphines and tetraarylphosphonium salts directly from P4. These useful organophosphorus compounds are obtained from P4 and aryl iodides using an iridium photocatalyst and blue light irradiation in the presence of triethylamine. We present the scope of this catalytic system and we propose an outline mechanism based on NMR monitoring and other spectroscopic observations.

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Code: CHEMRedox_T7

Presenter: Suong Nguyen (USA)

Abstract Title: PCET-Enabled Olefin Hydroamidation Reactions with N-Alkyl Amides

Co-Author(s): Qilei Zhu, Robert R. Knowles

Abstract: Oxidative proton-coupled electron transfer (PCET) has emerged as a promising technology for catalytic radical generation, enabling formal H• abstraction from strong E–H bonds found in many common protic functional groups. In this context, a number of light-driven PCET methods for olefin amination have been reported in recent years that utilize N-radical intermediates derived from the homolytic activation of the N–H bonds in anilides and sulfonamides (N–H bond dissociation free energies (BDFEs) ~100 and ~105 kcal/mol, respectively). However, analogous PCET-based olefin aminations with N-alkyl amides have proven more challenging to develop. This stems in part from the unusually strong N–H bonds in these amide derivatives (N–H BDFEs ~ 110 kcal/mol), which makes them difficult substrates for PCET activation. Moreover, as suggested by their high BDFEs, this class of amidyls is highly reactive and capable of engaging in numerous non-productive pathways that can compete kinetically with olefin addition. We recently addressed the thermodynamic constraints associated with N-alkyl amide activation in the development of a catalytic PCET method for amidyl-directed C–H alkylation. Building on this work, we report here a PCET-based protocol for catalytic olefin hydroamidation reactions of N-alkyl amides for the preparation of γ-lactams and cyclic N-acyl amine derivatives. This method exhibits a broad substrate scope, high functional group tolerance, and amenability to use in cascade polycyclization reactions. The feasibility of this PCET protocol in enabling the intermolecular anti-Markovnikov hydroamidation reactions of unactivated olefins is also demonstrated.

Institution: Princeton University

Code: CHEMRedox_T8

Presenter: Shunya Yoshino (JPN)

Abstract Title: Z-Scheme Shotocatalyst Employing Metal Sulfide and BiVO4 Photocatalysts for Water Splitting under Visible Light

Co-Author(s): Akihide Iwase, Akihiko Kudo

Abstract:

Photocatalytic water splitting is a promising reaction to convert solar energy to chemical energy. Metal sulfide photocatalysts are an attractive material group because they show high ability for H2 evolution from an aqueous solution containing sacrificial reagents under visible light. However, they can not oxidize water to form O2 due to photocorrosion. Recently, we have achieved Z-schematic water splitting using metal sulfides as an H2-evolving photocatalyst and an RGO-TiO2 composite as an O2-evolving photocatalyst. However, the Z-scheme systems respond only to UV light because of the limitation of TiO2 (BG = 3.0 eV). In this study, we demonstrated Z-schematic water splitting under visible light irradiation using BiVO4 (BG = 2.4 eV) as an O2-evolving photocatalyst with visible light response instead of TiO2.

When RGO-BiVO4 was used as an O2-evolving photocatalyst by combined with a metal sulfide photocatalyst, stoichiometric amounts of H2 and O2 did not evolve. On the other hand, Z-schematic water splitting proceeded by employing RGO-(CoOx/BiVO4) as an O2-evolving photocatalyst under visible light irradiation. To clarify the role of CoOx in the present Z-scheme system, photoelectrochemical measurements were carried out. The onset potential of anodic photocurrent of BiVO4 shifted to negative direction upon loading CoOx due to the promotion of water oxidation. This suggests enhancement of an electron injection from BiVO4 to metal sulfide, resulting in Z-schematic water splitting.

Institution: Tokyo University of Science

Code: CHEMRedox_T9

Presenter: Jayaraman Sivaguru (USA)

Abstract Title: Uncovering Novel Excited State Reactivity Of Organic Molecules

Co-Author(s): Sunil kumar Kandappa, Sapna Ahuja

Abstract:

Uncovering new excited state reactivity provides opportunities to build complex molecular architectures often with unique stereochemistry. A fundamental challenge in such a process involves controlling excited state reactivity of organic molecules due to the short lifetimes of the reactive species leading to stereo-enriched products. We have been interested in developing strategies for controlling the stereochemistry of products where the reactants reach the excited state(s) upon UV and/or visible light irradiations. This presentation will highlight our methodology of employing UV and/or visible light for performing photoreactions with excellent control over reactivity and selectivity. Based on photochemical and photophysical investigations, the presentation will highlight novel excited state reactivity of organic molecules, the role of restricted bond rotations in influencing the excited state chemistry and provide a mechanistic rationale for the observed reactivity in different systems.1-4

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Code: CHEMRedox_T10

Presenter: Kangmin Kim (USA)

Abstract Title: Radical Photopolymerization with Dark Curing: Overcoming Intrinsic Issue of Photopolymerization

Co-Author(s): Charles B. Musgrave, Jeffrey W. Stansbury

Abstract:

Radical photopolymerization (RPP) is widely recognized and rapidly growing as an important green technology relative to conventional thermal polymerization because of its potential to reduce energy consumption and waste, while increasing productivity. The spatial and temporal controls afforded by light initiation are highly desirable in applications like photolithography and 3-D printing, yet restrict the use of RPP in numerous polymeric applications due to immediate termination of radical polymerization upon irradiation discontinuation. Any low/moderate conversion regions within an undercured polymer contribute to compromised properties that cannot be rectified without additional irradiation. This limitation severely limits RPP implementation in applications that involve curing of dimensionally thick/expansive samples as well as light-attenuating situations including composites, adhesives, pigmented materials, and irregular surfaces. Herein, we demonstrated the first example of a solvent-free radical photopolymerization of common (meth)acrylate resins, which enables rapid surface and subsequent dark curing to near-vitrification-limited conversion in initially under-cured regions after brief irradiation. We compared the radical-based dark curing photoinitiator (DCPI) to a conventional type II photoinitiator (CVPI), using a commercially available 365nm LED. DCPI can dark cure the initial 20% conversion up to 80% without additional light while CVPI remains at 20% conversion after irradiation discontinuation. We also probed unique dark curing behaviors in bulk resins, providing insights into a hitherto unstudied phenomenon in RPP. We believe that practical DCPIs will be utilized as the next green technology, expanding the use of RPP into applications that were not previously feasible with automatic built-in correction of under-cured regions.

Institution: University of Colorado Boulder

Code: CHEMRedox_T11

Presenter: Nicholas A. Till (USA)

Abstract Title: Mechanistic Analysis in Dual Catalytic C–N Coupling

Co-Author(s): Lei Tian, Megan H. Shaw, Emily B. Corcoran, David W. C. MacMillan

Abstract: The combined use of photocatalyst structure-activity relationships, ultrafast spectroscopy, and stoichiometric organometallic studies has enabled the elucidation of the mechanistic underpinnings in a photocatalytic C–N cross-coupling reaction. The catalytic relevance of a high-valent Ni(III) species has been confirmed by precise tuning of photocatalyst properties, and stoichiometric reductive elimination studies. These studies provide insight into multiple roles for the photocatalyst in promoting product formation, in addition to addressing the mechanistic underpinnings to both N–H deprotonation and C–N reductive elimination steps.

Institution: Princeton University

Code: CHEMRedox_T12

Presenter: Justin Cole (USA)

Abstract Title: Translating Organic Photoredox Catalyst Design from Polymer Synthesis to New Reactivity for Small Molecules

Co-Author(s): Garret Miyake

Abstract: Organocatalyzed atom transfer radical polymerization (O-ATRP) using dihydrophenazine catalysts has led to an unprecedented understanding of the mechanism and photophysical properties of this photoredox catalyst family. This work seeks to exploit this advanced understanding and control of dihydrophenazine photoredox catalysts by tailoring their properties in order to operate orthogonally to a wide variety of functional groups at extremely low catalyst loading. Guided by computations, a library of catalysts was developed that possesses a wide range of excited state reduction potentials and radical cation oxidation potentials. These catalysts were then used to form inter- and intramolecular C-C, C-N, and C-O bonds.

Institution: Colorado State University

Code: CHEMRedox_T13

Presenter: Mahima Sneha (GBR)

Abstract Title: Unravelling Photoredox Catalysis Mechanism with Ultrafast Transient Absorption Spectroscopy

Co-Author(s): Aditi Bhattacherjee, Luke Lewis-Borrell, Jasper Tyler, Ian Clark, Andrew Orr-Ewing

Abstract: Recent advancements in the field of photoredox catalysis has been in the direction of replacing traditionally used transition metal catalysts with organic catalysts, which provide access to new and unique chemistry and do not suffer the same problems of toxicity and scarcity.1 However, while new synthetic methodologies and applications for these organocatalysts are emerging fast, quantitative understanding of their mechanistic underpinnings remains scarce.

Here, we report a detailed kinetic and mechanistic investigation of organocatalyzed atom transfer radical polymerization (O-ATRP) reactions using ultrafast transient electronic and vibrational absorption spectroscopies. O-ATRP operates through a multistep photoredox catalytic cycle and while the complete process takes ????-ms, the individual steps occur over a wide range of timescales from femtosecond (fs) upwards. Ultrafast spectroscopies can allow us to quantitatively characterize each step of this multistep pathway alongside building a complete picture of the reaction from initiation to completion. 2

Building on prior work,3 we have investigated OATRP reactions involving phenhydrazine and phenoxazine based catalysts developed by Miyake and coworkers.4,5 We have performed these studies accessing timescales all the way from 200 fs to 10 ms. Our observations challenge the previously proposed mechanisms and offer new insights about the structure-function-dynamic relationship of these photocatalysts.

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Institution: School of Chemistry, University of Bristol

Code: CHEMRedox_T14

Presenter: Alan Aguirre-Soto (MEX)

Abstract Title: Photocatalysis with Multiple Frequencies of Visible Light

Co-Author(s): NA

Abstract: The excitation of metastable intermediates in organic photoredox catalysis is discussed as a tool selectively promote desired over undesired pathways. It has recently been reported that the excitation of photoredox intermediates can be used to enable previously unattainable transformations (1) and to reduce the degradation of organic photocatalysts (2). In this study, we expand on this idea to broaden the set of photoredox systems amenable to multi-photon excitation. Steady-state and transient kinetics of organic photocatalysts and their intermediates were investigated under different irradiation regimes using multiple LED and laser combinations. A range of organic molecules were first tested for their ability to produce sufficiently stable intermediates after the initial photoredox event with sacrificial donors or acceptors. Then, the effect of the concentration of the secondary donor or acceptor molecule was tested. Once the photocatalyst/donor/acceptor combinations were screened, the effect of light intensity of the secondary light source was analyzed. The chosen systems were then studied in the presence of additional substrates that may lead to undesired reactions and by-products to show that the desired chemical transformation may be promoted with the present strategy. The benefits of controlling the selectivity of photocatalytic reactions is discussed and an outlook of possible applications of this approach presented.

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Institution: Tecnologico de Monterrey

Code: CHEMRedox_T15

Presenter: Yisrael M. Lattke (USA)

Abstract Title: Competitive Singlet and Triplet Reactivity in O-ATRP Activation

Co-Author(s): Steven M. Sartor, Blaine G. McCarthy, Niels H. Damrauer, Garret M. Miyake

Abstract: Organic photoredox catalysts show great promise in organocatalyzed atom-transfer radical polymerization (O-ATRP) since they are modular synthetic platforms and allow for light to be used as a toggle switch for the polymerization process. However, these photocatalysts are not all created equal; only some exhibit control over polymerizations, and design principles that promote this are still being established, with relevant molecular characteristics arising from correlations with computational studies and polymerization data. Questions remain regarding the roles of S1 and T1 excited states, the necessity of charge-transfer states, and the impact of excited-state reduction potentials on the activation step in the catalytic cycle. Activation is expected to proceed through outer-sphere electron transfer from an excited-state photocatalyst to an alkyl-bromide, resulting in homolytic cleavage of the R-Br bond. To probe this reaction, we utilize Stern-Volmer quenching studies with four phenoxazine-based photocatalysts, and an alkyl-bromide ATRP initiator as our model system. Conducting these investigations with both the S1 and T1 states of these photocatalysts yields bimolecular rate constants which we attribute to the activation process. While activation is certainly more rapid from the singlet manifold, the photocatalysts' short S1 lifetimes can limit their participation, whereas the molecules' long-lived T1 states are expected to react with unity yield, though they possess lower driving force for the electron transfer. We believe that measurement of these kinetic parameters provides insight into the first step in this catalytic cycle and will help to develop intuition regarding the reactivity of similar photocatalysts in related systems.

Institution: University of Colorado Boulder

Code: CHEMRedox_T16

Presenter: Tirthendu Sen (USA)

Abstract Title: Photoinduced Electron Transfer in Enhanced Green Fluorescent protein and its Mutants: An Insight to Oxidative Redding

Co-Author(s): Alexey M. Bogdanov, Konstantin A. Lukyanov, Anna I. Krylov

Abstract: Photoinduced reactions in fluorescent proteins (FPs) are becoming more attractive because of its diverse applications in advance fluorescence bioimaging. A mutant of green fluorescent protein (GFP) is designed with enhanced photostability (EGFP). Upon photoexcitation EGFP is transformed to a red form in presence of oxidants. Very little is known about the mechanism of this transformation and the characteristic of the red form. This process is known as oxidative redding. As it only occurs upon photoexcitation in presence of an oxidant, it has been hypothesized that this includes an electron transfer/ charge transfer reaction which determines the yield of redding. To understand the ET/CT pathway in EGFP, a series of random point mutations are performed and experimental relative photostabilities (PS) are compared to the theoretical rates of electron transfer via different residues. Along with experimental FQY, relative brightness (RB), PS etc. we conclude a theoretical model of competitive ET/CT channels via different residues in EGFP and mutants. This model not only contributes in mechanistic understanding of oxidative redding, but also, explains the differences in impact of mutation in different positions on FQY, based on other competitive processes like nonradiative decay, quenching by water close to the chromophore etc. On the whole, we propose a detail study on competitive ET/CT pathway in EGFP and its mutants along with impact of individual mutants role in initiating radiational relaxation.

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Institution: Department of Chemistry, University of Southern California

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Code: CHEMRedox_T17

Presenter: Kei Ohkubo (JPN)

Co-Author(s): N/A

Abstract Title: Light-Driven C-H Oxygenation of Methane into Methanol and Formic Acid by Chlorine Dioxide

Abstract: Selective aerobic oxygenation of CH4 into liquid products without the concomitant formation of CO2 and CO has served as an elusive target reaction. The one-step transformation of CH4 into methanol (CH3OH) is carried out in nature using methane monooxygenases. However, under chemical conditions, the selective oxygenation of CH4 to CH3OH with molecular oxygen (O2) has been unknown because the oxidation of oxygenated products, CH3OH and formic acid (HCOOH) is much easier than that of CH4, leading to over-oxidation products such as CO and CO2.

Here we show that chlorine dioxide radical (ClO2•) acts as an efficient oxidizing agent in the selective oxygenation of methane under photoirradiation. The product yields of CH3OH and HCOOH were 14% and 85%, respectively, without aerobic combustion under ambient conditions (298 K, 1 atm) [1]. In the case of ethane, the photooxygenation occurred under the otherwise same conditions to form ethanol and acetic acid with the yields of 19% and 80%, respectively. The photochemical oxygenation of methane is initiated by generation of chlorine radical and singlet oxygen from photoexcited state of ClO2•, leading to the final products by aerobic radical chain processes. Thus, the present study provides an environmentally benign approach towards the photooxidation of organic compounds. The photochemical oxygenation using ClO2• reported herein could be generalized to provide novel chemical reactions, which may have significant implications in synthetic and pharmaceutical chemistry.

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Institution: Osaka University

Code: CHEMRedox_T18

Presenter: Anabel E. Lanterna (CAN)

Co-Author(s): Bowen Wang, Kieran Duke, Juan C. Scaiano

Abstract Title: Cobalt-Molybdenum Co-Catalyst for Heterogeneous Photocatalysis

Abstract: The use of earth-abundant materials for applications in heterogeneous photocatalysis is a promising technology that adds to the easy separation and potential reusability of the material the advantage of developing cost-effective methodologies. Thus, Cu, Co, Mo, or Ni are alternatives to expensive traditional catalysts based on Ru, Pd, Pt or Ir complexes. In particular, we focus on the use of Mo-based materials as co-catalysts, as it has been demonstrated they have great potential in light-harvesting processes – especially for photogeneration of H2, where MoS2 is used as an alternative to Pt- or Pd-based catalysts. Nevertheless, Mo-based materials are practically unexplored in the field of photocatalytic organic transformations, with only a few examples reported for applications in fine chemistry.

In this contribution we focus on the use of non-precious Co and Mo elements as co-catalysts for the light-induced semi-hydrogenation reaction of internal and terminal alkynes using alcohols as H-source. It is known that TiO2 can readily oxidize alcohols to generate H2 gas, however the decoration of the semiconductor surface with other metals can greatly increase its reactivity. The Co-doped MoS2 structures can act as active sites for the formation of hydride species that can undergo H2 formation or H-mediated reactions affecting drastically the product ratios. This work constitutes a first step towards the use of Mo/Co-based catalysts with better efficiencies than Pd-based materials for uses in reductant-free heterogeneous organic transformations.

Institution: University of Ottawa

POSTERS

Code: CHEMRedox_P1

Presenter: Mulu Alemayehu Abate (ETH)

Co-Author(s): Hagos Feleke

Abstract Title: Transition State Structure Modeling and Mechanistic Study of Purine Derivatives

Abstract: Xanthine oxidase is one of the members of molybdo-enzymes known to catalyze the oxidative hydroxylation of various purine derivatives. The mechanistic transformation of the tetrahedral Michaelis-Menten type complex ((EOX)-[Mo(VI)-Oeq-CCRH]) to the product bound intermediate ((EOX)-[Mo(IV)-Oeq-CCR]) is expected to pass through the tetrahedral transition state complex ((EOX)-[Mo(VI)(-Oeq-CCRH---HRH---)(=SMo)]#). Although several accounts are made regarding the events taking place at the transition state, they have never been fully explored nor quite understood. Similarly, the description of the formation of Oeq-CCRH bond, cleavage of CCRH-HRH bond, migration of HRH to SMo terminal, and reduction of (EOX)-Mo(VI) to (ERED)-Mo(IV) was not well understood. In order to understand the events taking place during catalysis, new computational models have been used to perform an electronic structure calculation. The calculations were performed on the active site model compound bound to purine derivatives, mainly 2-hydroxy-6-methyl purine (HMP) that has never been investigated computationally. The transition state structure for HMP, Purine and hypoxanthine with one imaginary frequency was shown at -399.508 s-1, -214.505 s-1 and -920.217 s-1, respectively. The transition state modeling also reveals a reactant like transition state for the reaction of HMP with the active site. Understanding the transition state geometry is a prime importance in developing a plausible reaction mechanism. From the four alternative paths, path one has small energy barrier compare to the three alternative paths. Understanding the mechanism may be used in the drug design process. From our mechanistic study HMP favor concerted mechanism rather than step wise mechanism.

Institution: Arba Minch University, Arba Minch, Southern Region, Ethiopia

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Code: CHEMRedox_P2

Presenter: Chern-Hooi Lim (USA)

Co-Author(s): Garret Miyake

Institution: Colorado State University, New Iridium LLC

Abstract Title: Strongly Reducing Organic Photoredox Catalysts for Visible Light-Driven Synthesis of Polymers and Small Molecules

Abstract: Visible light photoredox catalysis has emerged as a power synthetic method for small molecule transformations and material synthesis. It accesses non-classical chemistry that target compounds can be synthesized in reduced synthetic steps under mild conditions. Despite these benefits, the required use of precious metal photoredox catalysts (PCs) such as Ir(ppy)3 or Ru(bpy)32+, can impede its industrial use. Through combined computational and experimental approach, we have developed strongly reducing dihydrophenazine and phenoxazine organic PCs as alternatives to these precious metals. Guided by DFT calculations, dihydrophenazine and phenoxazine organic PCs were designed to exhibit strongly reducing excited state, long-lived and high triplet quantum yield, charge transfer excited state, and redox reversibility. These traits are important for high performance PCs in oxidative quenchings. In particular, we have successfully applied these organic PCs for the synthesis of polymer via atom transfer radical polymerization (ATRP) and small molecules via trifluoromethylation and dual nickel/photoredox catalyzed C-N and C-S cross-couplings.

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(a) Theriot, J. C.; Lim, C.-H.; Yang, H.; Ryan, M. D.; Musgrave, C. B.; Miyake, G. M. Science 2016, 352, 1082.
(b) Pearson, R. M.; Lim, C.-H.; McCarthy, B. G.; Musgrave, C. B.; Miyake, G. M. JACS 2016, 138, 11399.
(c) Lim, C.-H.; Ryan, M. D.; McCarthy, B. G.; Theriot, J. C.; Sartor, S. M.; Damrauer, N. H.; Musgrave, C. B.; Miyake, G. M. JACS 2017, 139, 348.
(d) Du, Y.; Pearson, R. M.; Lim, C.-H.; Sartor, S. M.; Ryan, M. D.; Yang, H.; Damrauer, N. H.; Miyake, G. M. Chem. Eur. J. 2017, 23, 10962.

Code: CHEMRedox_P3

Presenter: Bryan Kudisch (USA)

Co-Author(s): Michael Black, Daniel G. Oblinsky, Todd K. Hyster, Gregory D. Scholes

Institution: Princeton University

Abstract Title: Mutagenesis Studies on Photobiocatalytic ‘Ene’-Reductases Reveal the Role of Internal Conversion in Their Excited-state Deactivation

Abstract: Photobiocatalysis merges the most useful and powerful aspects of both photoredox catalysis and biocatalysis by both selectively harnessing the energy of a photon to affect energetically intensive chemical transformations and by imparting stereoselectivity on the resultant product. Flavoproteins are emerging as the leading catalyst in this subfield of photocatalysis, boasting stability of multiple oxidation states, a high energy lowest singlet state (2.3 eV), and in some cases exposed active sites. Our groups have been working to understand the photochemical mechanism of a newly discovered light-promoted reaction which uses 12-oxophytodienotate reductase 1 (OPR1), an ‘ene’-reductase with a flavin mononucleotide (FMN) cofactor, in the presence of cyan light to induce the enantioselective cyclization of a non-natural substrate. Ultrafast spectroscopic investigations of OPR1 reveal an excited state lifetime on the tens of picosecond timescale, without the appearance of any charge transfer intermediates. Mutagenesis of the redox-affecting amino acids within 5Å of the FMN in OPR1 is discovered to not affect the overall deactivation pathway of the FMN cofactor excited state, while mutating select tyrosines further than 6Å from the FMN prompts ultrafast charge transfer to form a short-lived radical ion pair. We hypothesize that wild-type OPR1 undergoes an ultrafast internal conversion which is sensitive to the protein environment, either via specific nearby amino acids or the hydrogen bonding network. This work marks some of the first steps towards the understanding of photochemical mechanisms of non-natural ‘ene’-reductase photobiocatalysis through the discovery of the unique photophysics of OPR1.

Code: CHEMRedox_P4

Presenter: Luke Lewis-Borrell (GBR)

Co-Author(s): Mahima Sneha, Aditi Bhattacherjee, Varinder Aggarwal and Andrew Orr-Ewing

Institution: University of Bristol

Abstract Title: Unravelling the Mechanism of Organocatalysed Atom Transfer Radical Polymerisation (O-ATRP) with Ultrafast Spectroscopy

Abstract: Photoredox catalysis has transformed synthetic chemistry methodologies, and the field is now entering a mature phase where in-depth mechanistic studies around both catalysts and intermediates must be done to sustain the current levels of innovation. To date these mechanistic studies remain scarce.[1] In this study, we reveal kinetic and mechanistic details of photoredox catalysed reactions using ultrafast transient vibrational absorption spectroscopy. The focus is on organocatalyzed atom transfer radical polymerization mechanisms, using organic photocatalysts based on diphenyl dihydrophenazine and other conjugated ring structures.[2-3] The vision is to observe the full catalytic cycle from ultrafast (sub-picosecond) photoexcitation of the catalyst to radical termination and catalyst regeneration on nano, micro and milli second timescales in a single continuous measurement. These unprecedented studies identify the reactive intermediates involved in the electron transfer driven radical chemistry, revealing the molecular properties most important for controlling the photocatalytic efficiency. Overall leading to a greater understanding of O-ATRP, giving synthetic chemists the foundation from which they can further innovate.
1.Buzzetti, L.; Crisenza, G. E. M.; Melchiorre, P., Angew. Chem. Int. Ed. 10.1002/anie.201809984 2018.
2.Theriot, J. C.; Lim, C.-H.; Yang, H.; Ryan, M. D.; Musgrave, C. B.; Miyake, G. M., Science 2016, 352, 1082-1086.
3.Koyama, D.; Dale, H. J. A.; Orr-Ewing, A. J., J. Am. Chem. Soc. 2018, 140, 1285-1293.

Code: CHEMRedox_P5

Presenter: Sergio Adan Bermudez (GBR)

Abstract Title: Highly Sensitive Detection of Photosensitized Singlet Oxygen within Photonic Crystal Fibres

Co-Author(s): Anita C. Jones

Abstract: Singlet oxygen is an important reactive species in many areas of chemistry and biology and the principal component in a wide range of photodynamic therapy regimes. Consequently, the efficient photosensitized production and detection of singlet oxygen is an active area and attracting interest. Hollow-core photonic crystal fibres (HC-PCFs) are novel optofluidic systems in which light and chemical samples can strongly interact for quantitative spectroscopic analysis or photo-activation purposes [1,2]. Single-ring anti-resonant reflection (ARR) fibre is a newly developed type of HC-PCF that significantly reduces the complexity and guidance losses in the core, compared to previous generations [3]. We will report an investigation of the use of ARR HC-PCF for the detection of photosensitized singlet oxygen, using a well-established fluorescent probe, singlet oxygen sensor green (SOSG). This novel approach exploits the long path-length over which excitation can be sustained and the co-confinement of both photosensitizer and fluorescent probe along this extended excitation path.

References
[1] A. M. Cubillas, S. Unterkofler, T. G. Euser, B. J. Etzold, A. C. Jones, P. J. Sadler, P. Wasserscheid, P. St.J. Russell, Photonic crystal fibres for chemical sensing, and photochemistry, Chem. Soc. Rev. 2013, 42, 8629-8648.
[2] G. O. S. Williams, T. G. Euser, P. St.J. Russell, A. J. MacRobert and A. C. Jones, Highly Sensitive Luminescence Detection of Photosensitized Singlet Oxygen within Photonic Crystal Fibers, ChemPhotoChem, 2018, 2, 616-621.
[3] A. M. Cubillas, X. Jiang, T. G. Euser, B. J. Etzold, P. Wasserscheid and P. St.J. Russell, Photochemistry in a soft-glass single-ring hollow-core photonic crystal fibre, Analyst, 2017, 142, 925-929.

Institution: University of Edinburgh

Code: CHEMRedox_P6

Presenter: Matthew Bird (USA)

Abstract Title: Gaining Insight into Mechanisms of Photosensitized Reductive Elimination from Ni(II) Photocatalysts using Pulse Radiolysis

Co-Author(s): Jake Aquilina, Nick Till, Lei Tian

Abstract: It has been reported that Ni(II) complexes can undergo efficient reductive elimination from an electronically excited state, sensitized by energy transfer from an Ir photocatalyst.[1] Distinguishing between energy transfer and single electron transfer (SET) mechanisms[2] in these dual photocatalyst systems is not always straightforward. Knowledge of redox potentials helps to determine what reactions are possible, but many organometallic compounds show irreversible cyclic voltammograms and dark lowest electronic excited states.

Pulse radiolysis enables the rapid, selective addition of charge or energy to solute compounds in a controlled manner. The differing radiation chemistry of various solvents gives control over whether reduction, oxidation or triplet energy transfer can occur. With UV/vis/IR transient absorption techniques, short-lived intermediate species in a well-defined electronic state can be studied on a nanosecond timescale. Through electron transfer equilibria with other solutes, redox potentials were estimated for three Ni(II) compound that have been shown to undergo reductive elimination by photosensitization. We also use transient IR absorption to investigate whether the reductive elimination can be followed in real time to demonstrate unambiguously what electronic configuration initiates the reaction.

1.Welin et al., Science 355, 380-385 (2017)
2.Corcoran et al. Science 353, 279-283 (2016)

Institution: Brookhaven National Laboratory

Code: CHEMRedox_P7

Presenter: Lianfeng Zhao (USA)

Abstract Title: Solid-State and Solution Phase Room-Temperature Phosphorescence from Naphthalene Functionalized 2D Perovskites

Co-Author(s): Barry P Rand

Abstract: Long-lived triplet excitons, especially those with high energy, have attracted considerable attention because of their potential to be used in triplet-triplet-annihilation for visible-to-UV upconversion and photoredox catalysis. Naphthalene, a simple polycyclic aromatic hydrocarbon, is interesting owing to its high triplet energy (approximately 2.6 eV). However, triplet excitons cannot be directly generated by optical excitation because of the very high singlet energy and lack of efficient intersystem crossing. In this work, using 2D organic-inorganic hybrid perovskites as a sensitizer, we report room-temperature phosphorescence from naphthalene triplets in both solid-state and solution.

We used a combination of phenethylammonium (PEA) and 1-naphthylmethyl ammonium (NMA) as organic cations to form PEAxNMA (2-x)PbBr4 polycrystalline thin films. Room-temperature phosphorescence emission at 472 nm, 507 nm and 550 nm from the naphthalene group is observed when excited at 403 nm, a wavelength that corresponds to strong excitonic absorption of the 2D perovskite. Lifetime of these phosphorescence emission is calculated to be roughly 5 ms from their time resolved transient luminescence decays.

Colloidal 2D perovskite nanoplatelets suspended in toluene were synthesized through a nonsolvent crystallization process. We used a mixture of n-dodecylammonium (DDA) and NMA as organic cations to form DDAxNM2-xPbBr4 2D perovskite nanoplatelets. The bulky DDA cations were used to prevent 2D perovskite nanoplatelets from aggregating. Similarly, room-temperature phosphorescence emission is observed when excited at 388 nm.

Institution: Princeton University

Code: CHEMRedox_P8

Presenter: Remi Fayad (USA)

Co-Author(s): Anh Thy Bui, Felix Castellano

Abstract Title: Photochemical Upconversion in Water by Copper (I) Complexes for Photoredox Applications

Abstract: Photochemical upconversion (UC) through triplet-triplet annihilation (TTA), which employs a visible absorbing triplet photosensitizer and an acceptor/annihilator, is a process that generates a high energy photon from two lower energy photons. UC-TTA has been so far largely limited to pure organic solvents and solid-state polymeric constructs while being tied to the near exclusive use of rare and expensive metals in the photosensitizer component. In this work, we demonstrate that UC-TTA from the earth abundant photosensitizer [Cu(dsbtmp)2](PF)6 (dsbtmp = 2,9-di(sec-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline) operates in water through encapsulation within cationic-based micelles. Cetyltrimethylammonium bromide (CTAB) was the surfactant of choice here as it can electrostatically bind the negatively charged water-soluble 10-phenylanthracene-9-caboxylate acceptor/annihilator to facilitate energy transfer across the micellar interface. Efficient and diffusion limited triplet-triplet energy transfer (TTET) from the Cu(I) complex to the phenylanthryl-based annihilator was achieved from this design. The lack of mobility of the acceptors/annihilators ultimately hindered the annihilation process and this was reflected in attenuated TTA rates and efficiencies. The combined experimental data illustrates that the water soluble phenylanthracene acceptor was able to extract excited triplet energy from the Cu(I) photosensitizers contained within the micelles, ultimately delivering it to the bulk aqueous solution engaging in excited state electron transfer with various acceptors. This is particularly important for remotely operating photoredox reactions in water while rendering the Cu(I) photosensitizer spatially confined in the hydrophobic core of the micelles.

Institution: North Carolina State University

Code: CHEMRedox_P9

Presenter: Yoshinao Shinozaki (JPN)

Co-Author(s): Chiasa Uragami, Hideki Hashimoto, Hitoshi Tamiaki

Abstract Title: Fullerene-appended Chlorophyll Dimer as a Model of Photosynthetic Special Pair

Abstract: A pair of chlorophyll molecules called “special pair” plays a vital role in natural photosynthesis. The special pair is capable of functional junction between light-harvesting antenna and charge separation systems: this pair traps the excitation energy generated within antenna systems, which is in turn used for driving force for the charge separation. In an attempt to mimic structure and function of the special pair, several model compounds have so far been proposed. While majority of the models is based on tetrapyrrole macrocycles, (bacterio)chlorophyll-based models are limited as the chemical modification of natural chlorophylls is more difficult than that of porphyrins.

We recently reported a novel chlorophyll dimer in which two chlorophyll molecules are coupled via a dimethylamine linker. An amidation of this amino group with benzoic acid compelled the two chlorophyll components to be in close proximity each other in a dyad, which were interacted as in the special pair.1 Aiming at conferring the charge-separation function to the dimer, we introduced an electron-accepting fullerene into the chlorophyll dimer via amide bond. Time-resolved fluorescence measurements of this chlorophyll dimer–fullerene compound gave the very rapid decay component with the lifetime of 380 ps, which shortened as the solvent polarity increased. In this presentation, we will report synthesis of the chlorophyll dimer–fullerene compound and result for its spectrometric analyses including time-resolved fluorescence as well as transient absorption measurements.

H. Tamiaki, T. Tatebe, Y. Kitagawa, Tetrahedron Lett. 2018, 59, 3120–3123.

Institution: Graduate School of Life Sciences, Ritsumeikan University

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Code: CHEMRedox_P10

Presenter: Krishna Nand Tripathi (IND)

Co-Author(s): Md. Belal, Ravi P. Singh

Abstract Title: Organo Photoinduced Decarboxylative Alkylation of Coumarins with N-(Acyloxy)phthalimide

Abstract: Visible light catalyzed selective construction of carbon-carbon bond has started to garner attention from chemists recently.1 Coumarins are naturally occurring compounds recognized in organic materials for optical property and in many pharmaceuticals for impeccable bio-activities.2 The alkylation of coumarins yielding chain alkylated derivatives and other highly functionalized scaffold installation through alkylation via oxidative coupling reaction is still an arduous task. A metal/oxidant free and mild, photo-induced decarboxylative 4-position alkylation of coumarins has been disclosed. Photo-induced single electron transfer has been initiated by utilizing the visible-light absorptivity of Eosin Y3 for a reductive generation of alkyl radicals from N-(acyloxy)phthalimide esters.4 Depending on the nature of N-(acyloxy)phthalimide esters (primary, secondary, and tertiary carboxylic acid derived) several saturated and unsaturated C-4 alkylated coumarins were synthesized (34 examples) with excellent (upto 99%) yield. Control experiments photophysical and electrochemical studies supported a radical based mechanism for the selective alkylation.

References:
1) Tellis, J. C.; Primer, D. N.; Molander, G. A. Science 2014, 345, 433
2) (a)Tasior, M.; Kim, D.; Singha, S.; Krzeszewski, M.; Ahn, K. H.; Gryko, D. T. J. Mater. Chem. C 2015, 3, 1421. (b) Singh, L. R.; Avula, S. R.; Raj, S.; Srivastava, A.; Palnati, G. R.; Tripathi, C. K. M.; Mukesh Pasupuleti, M.; Sashidhara, K. V. The Journal of Antibiotics, 2017, 70, 954
3) Hari, D. P.; Konig, B. Chem. Commun. 2014, 50, 6688
4) Sandip, M. Adv. Synth. Catal. 2018, 360, 1735.

Institution: Research scholar

Code: CHEMRedox_P11

Presenter: Stephanie M. Hart, Minjung Son, Beryl X. Li, Talia J. Steiman (USA)

Abstract Title: Enhancing Transition Metal Photocatalytic Efficiency with Natural Light Harvesting Systems

Co-Author(s): Abigail G. Doyle, David W.C. MacMillan, Gabriela S. Schlau-Cohen

Abstract: The light-harvesting machinery of natural photosynthetic organisms such as plants and bacteria absorb over a broad range of visible and near-infrared wavelengths with a large absorption cross section. This allows numerous light-harvesting pigments bound to the antenna protein scaffold to concentrate dilute sunlight to the reaction center for efficient charge separation. In contrast, synthetic chemistry commonly uses transition metal-bearing photoredox catalysts to facilitate similar electron procceses for a variety of carbon bond-forming reactions. These photoredox catalysts have a significantly lower absorption cross section over a narrower spectral range, thus limiting the photocatalytic efficiency of many chemical reactions. To overcome this limitation, we have generated a biohybrid photocatalytic system by conjugation of phycoerthyrin, a red-algae-derived antenna protein, to transition metal based photoredox catalysts. By leveraging the optimal light harvesting properties of natural systems we aim to enhance the excitation flux to the photocatalyst via energy transfer from phycoerythrin to improve catalyst efficiency in photon-limited cases. The photophysical properties and photocatalytic properties of these biohybrid catalysts for carbon bond-forming reactions will be investigated. In addition to enhancing photocatalysis, this work also serves as a proof-of-principle demonstration of using natural photosynthetic systems to sensitize commonly available transition metal photoredox catalysts and has the potential to be expanded to multielectron chemistries that could serve as a synthetic analogue to the naturally occurring Z-scheme.

Institution: Massachusetts Institute of Technology (Hart & Son), Princeton University (Li & Steiman)

Code: CHEMRedox_P12

Presenter: Michael J. Black (USA)

Abstract Title: Photoenzymatic Catalysis in Flavin-Dependent 'Ene'-Reductases

Co-Author(s): Andrew J. Meichan, Kyle F. Biegasiewicz, Bryan J. Kudisch, Daniel G. Oblinsky, Gregory D. Scholes, Todd K. Hyster

Abstract: Flavin-dependent ‘ene’-reductases have a long history as useful biocatalysts for the stereoselective reduction of activated olefins. However, despite the known mechanistic versatility of flavin, ‘ene’-reductases are commonly viewed to only catalyze a single type of reaction. Here we describe a new approach to elicit new radical mediated C—C bond forming reactions through the irradiation of ‘ene’-reductases with visible light. Under this strategy, an asymmetric synthesis of pharmaceutically relevant oxindoles was achieved in a redox-neutral mechanism currently unknown to nature. This presentation will focus on the development of photoenzymatic catalysis in ‘ene’-reductases and the mechanistic underpinnings thereof. Further applications of photoenzymatic catalysis in future reaction design will be discussed.

Institution: Princeton University

Code: CHEMRedox_P13

Presenter: Lei Tian (USA)

Abstract Title: Ultrafast Spectroscopy Offers Mechanistic Insights for an Iridium-Nickel Photocatalytic C-O Coupling

Co-Author(s): Nicholas A. Till, Bryan Kudisch, David W. C. MacMillan, and Gregory D. Scholes

Abstract: The merger of transition metal and photocatalysis (termed as metallaphotocatalysis) has succeeded in invoking unprecedented over the past few years. In general, two types of “one-photon” initiated mechanisms, energy transfer and single electron transfer (SET) with photoexcited chromophores, are acknowledged to explain the enhanced reactivities of metal complexes. Contrary to the prevalence of photoinduced SET pathways where new redox species are accessed, energy transfer approach that utilizes the excited states of metal complexes to enhance reactivities remains relatively underdeveloped in metallaphotocatalysis.

Herein we report our mechanistic insights into an iridium-nickel photocatalytic C-O coupling[1] from ultrafast spectroscopic studies, where the product is formed via photoactivated reductive elimination from a square planar nickel(II) ester intermediate. By recording transient absorption signals of a mixture of iridium photocatalyst and the nickel intermediate, we observed a correlated excited state decay and ground state recovery for iridium transient signals. In conjunction with the lack of signals from any redox species, a triplet-triplet energy transfer mechanism for photoactivation from iridium excited state to the nickel intermediate is suggested. The mechanism of the following reductive elimination was also clarified to be a direct one-step process occurring on the 3MLCT state of the nickel intermediate. Based on these mechanistic insights, new strategies of energy transfer mediated photochemistry could be developed.

1. Welin et al., Science 355, 380-385 (2017)

Institution: Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States

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Code: CHEMRedox_P14

Presenter: Stephen I. Ting (USA)

Abstract Title: Characterization of Nickel Excited States Relevant to Nickel-Photoredox Catalysis

Co-Author(s): Sofia Garakyaraghi, Chelsea M. Taliaferro, Gregory D. Scholes, Felix N. Castellano, Abigail G. Doyle*

Abstract: Synthetic organic chemistry has been revolutionized by the merger of nickel and photoredox catalysis. This dual-catalytic platform, often called Ni-photoredox, enables many difficult bond formations under mild conditions. Canonically, photoredox catalysts modify the nickel catalyst and/or substrates by electron transfers. However, an increasing number of transformations are proposed to involve generation of excited nickel species, sometimes even in the absence of added photosensitizers. Thus, the excited states of nickel complexes relevant to Ni-photoredox are clearly important, although they have been scarcely studied. This study sought to experimentally characterize the excited states of complexes with the general structure Ni(2,2'-bipyridine)(aryl)(halide), which are believed to be intermediates in many Ni-photoredox reactions. The available evidence suggests that a metal-to-ligand charge transfer (MLCT) state is generated initially upon excitation, but decays to a tetrahedral d-d state that is ~11 kcal/mol (~0.48 eV) above the ground state. This necessitates a revision of a previous computational assignment from two of our groups, that the longest-lived component is an MLCT state with an energy of 38 kcal/mol (1.6 eV).[1] Mechanistic implications for Ni- and light-mediated reactions are discussed.

References:
[1] Shields, B. J.; Kudisch, B.; Scholes, G. D.; Doyle, A. G. J. Am. Chem. Soc. 2018, 140, 3035–3039.

Institution: Princeton University

Code: CHEMRedox_P15

Presenter: Nancy Awwad (USA)

Abstract Title: Photochemical Upconversion Induced Polymerization

Co-Author(s): Phil Castellano, Anh Thy Bui

Abstract: The revolutionary technology of 3D printing is quickly pervading many industries, predominantly employing photopolymerization as its commonly used technique. The present work reports the study of photochemical upconversion through triplet-triplet annihilation (TTA) in pre-polymer systems to initiate electron transfer in radical chain polymerization. First, homomolecular TTA was investigated in zinc (II) tetra-phenylporphyrin (ZnTPP) in a variety of solvents following Q-band excitation at 514.5 nm. ZnTPP acts as both the sensitizer and upconverting emitter as the TTA process ultimately yields an S2excited porphyrin as evidenced through the observation of its characteristic fluorescence at 435 nm. Upon addition of the liquid-based monomer trimethylolpropane triacrylate (TMPTA), we propose that green excitation at 514.5 nm promotes an electron transfer from the TTA-produced ZnTPP S2excited state that induces free radical polymerization. Fluorescence upconversion experiments following direct excitation of the Soret band at 400 nm illustrated that TMPTA dynamically quenched the ZnTPP S2fluorescence whose lifetime reduced from 1.48 ±0.05 ps in pure toluene to 0.56 ±0.04 ps in a 15:1 TMPTA/toluene mixture ([TMPTA]= 3.47 M). Using methyl acrylate (MA) as a surrogate for TMPTA in model quenching studies avoiding polymerization, dynamic excited state quenching of the S2fluorescence was also observed (kq= 8 × 1011M-1s-1), whereas the respective S1and T1excited states remained completely unaffected in the presence of MA. The utility of our approach was finally illustrated by producing micron-sized structures in a confocal fluorescence microscope, utilizing a variety of low-power visible light sources.

Institution: NCSU

Code: CHEMRedox_P16

Presenter: Daniela M. Arias-Rotondo, Artem Tsymbal (USA)

Abstract Title: Merging Photoredox Catalysis and Photochemical Upconversion

Co-Author(s): David W. C. MacMillan

Abstract: In the past decade, photoredox catalysis has enabled the development of a large number of novel chemical transformations that are highly advantageous for molecular construction. The key feature of this catalytic platform is the use of visible light to excite a photocatalyst that can then engage in electron transfer with an organic or organometallic substrate or intermediate; such interaction allows access to synthetically valuable mechanistic pathways.

Photochemical upconversion is a nonlinear process that effectively combines the energy of two photons to generate a higher-energy exciton. This phenomenon has shown great promise in several applications but has been scarcely used in synthetic chemistry. We see the merger of photon upconversion and photoredox catalysis as a way to further the application of previously reported reactions, and to explore new reactivity patterns by accessing excited states that are currently prohibitively high in energy.

In this work, we explore the use of red-to-blue photochemical upconversion to drive a series of decarboxylative cross-coupling reactions which our group has previously reported with traditional Ir(III) photocatalysts under blue light irradiation. Our new approach uses a triple catalytic platform that includes a red-light-absorbing sensitizer, an annihilator/photocatalyst, and a Ni catalyst that effects the bond-forming step. We have identified several annihilators that are competent photocatalysts for the reactions of interest. Herein we present those results, along with our progress towards the use of red light irradiation in conjunction with platinum- and palladium-based sensitizers. New directions are also discussed.

Institution: Princeton University

Code: CHEMRedox_P17

Presenter: Matthias Schmalzbauer (DEU)

Abstract Title: Activation of (Hetero)aryl Chlorides Utilizing Excited State Organic Anions and Visible Light

Co-Author(s): Indrajit Ghosh, Burkhard Koenig

Abstract: Forming complex molecules from cheap and available starting materials has always been a ubiquitous challenge. Photoredox catalysis emerged to an attractive tool and permits bond forming reactions under remarkably mild conditions. Widely used photocatalysts are, among others, the positively charged acridinium or triarylpyrylium-based dyes, which are known to act as powerful oxidants from their excited states.[1] However, contrary to those cationic representatives only little is known about anionic organic dyes in photoredox catalysis.

The tricyclic aromatic ketone 9-anthrone and its derivatives are under basic conditions in equilibrium with their corresponding anionic forms. Moreover, unlike the uncharged 9-anthrone, 9-anthrolate can be excited with blue LED light and acts as a strong reductant (E*red = -2.6 V vs. SCE) from its photoexcited state. To demonstrate the synthetic applicability of the catalytic system, various (hetero) aryl chlorides were converted in C–C and C–Het bond-forming reactions affording the corresponding arylation products in moderate to excellent yields. The reactions proceed under very mild conditions without the need for a sacrificial electron donor. Besides 9-anthrone, other closely related derivatives were synthesized and investigated concerning their ability to catalyze demanding reductive transformations. Based on spectroscopic findings and radical trapping experiments a conceivable mechanism is proposed.[2]

[1] N. A. Romero, D. A. Nicewicz, Chem. Rev. 2016, 116, 10075-10166.
[2] M. Schmalzbauer, I. Ghosh, B. Koenig, Faraday Discuss. 2019, DOI:10.1039/c8fd00176f.

Institution: Institute of Organic Chemistry,
University of Regensburg

Code: CHEMRedox_P18

Presenter: Anna Lucia Berger (DEU)

Abstract Title: Photocatalytic Carbanion Generation – Benzylation of Aliphatic Aldehydes to Secondary Alcohols

Co-Author(s): Karsten Donabauer, Mitasree Maity, Gregory S. Huff, Stefano Crespi and Burkhard König

Abstract: The key aspect of most photocatalytic reactions is the generation and subsequent reaction of a radical species by single electron transfer (SET) from an excited state photocatalyst to an organic starting material. While this concept enables many unique transformations, most C–C bond forming reactions in classical organic synthesis proceed via ionic intermediates. For example, the Grignard reaction, one of the most typical C–C bond forming reactions, involves the reaction of an anionic intermediate with an electrophile. Developing a photocatalytic method for the generation of carbanionic intermediates would be an interesting method to expand the limits of photoredoxcatalysis.

In this work, we present a redox-neutral method for the photocatalytic generation of carbanions from carboxylic acids. Benzylic carboxylates are photooxidized by single electron transfer; immediate CO2 extrusion and reduction of the in situ formed radical yields a carbanion capable of reacting with aliphatic aldehydes as electrophiles giving the Grignard analogous reaction product.

Reference:
K. Donabauer, M. Maity, A. L. Berger, G. S. Huff, S. Crespi, B. König, Chem. Sci. 2019, DOI: 10.1039/c9sc01356c.

Institution: Faculty of Chemistry and Pharmacy,
Institute of Organic Chemistry,
University of Regensburg

Code: CHEMRedox_P19

Presenter: Daniel Kim (USA)

Abstract Title: Selective Tyrosine Bioconjugation Mediated by Photoredox Catalysis

Co-Author(s): Beryl Li and Dave W. C. MacMillan

Abstract: The ability to reliably and site-specifically functionalize native amino acid residues of peptides and proteins is an important pursuit in the field of chemical biology. Bioorthogonal conjugation reactions have emerged as a powerful tool useful for imaging, biophysical investigations, photopatterning, and for the synthesis of antibody-drug conjugates for therapeutic applications. Photoredox catalysis has emerged as a powerful platform for cross-coupling reactions of native functional groups. To this end, by targeting native residues based on single-electron transfer versus nucleophilicity can offer complementary reactivity when compared to traditional bioconjugation reactions based on lysine and cysteine. Herein, we will explore the site-selective bioconjugation of tyrosine via a photoredox manifold and further diversify the toolbox of photoredox catalytic toolbox.

Institution: Princeton University

Code: CHEMRedox_P20

Presenter: Walter Damian Guerra (USA)

Abstract Title: Synthesis of a PCET-based Redox Relays: Ir-quinone-bipyridine Complexes for Improved Quantum Efficiency in Photocatalytic

Co-Author(s): Hunter H. Ripberger, Robert R. Knowles, Ana L. Moore, Thomas A. Moore

Abstract: Many transformations in photoredox catalysis are limited either in scope or quantum efficiency by electron-hole recombination between the radical (or radical ion) of the organic substrate and the oxidized/reduced form of the photocatalyst. Our approach addresses this limitation by using PCET-based redox relays attached directly to the photocatalyst to generate a rapid intramolecular PCET process that competes with the recombination reaction resulting in the extension of the lifetime of the reactive radical (1). As a result, a higher quantum yield of the desired product could be obtained and would open the door to the use of new substrates and applications in useful bimolecular processes.

We report the design, synthesis, and characterization of several naphthoquinone-bipyridine derivatives. These compounds serve as ligands in heteroleptic complexes of Iridium photocatalysts. Preliminary results using these catalysts for olefin hydroamination (2) and hydroamidation (3) reactions will be presented.

References:
1) Ruccolo, S.; Qin, Y,; Schnedermann, C.; Nocera, D. G. J Am Chem Soc. 2018, 140, 14926-14937.
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Institution: Arizona State University

Code: CHEMRedox_P21

Presenter: Hannah Sayre (USA)

Abstract Title: Supramolecular Nickel Photoredox Catalysts

Co-Author(s): Greg Scholes

Abstract: Polypyridyl Ni complexes catalyze cross-coupling reactions in photocatalytic systems with Ir(ppy)3 photosensitizers. The 3MLCT excited state of the Ni complex is important to the photocatalysis mechanism but has an excited state lifetime of only 4 ns. Electron acceptors have been coordinated to Ni catalysts to facilitate population of a long-lived charge transfer excited state for reductive elimination. Ru(II) polypyridyl photosensitizers have been coordinated to Ni catalysts to promote photoinitiated reduction of Ni for the oxidative addition step of cross-coupling catalysis.

Institution: Princeton University

Code: CHEMRedox_P22

Presenter: Xiao Liu (USA)

Abstract Title: Photochemical Properties of Solid-state Organic Semiconductor Photocatalysts

Co-Author(s): Daniela Arias-Rotondo, Dave MacMillan, Barry P. Rand

Abstract: Applications of prototypical organic optoelectronic semiconductors, i.e. light emitting and photovoltaic materials have opened new avenues in the field of organic photocatalysis. Various solid-state thin-film structures and combinations of earth abundant organic materials make their photochemical (redox) properties highly interesting. Here, we study the energy and charge transfer process in a tetracene film doped with 10%wt. platinum (II) tetraphenyltetrabenzoporphyrin (PtTPBP). The film is submerged in dimethyl sulfoxide as the photocatalyst for decarboxylative arylation of α-amino acids to produce benzylic amines. Steady state and time-resolved photoluminescence are used to measure the dynamics of tetracene singlet states that are generated via PtTPBP sensitized triplet-triplet annihilation in the film, where selective excitation of PtTPBP at a wavelength of 638 nm results in the observation of tetracene fluorescence peaked at 533 nm. Furthermore, we combine the doped tetracene with an electron acceptor material, e.g. Alq3 (tris-(8-hydroxyquinoline)aluminum) and TmPPPyTz (2,4,6-tris[3'-(pyridin-3-yl)biphenyl-3-yl]-1,3,5-triazine), forming a type II heterojunction that results in charge separation at a rate constant exceeding that for singlet decay in tetracene, leading to a significant increase of excited state lifetime that facilitates charge transfer from solid to liquid phase and thus the photocatalytic process.

Institution: Princeton University Department of Electrical Engineering

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Code: CHEMRedox_P23

Presenter: Hunter H. Ripberger and Emmanuel Odella (USA)

Abstract Title: Synthesis and Characterization of a Benzimidazole-phenol Based Ir-complex. Evaluation on Ketone-olefin Cyclization Reaction

Co-Author(s): S. Jimena Mora, Daniel A. Heredia, Thomas A. Moore, Robert R. Knowles and Ana Moore.

Abstract: The quantum efficiency of selected photoredox-based catalysis is frequently limited by the rapid charge recombination process between oxidizing equivalents (h+) and reducing equivalents (e-) formed upon initial illumination of the photocatalyst.(1) An alternative to favor the forward processes over recombination reactions is the introduction of redox relays featuring proton-coupled electron transfer (PCET),(2) which add fast redox-equivalent transfer steps that effectively compete against deleterious charge recombination at the charge-separating site.

Herein we report the rational design, synthesis, electrochemical and spectroscopic characterization of a bioinspired Ir-based photocatalyst complex bearing a benzimidazole-phenol (BIP) moiety (Ir-BIP complex) and its evaluation on a model ketone-olefin cyclization.

Preliminary results show remarkable fluorescence quenching of the Ir-BIP complex compared with the standard photocatalyst lacking the BIP moiety, suggesting a fast intramolecular PCET event, generating ground state Ir(II) and oxidized phenol. Initial evaluation of the Ir-BIP complex in a previously reported ketyl-olefin cyclization(3) established that it is a competent photocatalyst in reductive PCET chemistry. Further spectroscopic characterization of the Ir-BIP complex, as well as a preliminary results in the application of the complex to improve quantum efficiency in the ketyl-olefin coupling, will be presented.

In summary, we have developed a novel procedure for ketyl-olefin coupling allowed by PCET activation. These findings could be transferred to other photoinduced reactions, providing new strategies in the development of photocatalysts for reductive chemistry.

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Institution: Princeton University and Arizona State University

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Code: CHEMRedox_P24

Presenter: Kamila Kočí (CZE)

Abstract Title: Utilization of Advanced Oxidation Processes for Mitigation of Xylene from Waste Gas Stream

Co-Author(s): T. Prostějovský, M. Reli, R. Žebrák, T. Konečná, L. Obalová,

Abstract: Air pollution is one of the biggest environmental problems these days. The best option to lower the negative effects on the environment is to decrease or remove the emissions of pollutants and there are many ways how to do that. Advanced oxidation processes (AOPs), as a set of chemical reactions to generate hydroxyl radicals (OH·), are considered as an alternative technology for decreasing of emission of pollutants.

The experimental unit using advanced oxidation processes consisted of two consecutive steps. The first step was a stainless steel photolytic flow reactor with 16 UV lamps (peak intensity at 185 and 254 nm), which generated O3. The second step was a wet scrubber with 15 UV lamps in the upper part and with 8 UV lamps in the water reservoir (both sections of lamps with peak intensity at 254 nm). The scrubber worked as a photochemical reactor that used H2O2 water solution. The xylene was chosen as a model pollutant.

Photochemical pilot plant unit for the removal of volatile organic compounds was successfully constructed, tested and its efficiency was evaluated. The conversion of xylene decreased with increasing initial xylene concentration and decreasing residence time (higher flow rate) of waste gas. The highest conversion of xylene was 95 % and it was achieved under the lowest initial xylene concentration (50 ppm) and lower flow rate of 56.6 m3/h (mean residence time of 0,3 min in first step and of 2.5 min in second step).

Institution: Institute of Environmental Technology, VSB-Technical University of Ostrava, 17. listopadu 15, Ostrava-Poruba, Czech Republic

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Code: CHEMRedox_P25

Presenter: Justin Earley (USA)

Abstract Title: Dipole Strength and Charge Delocalization of Donor-Bridge-Acceptor Molecules

Co-Author(s): Obadiah Reid

Abstract: Photoredox catalysts are molecules that harvest light to drive thermodynamically unfavorable reactions by oxidizing or reducing the reactant species. It is key for these molecules to have a long-lived excited state and sufficient charge separation to enable charge transfer processes from the photoredox catalysts to the reactant species. Additionally, the separated charge’s spatial character, or delocalization, provides useful mechanistic insight into how the intermediate charge transfer state of a photoredox catalyst evolves.

Time-resolved dielectric loss spectroscopy is a technique sensitive to changes in the charge distribution of molecules in solution. Given a charge separated lifetime greater than a few tens of nanoseconds, time-resolved dielectric loss spectroscopy can measure the strength and lifetime of a dipole as well as how a charge is delocalized over a molecule. Donor-bridge-acceptor molecules have similar charge kinetics of photoredox catalysts; however, they stereotypically have more distinct and longer-lived signals, making them better model systems to study before moving to the more complicated charge kinetics of photoredox catalysts. This study utilizes time-resolved dielectric loss spectroscopy to map the charge kinetics of various donor-bridge-acceptor molecules to better understand the molecules' excited state behavior.

Institution: University of Colorado Boulder

Code: CHEMRedox_P26

Presenter: Md Islam (USA)

Co-Author(s): Radini Dissanayaka, Brendan T. Higgins, S. Adhikari, G. Mills

Institution: Postdoctoral research fellow, University of Notre Dame

Abstract Title: Photoreduction of CCl3F in Aqueous Solutions Containing Sulfonated Poly(ether etherketone) and Formate Buffers

Abstract: Irradiation of aqueous solutions containing the sodium salt of sulfonated poly(ether etherketone), and HCO2H/HCO2- buffers with 350 nm photons induced photoreduction of CCl3F to CHCl2F and Cl-. In situ determinations of chloride ion concentrations enabled evaluation of the quantum yield, φ(Cl-), which amounted to 0.46 in air-free, neutral solutions. A delayed formation of F- was noticed with a quantum yield of 0.18 probably due to a secondary transformation. High concentrations of the halide ions inhibited somewhat the photoreduction whereas phase-separated CFC droplets increased the reaction rate. Despite the high quantum efficiencies obtained, no post-irradiation formation of Cl- occurred. This observation together with other findings indicated that a chain process was not involved in the transformation. Most of the kinetic features of the photoreaction are explained in terms of a mechanism involving radicals of the reactants and of the polymer. Efficient photoreductions of CCl3F also took place in sulfonated poly(ether etherketone) solutions containing air.

Code: CHEMRedox_P27

Presenter: Russ Schmehl (USA)

Co-Author(s): Kristina Martinez, Jared Paul

Institution: Tulane University

Abstract Title: In Search of True Excited State Proton Coupled Electron Transfer Reactions

Abstract: Numerous reports exist of bimolecular excited state photoprocesses that experimentally appear to involve coupled electron and proton transfer (PCET), implying that both reactions occur within an encounter complex and the PCET products emerge from the reactant cage. However, direct spectroscopic evidence for such coupled reactions is lacking. We have recently been investigating photoinduced electron and proton transfer reactions between Ru(II) diimine chromophores with one 4-hydroxy-2,2'-bipyridine ligand and mono-quaternarized 4,4'-bipyridines (MQ(+)) that can serve as an electron and proton acceptor. In aprotic solvents these systems have explicit spectroscopic signatures that allow unambiguous identification of excited state proton transfer (ESPT), excited state electron transfer (ESET) and proton coupled electron transfer (ESPCET) photoproducts. Systems examined thus far follow an ESET / PT sequence that is complete in a few microseconds. The initial ESET product, MQ(0), reacts under pseudo first order conditions with protons available on the hydroxybipyridine Ru(II) complex in solution to yield the ET/PT product. These reactions will be discussed in terms of the free energy for competing excited state processes as well as the involvement of hydrogen bonded complexes formed in the ground and excited state. The current results also point to chromophore-proton/electron acceptor systems that might exhibit ESPCET.

Code: CHEMRedox_P28

Presenter: Matthew D Woodhouse (USA)

Co-Author(s): James K. McCusker

Institution: Michigan State University

Abstract Title: Excited-State Ligand Field Reactivity of an Iron(II) Polypyridyl

Abstract: Photoredox catalysis and solar energy conversion using 4th and 5th row transition metals, such as ruthenium and iridium, have been thoroughly studied. The natural abundance of these elements are among the lowest on the periodic table, leading to an interest in finding alternative earth-abundant transition metals. There have been reports of using FeII polypyridyls as catalysts in photoredox chemistry, but there is limited mechanistic evidence pertaining to the excited-state reactivity of the iron(II) catalyst. In this work, we have observed direct evidence of electron transfer from the lowest-energy ligand field excited state of [Fe(tren(py)3)]2+ (tren(py)3 = tris (2-pyridyl-methyliminoethyl)amine) to a variety of benzoquinones in bimolecular quenching studies using transient absorption spectroscopy. From these data it is possible to calculate an excited-state oxidation potential ranging from 0.15 V to 0 V (vs. SCE) and an approximate range of the zero-point energy difference between the ground state and lowest-energy excited state ranging from 0.9 eV (7200 cm-1) to 1.0 eV (8100 cm-1). These results provide a guideline for designing photoredox reactions using Fe(II) polypyridyls as photocatalysts.

Code: CHEMRedox_P29

Presenter: Suryansh Singh, Hanna Lyle (USA)

Co-Author(s): Ilya Vinogradov, Aritra Mandal, Tanja Cuk

Institution: CU Boulder

Abstract Title: Spectroscopic Investigation of Charge-Trapping intermediates of Photo-triggered O2 Evolution on n-SrTiO3

Abstract: Understanding the mechanistic details of water oxidation is key to developing efficient methods for water splitting. In that context, we aim to resolve the chemical bond dynamics taking place during photo-oxidation of water at a n-SrTiO3 catalytic surface from picosecond to microseconds timescales. Previously, two intermediates that trap charge and of the form Ti-O• and Ti-O•-Ti were identified on the n SrTiO3 surface during photo-triggered O2 evolution with 266 nm light. In order to fully characterize these intermediates, we have performed transient reflectance (TR) measurements with a pump pulse centered at 266 nm and a broadband white light continuum probe pulse spanning from 365 nm to 700 nm. The TR experiments performed during O2 evolution exhibit polarization dependence due to the difference in relative orientation of the intermediates with respect to the surface. Furthermore, the broader bandwidth of the white light probe and probing the surface under different conditions (closed circuit and open circuit) allows us to differentiate these intermediates both spectrally and kinetically from valence band holes and other nonlinearities. In the future, we would like to perform stimulated resonance Raman measurements on this model system to reveal their detailed structural evolution over a broad range in time.

The 29th International Conference on Photochemistry
Boulder, Colorado
July 21 – 26, 2019

INORGANIC PHOTOCHEMISTRY (INORGPhoto)
ABSTRACTS

INVITED TALKS

Code: INORGPhoto_I1

Presenter: Oliver S. Wenger (CHE)

Abstract Title: Luminescent 3d6 and 4d6 Complexes with Earth-Abundant Metals

Co-Author(s): Patrick Herr, Jakob Bilger, Laura A. Büldt, Christopher B. Larsen, Christoph Kerzig

Abstract: This talk will begin with an introduction to some of the basic challenges faced when trying to obtain 3d6 complexes with long-lived (emissive) metal-to-ligand charge transfer (MLCT) excited states. Whilst much research in this context has focused on Fe(II), there are other isoelectronic alternatives that seem worthy of consideration. [1] New results from our research on complexes with Cr, Mo and other earth-abundant metals will be presented. [2] Particular focus will be on ligand design, excited-state relaxation pathways, luminescence color tuning, the interplay between singlet and triplet emission, and applications in triplet-triplet annihilation upconversion as well as in photoredox catalysis. [3]

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[3] Wenger, O. S.; J. Am. Chem. Soc. 2018, 140, 13522.

Institution: University of Basel

Code: INORGPhoto_I2

Presenter: James K. McCusker (USA)

Abstract Title: Tailoring the Photophysics of First-row Transition Metal Complexes for Photo-induced Electron Transfer Chemistry

Co-Author(s): (none)

Abstract: Fundamental research on solar energy conversion – which will ultimately lead to the next generation of solar energy technologies – has sought to replicate Nature's solution through the creation of artificial constructs that mimic various aspect of photosynthesis. Indeed, the prospect of direct solar-to-fuel conversion represents one of the most promising pathways for carbon-neutral energy that can be scaled in a way not possible with the other renewables listed above. Whether it's the creation of potential gradients to generate current (i.e., photovoltaics) or more recent efforts to couple photo-excited species to catalysts for chemical conversion (e.g., reduction of protons to hydrogen), the critical first step is the absorption of light and the subsequent separation of charge. When considering large-scale (i.e., global) implementation of any solar energy conversion scheme, material availability becomes a critically important consideration in the light-capture part of the problem, particularly when one considers the projected two- to three-fold increase in energy demand over the next 30-40 years. Unfortunately, virtually all of the molecule-based approaches for solar energy conversion that have been proven successful rely on some of the least abundant elements on earth.

An obvious alternative is to employ chromophores based on earth-abundant materials: for transition metal-based approaches, this means moving away from the second- and third-row transition series elements (e.g., ruthenium) and develop photoredox-active chromophores based on the more widely available, first-row metals like iron and copper. Unfortunately, efforts to achieve this goal have met with limited success due primarily to ultrafast dynamics that rapidly depopulate the charge-transfer states that are formed upon light absorption: this is a debilitating feature that serves to undercut the use of these earth-abundant components in virtually any application that relies on charge separation following photon capture. This presentation will describe the origin(s) of this dramatic difference between first-row chromophores and their heavier congeners, as well as provide an overview of our efforts to understand the factors that determine the dynamics associated with excited-state evolution in first-row transition metal-based chromophores with the ultimate goal of circumventing and/or redefining their intrinsic photophysical properties in order to make feasible their use as light-harvesting components in photo-induced electron transfer chemistry.

Institution: Department of Chemistry, Michigan State University

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Code: INORGPhoto_I3

Presenter: Mark Thompson (USA)

Abstract Title: Modern Alchemy: Making Coinage Metals Look Like Iridium or Platinum

Co-Author(s): Rasha Hamze, Shyuang Shi, Peter Djurovich, Rodolphe Jazzar, Michele Soleilhavoup, Guy Bertrand, Caleb Coburn, Stephen Forrest

Abstract: There has been a great deal of effort targeted at finding alternatives to iridium-based emitters in organic LEDs (OLEDs), with Cu(I) complexes attracting a great deal of attention. In this paper I will discuss the synthesis, structural characterization and photophysical properties of several, two coordinate copper, silver and gold carbene complexes. Here we will focus on a number of different N-heterocyclic carbenes (NHCs). Using different carbene and X ligands, the emission color can be shifted from violet to deep red. These complexes show good phosphorescence quantum yield (□PL = 0.3 – 1.0), with radiative lifetimes in 0.4-3 microsecond regime in fluid solution and in thin film form. We have carried out cryogenic photophysical measurements and show that these compounds emit via E-type delayed fluorescence (also called thermally assisted delayed fluorescence, TADF), with a singlet-triplet gap as low as 200 cm-1 (25 meV) for the Ag-based materials and zero filed splitting values as high as 85, 75 and 225 cm-1, for Cu-, Ag- and Au-based compounds, respectively. Both of these values are exceptional for TADF emitters and copper-based compounds. I will discuss our modelling studies to determine the origin of these exceptional properties. I will discuss the photophysical properties and our understanding of them through the theoretical modelling and photophysical studies of these complexes.

We have prepared organic LEDs with these dopants and achieved > 20% EQE for green emissive OLEDs and > 12% for blue emissive OLEDs, both at comparatively low drive voltages.

Institution: University of Southern California

Code: INORGPhoto_I4

Presenter: Rebecca Abergel (USA)

Abstract Title: Actinide Luminescence Sensitization in Molecular and Nanocrystalline Assemblies

Co-Author(s): Peter Agbo, Korey Carter, Gauthier Deblonde, Abel Ricano, Leticia Arnedo-Sanchez

Abstract: From potential contamination of individuals with radioactive fission products after a nuclear accident to the therapeutic use of radio-isotopes for cancer diagnostics and treatment, the biological chemistry of actinides has become increasingly relevant to a number of applied problems. Understanding the fundamental bonding interactions of selective metal assemblies presents a rich set of scientific challenges and is critical to the characterization of f-element coordination chemistry in environmentally and biologically relevant species, and to the development of highly efficient detection methods, separation reagents or new therapeutic agents. Our approach to these challenges uses a combination of biochemical and spectroscopic studies on both in vitro and in vivo systems to characterize the selective binding of f-block metal ions by natural and biomimetic hard oxygen-donor architectures.

Several actinides, including AmIII, CmIII, and BkIV, are known to display specific luminescence properties, which can provide important information on the electronic and chemical differences between the 4f and 5f elements and may be in turn used for speciation determination. Most prior actinide photo-luminescence studies have been performed in the solid state and are based on direct excitation of the metal centered transitions, which necessitates high excitation power in order to populate emissive states and generate weak luminescence signals attributed to Laporte-forbidden f-f transitions. In contrast, most of our recent work has focused on the indirect modulation of actinide luminescence through the use of sensitizing antenna chelators. In this process, luminescence of the metal ion is prompted by the excitation of the ligand and subsequent intramolecular energy transfer from a triplet excited state or a singlet intra-ligand charge-transfer excited state of the ligand to the metal ion. Using the so-called “antenna” effect therefore leverages the much larger molar absorption coefficients of organic chromophores as compared to those of the weakly absorbing f-f transitions of actinide and lanthanide ions.

We will discuss the single- and multi-photon excitation of f-element molecular complexes as well as lanthanide/actinide nanocrystals decorated with strongly sensitizing chelators. Emphasis will be placed on the importance of luminescence-based processes to exploit the fundamental knowledge of the role of f-electrons in actinide bonding as well as on the generality of the proposed material architectures for realizing ligand-pumped, multi-photon downconversion.

Institution: University of California, Berkeley

Code: INORGPhoto_I5

Presenter: Matthew P Shores (USA)

Abstract Title: Investigating Impact of Noncovalent Interactions on Photoreactivity in Chromium Complexes

Co-Author(s): Anthony Rappe, Niels Damrauer, Eric Ferreira, Robert Higgins

Abstract: Employing Earth-abundant reagents in photocatalysis offers access to alternative mechanistic pathways, possibly leading to novel products or regio- or stereochemical control of product structures. Our current research efforts comprise several variations on a theme of understanding how non-covalent interactions can influence spin states, magnetic interactions, and reactivity in base metal-centered complexes. We seek detailed knowledge of the properties of Earth-abundant compounds, and accurate descriptions and synthetic control of electronic structure in ground and (photo)excited states. I will focus on the interplay of intermolecular interactions and electronic spin in mononuclear chromium complexes, toward understanding reaction mechanism(s) in photocatalytic Diels Alder cycloadditions, where spin considerations in photocatalyst interaction with substrates and dioxygen generate significant effects on observed products and pathways relative to more commonly used Ru and Ir photosensitizers.

Institution: Colorado State University

Code: INORGPhoto_I6

Presenter: Katja Heinze (DEU)

Abstract Title: Near-Infrared Emission with Earth-Abundant Metal Ions

Co-Author(s): Ute Resch-Genger, Christian Reber, Michael Seitz

Abstract: Emission, especially near-IR emission, from Earth-abundant 3d metal complexes is very difficult to achieve. If emission is observed, it is often short-lived and of low efficiency. By conceptual ligand design, we obtain luminescent and photoactive complexes with Earth-abundant metal ions with excited state lifetimes up to the millisecond range in solution at room temperature. Experimental (UV-VIS absorption, steady-state and time-resolved emission spectroscopy, transient absorption spectroscopy) and theoretical methods (DFT, TD-DFT, CASSCF-NEVPT2) give a deeper understanding of the unique photophysical properties. First applications of the complexes in optical sensing and photochemical synthesis already emerged.[1-6]

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[2] S. Otto, J. Harris, K. Heinze, C. Reber, Angew. Chem. Int Ed. 2018, 57, 11069.
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[6] S. Otto, N. Scholz, T. Behnke, U. Resch-Genger, K. Heinze, Chem. Eur. J. 2017, 23, 12131.

Institution: Johannes Gutenberg University Mainz, Germany

CONTRIBUTED TALKS

Code: INORGPhoto_T1

Presenter: Julien Christmann (CHE)

Abstract Title: Revealing the Mixing of the 4f55d1 and 4f6 States of Sm2+ in a Crystal Field

Co-Author(s): Prof. Hans Hagemann

Abstract:

The use of materials doped with Sm2+ in various applications (temperature and pressure sensing, optical data storage by hole burning, X-ray storage…) appeals for a better understanding of its electronic structure in a crystal field. One major difference between Sm2+ and the isoelectronic Eu3+ lies in the closeness between the 4f55d1 excited state and the 4f6 electronic levels in the divalent ion. This work reports luminescence data from several crystals doped with Sm2+ to address the influence of its 4f55d1 state on the 4f6 levels in a crystal field, and the corresponding results are compared to data previously published for Eu3+ [1]. The involvement of the environment-sensitive 4f55d1 state in the 4f6 mixing for Sm2+ is clearly evidenced by the relationship of the 5D0 – 7F0 transition energy with both the 5D0 – 7F1 energy and the 7F1 splitting, as well as the discrepancy of the ratio between the 5D1 and 7F1 splittings from its theoretical value [2].

[1] Tanner, P. A.; Yeung, Y. Y.; Ning, L. J. Phys. Chem. A 2013, 117, 2771.

[2] Christmann, J.; Hagemann, H. J. Phys. Chem. A 2019, submitted.

Institution: Department of Physical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

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Code: INORGPhoto_T2

Presenter: Lea Gimeno (FRA)

Abstract Title: New Chemical Design of Phenanthrolines to Achieve Reductive Quenching with Copper(I) Diimine Complexes

Co-Author(s): Jean-Noel Rebilly, Thierry Roisnel, E. Blart and Y. Pellegrin

Abstract:

Reductive quenching is the best way to do difficult reduction reactions. Using light, photosensitizer (PS) will be excited into (PS*). The key step is the reduction of PS* by a sacrificial electron donor (SD). Copper(I) bis(diimine) complexes ([CuL2]+, L = diimine) have the particularity to exhibit a very strong reduction potential (less than -2 V vs. Fc)[1]. For now, [CuL2]+ complexes are poorly oxidant at the excited state so the reduction of PS* by SD is thermodynamically impossible.

To make this step possible, we aim at increasing the photooxidation potential of copper(I)–bis(diimine) complexes (Eox*) by a new chemical design of phenanthrolines. We first worked on the excited state energy of the complexes which will directly impact Eox* by increasing the steric bulk within copper(I) coordination cage. However, increasing it too much raises stability issues. Molecular engineering guided us to break the symmetry of the phenanthroline, the two α positions of the nitrogen atoms were substituted by one bulky aliphatic group (to increase Eox*) and one aromatic group (phenyl or benzyl, to stabilize the coordination sphere by intramolecular π-stacking). We studied the impact of different substituents on electrochemical and optical properties of the complexes. Following this strategy we managed to increase Eox* by 150 mV for three new complexes compared to [Cu(dpp)2]+ (ca. -0.1V vs Fc).

This presentation will focus on the synthesis, optoelectronic characterizations, stability studies and reductive quenching trials of this new family of copper(I) complexes.

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Institution: CEISAM, Nantes University

Code: INORGPhoto_T3

Presenter: Peter Vöhringer (DEU)

Abstract Title: Exceptional Iron Complexes with Carbon Dioxide Radical Anion Ligands Dicovered by Ultrafast UV/MIR-Spectroscopy

Co-Author(s): Steffen Straub, Inga Majer, Jörg Lindner

Abstract:

The utilization of CO2 as an abundant, renewable carbon source in chemical synthesis represents a compelling strategy that may assist in the future to reduce greenhouse gas emissions. Inspired by biochemical CO2-fixation such an approach may rest on the activation of the inert gas by a suitable transition metal (TM). In the past, chemists have successfully prepared a number of different CO2-TM-complexes that can be classified according to the CO2-binding mode: (i) σ-bonding between TM and the central C-atom, (ii) π-„side-on"-bonding between TM and one of the two C=O bonds, and (iii) σ-"end-on"-bonding between TM and one of the two terminal O-atoms. Whereas in the former two modes the CO2-ligand is bent, it assumes a linear geometry in the „end-on" motif.

Here, we report on the observation of an exceptional "end-on" binding mode, in which the carbonaceous ligand is bent rather than linear. To this end, we photolyzed various oxalato complexes of iron, [LnFe(C2O4)(6-n)/2]n–3 (L=auxiliary ligand with denticity n), in liquid water as models for TM-CO2 binding/unbinding dynamics and ultrafast UV/IR spectroscopy to disclose the primary photochemical events resulting from their impulsive excitation. A single neutral CO2-molecule is expelled within 500 fs after excitation to generate a penta-coordinated ferrous species bearing a lone CO2-ligand. In low-spin complexes, the CO2 was found to bind in a "side-on" fashion, while in high-spin complexes, the "end-on" coordination is favored. In the latter case, the CO2 is coordinated as a radical anion and as such, it represents the reductively activated form of CO2 promising rich carbon-centered chemical reactivity.

Institution: Institute for Physical and Theoretical Chemistry, University of Bonn

Code: INORGPhoto_T4

Presenter: Sebastian Megow (DEU)

Abstract Title: Contradictions of the Ligand-Driven Light-Induced Spin Change (LD-LISC) Concept Revealed by Investigation of the Ultrafast Photo

Co-Author(s): Leonie Fitschen, Benedikt Flöser, Felix Tuczek, Friedrich Temps

Abstract: Light-induced spin crossover (SCO) in transition-metal complexes is a phenomenon that provides huge application potential, ranging from high-density magnetic data storage to medical applications. The concept of light-driven ligand-induced spin change (LD-LISC) is one of many promising approaches for the rational design of such compounds. The idea is to introduce a chromophore into the ligand environment that can undergo a photoreaction that changes the ligand field strength and thereby the spin state of the transition metal center.

We report on the ultrafast photodynamics of Fe(3AzoN4Py), an iron(II) polypyridyl complex functionalized with a photoswitchable azopyridine ligand suggested to be magnetically bistable in solution according to the LD-LISC concept. The results of femtosecond transient electronic absorption spectroscopy of Fe(3AzoN4Py), the free ligand 3AzoN4Py and the reference complex Fe(N4Py) show that initial excitation of the π,π* state of the azopyridine ligand at λpump = 312 nm is followed by an ultrafast energy transfer process leading to the formation of a metal-centered quintet state (5MC), often reported for similar complexes. This competing process diminishes the yield of the ligand's cis-isomer. Additional measurements carried out upon excitation of the singlet metal-to-ligand charge transfer (1MLCT) transition at λpump = 455 nm suggest that this energy transfer occurs via an MLCT state. Furthermore, the high-spin 5MC state is metastable and recovers to the low-spin ground state of the Fe(3AzoN4Py) complex with a time constant of ~3 ns. These results reveal intrinsic contradictions of the LD-LISC concept which will be discussed in some detail.

Institution: Christian-Albrechts-University Kiel

Code: INORGPhoto_T5

Presenter: Jannik Brueckmann (DEU)

Abstract Title: Introducing Oligothiophene Subunits into Ru(II) and Os(II) Polypyridine Complexes

Co-Author(s): Sylvia Schmid, Anne Stumper, Kilian R. A. Schneider, Djawed Nauroozi, Benjamin Dietzek, Peter Baeuerle, Sven Rau

Abstract: Recently, TLD1433 entered the clinical trials as the first Ru(II) containing photodynamic derivative. At the moment, a series of complexes bearing different oligothiophenes does exist, e.g. TLD1433 with a terthiophene moiety. Oligothiophenes are very attractive organic chromophoric units to be coupled with transition metal complexes. Such complexes exhibit 3LC states which are very reactive towards ROS production. Additionally, these ligand centered states make energy equilibrium between themselves and 3MLCT states possible. To achieve a more straightforward synthetic procedure, one has to widen the synthetic range, e.g. transition metal catalyzed cross-coupling reactions and functionalization of the aromatic backbone.
Herein, we want to present recent synthetic improvements and detailed photophysical investigations enabling the design of potent PDT drugs.

[1] C. G. Cameron, S. A. McFarland et al., Chem. Rev. 2019, 119, 2, 797-828. [2] L. Lilge, S. A. McFarland et al., Coord. Chem. Rev. 2015, 282-283, 127-138. [3] G. Gasser et al., Chem. Sci. 2015, 6, 2660. [3] J. Brückmann, A. A. Heidecker, D. Popovic, A. K. Mengele, D. Nauroozi, P. Bäuerle, S. Rau, Eur. J. Inorg. Chem. 2019, 1832-1838. [4] J. Brückmann, S. Schmid, A. Stumper, K. R. A. Schneider, D. Nauroozi, B. Dietzek, P. Bäuerle, S. Rau, manuscript in preparation. [5] W. Sun, S. A. McFarland et al., Photochemistry and Photobiology 2019, 95, 267-279. [6] A. Mandel, S. A. McFarland, L. Lilge et al., Photochemistry and Photobiology 2017, 93, 1248-1258.

Institution: Ulm University, Institute of Inorganic Chemistry I – Materials and Catalysis, 89081 Ulm, Albert-Einstein-Allee 11, Germany

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Code: INORGPhoto_T7

Presenter: Bryan C. Paulus (USA)

Abstract Title: From Vibrational Coherences to Synthetic Design Principles: Steric Control of MLCT Deactivation in Fe(II) Polypyridyls

Co-Author(s): Sara L. Adelman; James, K. McCusker

Abstract: Charge-separated, metal to ligand charge transfer (MLCT) excited states of ruthenium(II) coordination compounds have received intense interest for applications in solar energy conversion and photoredox catalysis. Efforts to use the vastly more earth abundant iron (II) congener, however, have often suffered from rapid deactivation of the initially generated MLCT excited state to an energetically lower ligand field excited state. The large geometric distortion concomitant with MLCT decay in these systems suggests a substantial amount of mixing between electronic and vibrational degrees of freedom and, by extension, implies that restricting the motions that drive this process may decrease the rate of MLCT decay. We performed ultrafast visible pump-probe spectroscopy measurements on a structurally tunable [Fe(cage)]2+ control molecule to monitor the coherently activated vibrational modes during the ultrafast MLCT decay process in an effort to understand the role of nuclear motion on the ultrafast decay mechanism of this class of compounds. Density functional theory calculations were used to visualize the rapidly dephased coherent vibrational modes of [Fe(cage)]2+, and subsequently inspired the synthesis of the more sterically encumbered [Cu2Fe(cage)]4+ analogue. It was shown that the Fe(II)-based MLCT lifetime of this [Cu2Fe(cage)]4+ derivative was 2.8 ps, representing a >20-fold increase relative to the [Fe(cage)]2+ control molecule. These results, in addition to the significantly longer dephasing times in [Cu2Fe(cage)]4+, suggest at least a partial decoupling of the electronic and vibrational degrees of freedom and illustrate the possibility for coherences to identify the reaction coordinate and therefore inspire synthetic design principles for tuning photophysical processes.

Institution: Michigan State University

Code: INORGPhoto_T8

Presenter: Julien Eng (USA)

Co-Author(s): Thomas J. Penfold

Abstract Title: On the Importance of Intermediate States in the TADF Mechanism: A Matter of Spin-vibronic Coupling

Abstract:

Thermally Activated Delayed Fluorescence (TADF) has been investigated in the last years as an efficient mean of harvesting the 75 % of triplet population generated upon electrical excitation of an OLED [1]. The TADF mechanism has been shown to be more complex than the simple two-states (S1/T1) picture.

To minimise the S1/T1 energy gap, and to favour reverse intersystem crossing (rISC) from T1 to S1, efforts have been put in the design of Donor-Acceptor type molecules exhibiting low lying charge transfer states. However, the spin-orbit coupling (SOC) between states of same nature and different spin is null and will lead to a decrease of the rate of the rISC. Even though this direct pathway (S1⇋T1) is closed, alternative routes via close-lying electronic states may provide a way of rISC [2,3].

Using quantum dynamics, we investigate the role of intermediate states in the TADF process in the [M(CAAC)(Cz)] (M=Cu, Ag, Au) series of compounds [4,5].

While the relative position of those intermediate states does not play a major role in the rate of ISC, their presence dramatically changes the dynamics depending on the intensity of the SOC between S1 and T1.

[1] F. B. Dias et al., Methods Appl. Fluoresc., 2017, 5, 012001.
[2] J. Gibson et al., ChemPhysChem, 2016, 17, 2956-2961
[3] M. K. Etherington et al., Nat. Commun., 2016, 7:13680
[4] S. Thompson et al., J. Chem. Phys., 2018, 149, 014304
[5] J. Eng et al., In preparation

Institution: Chemistry - SNES, Newcastle University

Code: INORGPhoto_T9

Presenter: Sara L. Adelman (GBR)

Co-Author(s): James K. McCusker

Abstract Title: Decoding the Nuclear Coordinate of Excited-state Deactivation in Low-spin Iron(II) Polypyridyls

Abstract:

Iron(II) polypyridyls represent an earth-abundant alternative to ruthenium-based complexes in photo-induced electron transfer applications, yet the sub-200 fs metal-to-ligand charge transfer (MLCT) excited-state lifetime endemic to low-spin Fe(II) polypyridyls has hampered their widespread use. One promising avenue towards achieving a longer-lived MLCT excited-state lifetime is through the exertion of kinetic control, made possible through the identification and subsequent disruption of the nuclear coordinate of excited-state deactivation. With this aim, a series of structurally similar iron(II) polypyridyl complexes spanning from low-spin to high-spin with a spin crossover intermediate were synthesized, which allowed for the determination of reorganization energy from the lowest-energy excited state (5T2) to the ground state (1A1) through a combination of variable temperature transient absorption and magnetic susceptibility measurements. In addition to experimentally determining the reorganization energy (4100 cm-1) and electronic coupling constant (2.1 cm-1) associated with this conversion, we will deduce the kinetically competent degree of freedom associated with this transition through a convergence of analyses from semi-classical to fully quantum mechanical non-radiative decay theories. Ruthenium (II)-based analogs of the spin crossover complexes provide insight into the geometric distortions coupled to the deactivation of the MLCT excited states. Coupled together, these results provide new guidelines for ligand design toward the goal of controlling excited-state dynamics in this class of iron(II)-based compounds.

Institution: Michigan State University

Code: INORGPhoto_T10

Presenter: Samuel G. Shepard (USA)

Co-Author(s): David Boston, Matt Shores, Niels Damrauer

Abstract Title: Salen Complexes as Candidates for Stereoselective Photocatalysis

Abstract:

Metal complexes with salen-derived ligands have found utility in a broad array of catalytic and, to a lesser extent, bio-sensing and fluorescence labeling applications, due to the ease and flexibility of their synthesis. The tetradentate salen ligand leaves two axial sites open on the metal center. The direction of substrate approach to these sites is determined by stereocenters on the ligand, allowing for stereoselective catalysis (e.g., in olefin epoxidation and epoxide ring opening). Despite the research on photoactive salen compounds, salen-based catalysis rarely exploits excited states and the enhanced reactivity they afford. This presentation will examine efforts to combine steady-state and time-resolved spectroscopy, electronic structure theory, and electrochemistry to explore the potential role of metallo-salen compounds as photocatalysts. Specifically, the axial binding of a pyridine substrate creates subtle changes in ground state absorption but shows marked effects on the excited state evolution of these complexes. DFT results suggest that the photoexcitation shifts electron density on to the pyridine in low-lying excited states. The possibility of stereoselective attack on the photoexcited pyridine-salen complex is a promising first step towards salen photocatalysis.

Institution: University of Colorado - Boulder

Code: INORGPhoto_T11

Presenter: Ahmed El-Zohry (SAU)

Abstract Title: Charge Dynamics on Material Surfaces

Co-Author(s):	Ahmed El-Zohry	**Abstract:**	Although ultrafast charge carrier dynamics in the bulk of solar cell materials are generally well understood using time-resolved laser spectroscopy, these processes on surfaces and interfaces continue to represent one of the largest challenges impeding the further development of solar cells, photodetectors, and light-emitting diodes. By utilizing four-dimensional scanning ultrafast electron microscopy (4D-SUEM) at various applied voltages, we can now visualize the evolution of photogenerated charge dynamics from the material's bulk towards its surface simultaneously in space and time domains under the influence of band-bending at the material surfaces, and at the terminating surfaces controlled by the crystal orientation. Cadmium telluride (CdTe), silicon (Si) single crystals wafer, and other materials were chosen as model systems to understand these processes.
Institution:	KAUST		

Code:	INORGPhoto_T12		
Presenter:	Peter Vöhringer (DEU)	**Abstract Title:**	The Femtochemistry of the Ferrioxalate Actinometer
Co-Author(s):	Steffen Straub, Paul Brünker, Jörg Lindner	**Abstract:**	Chemical actinometry is an indispensable analytical tool in preparative photochemistry that allows for a precise measurement of radiant fluxes inside photoreactors. An actinometer thus enables an absolute determination of the quantum yield of a photochemical reaction of interest. The "gold standard" of chemical actinometry in liquid systems is the Hatchard-Parker actinometer, i.e. an aqueous solution of potassium iron(III)oxalate, which is based on the light-induced net transformation of ferric into ferrous oxalate complexes. Although the absolute photochemical quantum yield for this fundamental standard system has been accurately known for many years, the underlying molecular-level mechanisms and time scales associated with a photoreduction of the ferrioxalate actinometer remained so far entirely obscured. Here, we use femtosecond mid-infrared spectroscopy combined with ultrafast laser photolysis to obtain unique structural-dynamical information associated with the primary light-triggered processes thereby finally providing the quantitative molecular foundations, without which a utilization of aqueous ferrioxalate as a true photochemical standard cannot be justified. The time-resolved spectra reveal that the metal's coordination sphere loses a neutral CO2 molecule within 500 fs after photoexcitation to generate a penta-coordinated dioxalatoiron(II) species that is still dressed with an anionic CO2 radical ligand. Subsequent oxalate sliding and twisting motions bring about a structural isomerization that changes the ligand binding geometry at the metal from initially octahedral and trigonal-bipyramidal to square-pyramidal. The cleavage of the CO2 radical anion ligand generates the final ferrous dioxalate product on a time scale of a few tens of picoseconds.
Institution:	Institute for Physical and Theoretical Chemistry, University of Bonn		

Code:	INORGPhoto_T13		
Presenter:	Matteo Mauro (FRA)	**Abstract Title:**	Light-responsive Supramolecular Metallopolymers as Self-healable Contractile Materials
Co-Author(s):	-	**Abstract:**	Smart functional materials that are able to translate an externally applied stimulus into a well defined, controllable, and reversible macroscopic response are one of the most fascinating materials nowadays. Soft and structurally dynamic functional materials are particularly attractive because of their intrinsic possibility to heal after damage. These materials possess appealing application in nanomedicine, drug delivery systems, tissue engineering as well as soft robotics and artificial muscles. Amongst all possible triggers, light represents an interesting stimulus due to its advantageous features such as remote application with high spatiotemporal resolution. During the talk, the straightforward molecular design of reversible and photo-switchable metallopolymers and their use as photo-responsive and autonomously healable gels will be presented. By simply mixing a proper metal salt and ligand(s) at the desired ratio, libraries of supramolecular metallopolymers have been straightforwardly prepared. In addition, judicious choice of the electronic properties of each building block allows to independently addressing luminescence and photo-isomerization by selection of the excitation wavelength. We found out that such materials can act as "supergelators" and either hydrogels or organogels have been obtained that display light-triggered reversible phase transition and large photo-mechanical actuation (gel contraction), respectively. Noteworthy, proper choice of the metal ion and its electronic excited-state features, i.e. Fe(II) vs. Co(II) and Zn(II), allowed control of the macroscopic photo-mechanical response in the gels state. Finally, the monitoring of the reversible photo-triggered expansion/contraction processes at the sub-molecular level was achieved by means of scanning tunneling microscopy on a highly oriented pyrolitic graphite surface, where these systems reversibly played as supramolecular "accordions" under light irradiation.
Institution:	Institut de Physique et Chimie des Matériaux de Strasbourg, University of Strasbourg, France		

Code:	INORGPhoto_T14		
Presenter:	Irene Jiménez Munguía (RUS)	**Abstract Title:**	Comparative Study of Porphyrin Photosensitizers on the Boundary of Lipid Membrane

Co-Author(s): Meshkov I.N., Birin K.P., Gorbunova Y. G., Sokolov V.S.

Abstract: Photosensitizers (PS) are commonly used in photodynamic therapy to treat skin cancer. Their molecules bind to cell membrane and damage it by singlet oxygen (SO) generated under illumination. In our laboratory, we study in vitro the processes involved in photodynamic therapy on a model bilayer lipid membranes (BLM) by measuring the boundary potential applying the Intramembrane Field Compensation Method (Sokolov and Kuz'min, Biofizika, 25:170, 1980). This method allowed to monitor the binding of PS on BLM and damage of target molecules (TM) of SO - di-4-ANEPPS under excitation of PS by light. In present investigation, we studied the adsorption and photodynamic efficiency of new positively charged porphyrins, namely β-imidazolyl substituted porphyrin and it's Zn(II) and In(III) complexes; and two phosphorus (V) complexes of meso-(p-pyridyl)-triphenylporphyrin bearing hydroxyl and ethoxyl axial ligands. We observed a linear dependence of the boundary potential change on the logarithm of concentrations of each PS. The photodynamic efficiency of these porphyrins was assessed by determining the rate of oxidation (R) of TM adsorbed either on the same or opposite surface of the BLM where molecules PS were present. The values R for both positions of TM were close indicating that BLM is highly permeable to singlet oxygen. The values R were proportional to surface density of the porphyrin molecules in the membrane. This investigation indicate that the main factor influencing the photodynamic efficiency of the porphyrins is their adsorption on the BLM.

Acknowledgements: This work was supported by the Russian Foundation of Basic Research (N 19-04-00694a) and the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of NUST «MISiS» (№ К4-2017-053).

Institution: National University of Science and Technology, NUST-MISiS

Code: INORGPhoto_T15

Presenter: Mika Inaba (JPN)

Abstract Title: Cooperative Doping Effect in both Bulk and Surface in Hematite for Efficient Solar Water Splitting by the Facile Method

Co-Author(s): Woon Yong Sohn, Kenji Katayama

Abstract: Hematite is one of the promising candidates for photoelectrochemical (PEC) water splitting because of its abundance, photo-stability, and narrow optimal bandgap. However, its low conductivity, the major drawback, intrinsically limits the effective water splitting. In order to address this problem, doping is a powerful approach because it increases both carrier concentration and carrier mobility. For example, it has been reported that the TiO2 interlayer between hematite and FTO serves as a Ti4+ source which promote the bulk conductivity, as well as blocking the back-diffusion of electrons and reducing the lattice mismatch.1 In addition, phosphorus doping on the surface of hematite, which does not act as the trapping site, results in a large number of the charge carriers.2 From these aforementioned achievements, we expect that there is a cooperative effect by introducing dopant in both bulk and surface of hematite film, leading to a drastically improved PEC performance. In this study, we fabricated a new type of hematite films with doping from both upper (phosphorus) and lower (titanium) side of hematite layer using a facial solution-based method. In addition, in order to expand the depletion layer, we employed very short and high temperature annealing, which is called gradient doping.2 We precisely controlled the annealing condition, inducing the gradient incorporation of elements that are designed to increase its conductivity and facilitate the charge separation in hematite, which promote the PEC performance.[1]Luo, Z. B., et al., Angew. Chem. Int. Ed., 2017, 56(42), 12878-12882.[2]Luo, Z. B., et al., Chem. Sci., 2017, 8(1), 91-100.

Institution: Chuo University

Code: INORGPhoto_T16

Presenter: Akihito Imanishi (JPN)

Abstract Title: Influence of Nano Structure of TiO2 Single Crystal Electrode on Water Photooxidation Reaction Process –Facet and Edge Effects–

Co-Author(s): Hideki Ishikawa, Ken-ichi Fukui

Abstract: The oxygen photoevolution reaction on TiO2 and related metal oxides has attracted strong attention from the point of view of solar water splitting. In our previous study, we reported that the generated holes are consumed not only by the O2 evolution reaction but also by three competitive paths possibly occur at different surface sites; photoluminescence, surface roughening (i.e. photocorrosion), and nonradiative recombination [1,2]. In this study, we investigated the influence of nanostructure formed on the TiO2 electrode on the branch ratio of 4 competitive photooxidation reactions.

Nanostructured 0.05wt% Nb doped-TiO2(110) (n-type) electrode were prepared by photoetching in 0.05 M H2SO4 [3] and used as a working electrode. We obtained the nanostructured surfaces on which shallow grooves are regularly arranged (We should note that formed surface of the nanostructure is composed by (100) facet faces [3]). Photooxidation process was observed in 0.1 M HClO4 under UV irradiation. We found that the overvoltage for O2 evolution on nanostructured electrode was decreased comparing with that on atomically flat (100) surface. In addition, the consumption ratio of the photogenerated holes by above mentioned 4 competitive reactions was largely different from that on the atomically flat (100) surface. We can explain these results by the spatial configuration of edge and facet sites which depends on the surface nanostructure.

[1] A. Imanishi et.al. J. Am. Chem. Soc., 129 (2007) 11569.
[2] A. Imanishi et. al. J. Phys. Chem. Lett., 5 (2014) 2108.
[3] A. Imanishi et. al. J. Phys. Chem. B, 110 (2006) 21050.

Institution: Department of Chemistry, Graduate School of Engineering Science, Osaka University

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Code: INORGPhoto_T17

Presenter: Ian Stanton (USA)

Abstract Title: Innovative Measurement Techniques and Sampling Accessories for Photoluminescence and Transient Absorption Spectrometers

Co-Author(s):

Abstract: Edinburgh Instruments has engineered sample holders for the most challenging photoluminescence and transient absorption measurements of solutions, solids, and device; absolute quantum yields down to 77 K, photoluminescence measurements up to 600 C, electroluminescence for steady-state and lifetime analysis, and ICCD integration for time gated nanosecond transient absorption spectra, to name a few. This presentation will not only highlight the tools needed to make the measurements, but show exemplary data from literature and internal measurements.

Institution: Edinburgh Instruments

POSTERS

Code: INORGPhoto_P1

Presenter: Salam Maloul (DEU)

Abstract Title: Pd and Pt Functionalized Anderson Polyoxomolybdate Clusters for the Photocatalytic Hydrogen Evolution

Co-Author(s): Prof. Carsten Streb

Abstract: Molecular hydrogen is considered one of the most promising alternative for fossil fuels, as it represents a clean fuel with high energy density [1]. One of the most promising approaches towards the generation of hydrogen is the use of molecular photocatalysts that utilize visible light to drive protons reduction [1,2]. Here, we represent three Pd and Pt functionalized Anderson polyoxomolybdate clusters [3]. These clusters are
-(nBu4N)3[MnMo6O18{(OCH2)3CNCH(C11H9N2)PdCl2}2]
-(nBu4N)3[MnMo6O18{(OCH2)3CNCH(C11H9N2)PtCl2}2]
-(nBu4N)3[MnMo6O18{(OCH2)3CNCH(C11H9N2)PtI2}2]
The photocatalytic activity of these clusters toward the hydrogen evolution were tested, and they showed higher activity compared to a reference compound of Pt(bpy)Cl2. This increased activity could be attribute to the increased negative charge on the clusters that leads to a higher electrostatic interaction between the catalyst and the photosensitizer which is [Ir(ppy)2(bpy)]PF6. This increased electrostatic attraction would lead to enhanced charge transfer between the photosensitizer and the catalyst.

1.Whang, D. R. & Young, S. Rational Design of an Electron-Reservoir Pt II Complex for Efficient Photocatalytic Hydrogen Production from Water. 3204–3207 (2015).
2.Pfeffer, M. G. et al. Palladium versus Platinum: The Metal in the Catalytic Center of a Molecular Photocatalyst Determines the Mechanism of the Hydrogen Production with Visible Light. Angew. Chemie - Int. Ed. 54, 5044–5048 (2015).
3.Schönweiz, S. et al. Covalent Photosensitizer–Polyoxometalate-Catalyst Dyads for Visible-Light-Driven Hydrogen Evolution. Chem. - A Eur. J. 22, 12002–12005 (2016).

Institution: Institute of Inorganic Chemistry I/ Ulm University Albert-Einstein-Allee 11, 89081 Ulm (Germany)

Code: INORGPhoto_P2

Presenter: Dajana Isakov (DEU)

Abstract Title: Two Long-lived Emissive Excited States in a Ruthenium Dipyridophenazine Type Complex

Co-Author(s): Robin Giereth, Djawed Nauroozi, Stefanie Tschierlei*, Sven Rau*

Abstract: Since the discovery of the function of ruthenium dipyridophenazine complexes as DNA sensors, great efforts have been made to understand the underlying photophysical properties of such complexes.[1]
Interestingly, in π-extended derivatives the existence of further ligand-centered excited states can be advantageous for the overall activity of such complexes in the fields of e.g. photodynamic therapy and solar energy conversion.[2-5]
Herein, we present a ruthenium complex, which incorporates the well-known dipyridophenazine ligand, modified by a conjugated imidazole moiety. We investigated this compound via transient absorption spectroscopy and emission lifetime measurements on nanosecond timescale and observed two long-lived excited states.[6] Notably, both these states are emissive in acetonitrile. Furthermore, we investigated the “light switch” behavior of the complex, as well as its electrochemical properties.
Literature:
[1] J. K. Barton et al., J. Am. Chem. Soc. 1990, 112, 4960-4962.
[2] C. Turro et al., Chem. Commun. 2010, 46, 2426-2428.
[3] S. A. McFarland et al., Inorg. Chem. 2014, 53, 4548-4559.
[4] B. Dietzek et al., J. Phys. Chem. C 2018, 122, 83-95.
[5] B. Dietzek and M. Chavarot-Kerlidou et al., Chem. Sci. 2018, 9, 4152-4159.
[6] D. Isakov, R. Giereth, D. Nauroozi, S. Tschierlei*, S. Rau*, manuscript submitted.

Institution: Ulm University, Institute of Inorganic Chemistry I – Materials and Catalysis, 89081 Ulm, Albert-Einstein-Allee 11, Germany

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Code: INORGPhoto_P3

Presenter: Takuhiro Otsuka (JPN)

Abstract Title: Quenching Reaction of Luminescence of Ru(II) Complex in Coexisting Liquid Phase Near the Eutectic Point of Aqueous Solution

Co-Author(s): Arinori Inagawa, Tetsuo Okada, Youkoh Kaizu

Abstract: As the aqueous solution is cooled, only water is frozen and the solution is gradually concentrated. At temperatures near the eutectic point, the concentrated liquid phase looks like a blood vessel in the human body. We have used this special coexisting liquid phase as a tube for transporting particles, and have studied the interface of the coexisting liquid phase and ice as a new reaction field. Recently, we focused on the quenching reaction of the [Ru(bpy)3]2+ emission by [Fe(CN)6]3- due to the diffusion-limited electron transfer reaction. From the results of the quenching experiments, we succeeded in estimating the viscosity of the coexisting liquid phase generated by freeze concentration 1). In this study, we focused on the fact that the concentration of the coexisting liquid phase generated by freeze concentration reached 50 times the concentration before freezing. The aim of this work is to clarify how the photo-excitation energy-transfer from [Ru(bpy)3]2+ to [Cr(CN)6]3- in this special solution is different from the bulk solution before freezing.
1) Arinori Inagawa, Tomoki Ishikawa, Takuma Kusunoki, Shoji Ishizaka, Makoto Harada, Takuhiro Otsuka, Tetsuo Okada. Viscosity of Freeze-Concentrated Solution Confined in Micro / Nanospace Surrounded by Ice, Journal of Physical Chemistry C, Vol. 121, page 12 -12328, 2017.

Institution: Department of Chemistry, Tokyo Institute of Technology.

Code: INORGPhoto_P4

Presenter: Ryan Dill (USA)

Abstract Title: Long-Lived Doublet MLCT States in Vanadium(II) Polypyridines

Co-Author(s): Ryan D. Dill, Samuel G. Shepard, Romeo I. Portillo, Anthony K. Rappé, Matthew, P. Shores, Niels H. Damrauer

Abstract: Transition metal (TM) complexes with 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and related ligands have proven useful in photochemical applications partly because they exhibit redox active charge-transfer states and high molar attenuation coefficients. Replacing conventional ruthenium complexes with cheaper first-row TM complexes has been a focus of our research group. [V(bpy)3]2+ and [V(phen)3]2+ have strong, panchromatic metal-to-ligand charge-transfer (MLCT) absorptions, a particularly useful characteristic in photosensitizers. Prior studies concluded that the long-lived excited state was a quartet MLCT. However, our sub-picosecond transient absorption studies in the visible and near-infrared, including at cryogenic temperatures, suggest that after initial excitation into the 4MLCT, the complexes undergo rapid interconversion (τisc < 100 fs) to a 2MLCT, which then equilibrates with a metal-centered (MC) state (τeq = 2.5-3 ps). Computational evidence suggests that the 2MLCT is lower in energy than the 4MLCT, which supports our conclusions and is consistent with previous reports from other authors. Population of the MLCT persists longer than in typical first-row TM complexes – ground state recovery lifetimes are 450 and 1600 ps for the bpy and phen complexes, respectively. Subtle synthetic modifications in future systems may shift the MLCT-MC equilibrium and substantially modify the dynamics.

Institution: University of Colorado, Boulder

Code: INORGPhoto_P5

Presenter: Andressa Vidal Müller (USA)

Abstract Title: Tuning the Electron Transfer Rates in DSSCs with Ru(II) Dyes Having N-Heterocyclic Aromatic Substituents

Co-Author(s): Kleber T. de Oliveira, Gerald J. Meyer, André S. Polo

Abstract: A series of cis-[Ru(R2-phen)(dcbH2)(NCS)2] compounds, dcbH2 = 2,2'-bipyridine-4,4'-dicarboxylic acid, phen = 1,0-phenanthroline and R = H, pyrrole (pyr), indole (ind) or carbazole (cbz), was investigated for application as dye-sensitizers in mesoporous TiO2 Dye-Sensitized Solar Cells (DSSCs). A systematic increase in the number of rings of the N-heterocyclic R substituents in the 4,7-positions of 1,10-phenanthroline allowed to tune the molecular size of the sensitizers and the energy stored in the excited state, while maintaining the same ground-state Ru(III/II) reduction potentials. These small structural changes had a significant influence on the rates and/or efficiencies of electron injection, recombination to oxidized species, lateral self-exchange electron transfer and regeneration through iodide oxidation that were reflected in distinct photoelectrochemical performance of full operating DSSCs. The global efficiencies, open-circuit voltages and short-circuit current densities of the DSSCs consistently followed the trend Ru(pyr2-phen) < Ru(ind2-phen) < Ru(phen) < Ru(cbz2-phen) and the most optimal performance of Ru(cbz2-phen) was ascribed to the significantly smaller recombination losses. Transient photovoltage and absorption data were correlated and demonstrated slow TiO2(e-) + I3- recombination for Ru(cbz2-phen). The molecular insights into the role of aromatic substituents on the electron transfer dynamics that govern energy conversion in these devices will be discussed.

Acknowledgements: FAPESP (2016/21993-6, 2016/24020-9, 2018/08038-0)

Institution: Universidade Federal do ABC (Brazil) / University of North Carolina at Chapel Hill (USA)

The 29th International Conference on Photochemistry
Boulder, Colorado
July 21 – 26, 2019

SOLAR FUELS: NATURAL AND ARTIFICAL PHOTOSYNTHESIS (SOLFuel)
ABSTRACTS

INVITED TALKS

Code: SOLFuel_I1

Presenter: Lisa Utschig (USA)

Co-Author(s): Karen Mulfort; Oleg Poluektov

Abstract Title: Photosynthetic Biohybrids for Solar Hydrogen Production

Abstract: The sustainable production of solar fuels via photochemical energy conversion is a promising means to replace fossil fuels and provide for long-term global energy needs. Currently, we are designing new biohybrid systems that capture and convert the sun's energy and store it in the energy-rich bond of hydrogen, a clean and renewable energy source. Specifically, we are (1) creating a new class of small protein-based photocatalytic complexes that enable the spectroscopic discernment of the structure and processes crucial to solar-driven proton reduction and (2) developing new energy conversion strategies that couple photon energy, captured as a stabilized charge separation across a native photosynthetic reaction center (RC), to the direct synthesis of hydrogen using abiotic inorganic catalysts. Recently, we have achieved complete solar water splitting by utilizing the native photosynthetic Z-scheme electron transport chain to drive hydrogen production from thylakoid membranes by directional electron transport to abiotic catalysts bound at the stromal end of the Photosystem I RC. Pt-nanoparticle and first-row transition metal molecular catalysts readily self-assemble with Photosystem I in spinach and cyanobacterial membranes. We show that, by self-assembling catalysts within the photosynthetic membrane, the system is self-sustaining as electrons that originate from the light-driven oxidation of water by the Photosystem II RC are transferred through Nature's inherent, highly tuned electron transport chain to the abiotic catalyst sites at Photosystem I for hydrogen generation. This work provides the basis for future studies implementing in vivo approaches to generate living photosynthetic systems as a viable energy solution.

Institution: Argonne National Laboratory

Code: SOLFuel_I2

Presenter: Etsuko Fujita (USA)

Co-Author(s): R. N. Sampaio, D. C. Grills, D. E. Polyansky, Y. Tamaki and O. Ishitani

Abstract Title: Roles of Triethanolamine in Photochemical CO2 Reduction with [Ru(dmb)2(CO)2]2+ and Ru(II)-Ru(II) Supramolecular Systems

Abstract: A supramolecular assembly in which Ru(II) photosensitizer and Ru(II) catalyst units are connected by an ethylene linker is among the most effective and robust photocatalysts for CO2 reduction to produce formate. While time-resolved infrared spectroscopy is a powerful tool for investigating the electron transfer and chemical transformations, interpretation of the results requires knowledge of the possible catalytic intermediates. Therefore, we investigated the electrochemical and spectroscopic characterization of [Ru(dmb)2(CO)X]n+ (dmb = 4,4′-dimethyl-2,2′-bipyridine, X = CO, CH3CN with n = 2; X = HCOO, COOH, H with n = 1) together with the photochemical reaction in Ar- and CO2-saturated CH3CN solution containing 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH) as an electron donor and triethanolamine (TEOA) as a proton relay. When we know the properties of the possible intermediates of Ru mononuclear catalysts, that knowledge can be translated into the study of the supramolecular catalysts in the BIH/TEOA/CH3CN solution.

We will discuss results with the mononuclear ruthenium carbonyl catalyst during the photocatalytic reduction of CO2 and how the presence of TEOA impacts the formation of reaction intermediates. An important finding was that TEOA – a commonly used sacrificial electron donor in homogeneous photochemical experiments – plays a crucial role in CO2 capture and formate selectivity.

The work at BNL was carried out with support from the U.S. Department of Energy, Office of Science, Division of Chemical Sciences, Geosciences & Biosciences, Office of Basic Energy Sciences under contract DE-SC0012704. The work in Japan was supported by the Japanese Ministry of Economy, Trade, and Industry and JST CREST (Grant Number JPMJCR13L1).

Institution: Chemistry Division, Brookhaven National Laboratory

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Code: SOLFuel_I3

Presenter: Brian Dyer (USA)

Co-Author(s): Monica Sanchez, Greg Vansuch, Tiffany Trieu

Abstract Title: Hybrid Nanocrystalline Semiconductor-enzyme Photocatalysts

Abstract: We have developed a modular artificial photosynthetic system that comprises a nanocrystalline semiconductor (NCS) photosensitizer with an enzyme catalyst to achieve efficient light driven chemistry. This approach integrates independent modules to perform each of the required functions of efficient light harvesting, charge separation and catalytic electron and proton transfer (ET/PT) reactions to produce high energy chemical bonds. This approach is inspired by natural photosynthesis in which each module is highly optimized for a specific function. Light harvesting and charge separation are accomplished by the NCS material, which can be optimized to efficiently absorb the solar spectrum and to generate long lived redox equivalents with high quantum efficiency. Oxidoreductases activate small molecules for efficient electron transfer with little overpotential and at rates that easily match the rate of generation of redox equivalents by the solar flux. Furthermore, the thermophilic versions of such enzymes are extremely stable, making them suitable to interface with NCS photosensitizers. Viologen derived mediators are used as electron relays to achieve efficient interfacial ET between modules. The mediators have long-lived, stable radicals, high water solubility and their redox potentials can be tuned to achieve efficient redox cycling. We describe the application of this approach in two different contexts: the reduction of protons to hydrogen catalyzed by [NiFe] and [FeFe] hydrogenases and the reduction of CO2 by CO dehydrogenase (CODH). We also describe time-resolved infrared and UV-Vis spectroscopic studies of the mechanisms of the light driven processes, from the exciton dissociation to the interfacial ET and enzyme turnover.

Institution: Emory University

Code: SOLFuel_I4

Presenter: Louise A. Berben (USA)

Co-Author(s): Atefeh Taheri, Cody R. Carr, Natalia D. Loewen

Abstract Title: Managing Proton and Electron Transfers in Fuel-Forming Mechanisms

Abstract: In this talk I will discuss metal carbonyl clusters as a platform to promote fast proton transfer (PT) reactions, and to promote reduction chemistry at modest potentials relative to single-site metal catalysts. I will also discuss how these properties may arise from the extended electronic structure that lowers overall Marcus reorganization energies for electron transfer (ET). The intermediate size of MCCs, between molecules and nanomaterials, preserves access to the powerful characterization tools of molecular chemistry to enable a thorough characterization of structures and reactivity. In one case study I will discuss the reduction of CO2 into C-H bond containing fuels using [Fe4N(CO)12]- and related small metal carbonyl clusters as electrocatalysts. At pH 6.5 or in MeCN/H2O (95:5), [Fe4N(CO)12]- promotes the selective formation of formate from CO2 saturated solution at -1.2 V vs. SCE which is about 440 mV of overpotential. Faradaic efficiency for formate is 97%. The intermediate hydride in this reaction is believed to be the iron-iron bridged hydride: [H-Fe4N(CO)12]- which forms via an ET, PT process.

In a second case study I will discuss the larger cluster [Co13C2(CO)14]4-, which promotes a fast and concerted ET, PT mechanism for H2 evolution. The kinetics of heterogeneous ET, diffusion properties, and reactivity with protons and CO will be presented to benchmark physical properties of the larger MCC, and a discussion of ET, PT, hydride migration chemistry, and H2 evolution mechanisms will be presented.

Institution: University of California Davis

Code: SOLFuel_I5

Presenter: Oleg Poluektov (USA)

Co-Author(s): Jens Niklas, Karen L. Mulfort, Lisa M. Utschig, David M. Tiede, Kristy L. Mardis

Abstract Title: Charge Separation and Triplet Exciton Formation Pathways in Small-Molecule Bulk Heterojunction Blends as Studied by Time-Resolve

Abstract: Photovoltaic system based on donor-acceptor BHJ are attracting renewed interest because of remarkable gains that have been achieved in the efficiency of charge separation and collection. Initially BHJ were made from semiconductor polymer donors and fullerene-derivative acceptors. However, low efficiency, ca. 10%, in combination with costly fullerene derivatives made these material not applicable for industrial production. Recently, breakthrough in efficiency of OPVs, ca. 16%, were reported for cells based on organic small molecules BHJ. Important question which is awaiting its resolution is what are the crucial factors which determines the higher solar energy conversion efficiency in small molecules OPV? As a first step to address this question we use advanced light-induced EPR spectroscopy in combination with DFT modeling to study the electronic excited states, charge transfer dynamics, and triplet exciton formation pathways across five representative of a widely studied dithienosilole, DTS, family of small-molecule electron donors with fullerene derivative PC61BM as aa acceptor. High-frequency EPR results have been compared with DFT calculations which revealed that the spin density of the positive polaron is distributed over a dimer or trimer of DTS molecules. Using TR-EPR the triplet exciton formation pathways were investigated. The polarization patterns provide the direct evidence that the excitons originate from both intersystem crossing and back electron transfer processes. The higher BET triplet exciton population is directly related to the slower charge separation dynamics observed in this blend. These data are compared with a previously obtained data on semiconductor polymers-fullerenes BHJ blends.

Institution: Argonne National Laboratory

Code: SOLFuel_I6

Presenter: Wilson Smith (NLD)

Co-Author(s): Nienke J. Firet, Anirudh Venugopal, Marijn A. Blommaert, Chiara Cavallari, Christoph J. Sahle, Alessandro Longo

Abstract Title: Chemisorption of Anionic Species Alters the Surface Electronic Structure and Composition of Photocharged BiVO4 Photoanodes

Abstract: Photocharging has recently been demonstrated as a powerful method to improve the photo-electrochemical water splitting performance of different metal oxide photoanodes, including BiVO4. In this work, we use near in-situ X-ray Raman scattering (XRS) spectroscopy to study the surface electronic structure of photocharged BiVO4. Through grazing incidence XRS spectroscopy measurements, it was found that the oxidation state of vanadium was reduced in the first 60 nm of the material. The O K edge spectrum was simulated using the Finite Difference Method Near Edge Structure (FDMNES) method, which revealed a change in electron confinement and occupancy in the conduction band. These insights, combined with ultraviolet-visible spectroscopy (UV-vis) and X-ray photoelectron spectroscopy (XPS) analyses, reveal that a surface layer formed during photocharging that creates a heterojunction with BiVO4, leading to favorable band bending and strongly reduced surface recombination. In addition, plasmonic features were discovered which may further reduce surface recombination. The XRS spectra presented in this work exhibit good agreement with soft X-ray XANES spectra from literature, demonstrating that XRS is a powerful tool to study the electronic and structural properties of light elements in semiconductors. Our findings provide direct evidence of the electronic modification of a metal oxide photoanode surface as a result of the adsorption of electrolyte anionic species under operating conditions. This work highlights that the surface adsorption of these electrolyte anionic species is likely present in most studies on metal oxide photoanodes, and has serious implications for the photoelectrochemical performance analysis and fundamental understanding of these materials.

Institution: Delft University of Technology

Code: SOLFuel_I7

Presenter: Alberto Mezzetti (FRA)

Abstract Title: Photoprotective Mechanism in Photosynthesis Studied by Time Resolved FTIR Spectroscopy In Vivo and In Vitro

Co-Author(s): Silvia Leccese, Maxime Alexandre, Adrien Thurotte, Adjelé Wilson, Claudia Buchel, Bruno Robert, Diana Kirilovsky

Abstract: Time-resolved FTIR difference spectroscopy (TR-FTIR-DS) is a powerful technique in the investigation of biochemical reactions, providing time-resolved details at the atomic level on the reaction mechanisms (H+ transfer, e- transfer, chemical modification of molecules,...) [1].

We have studied photoprotection mechanisms in photosynthesis by TR-FTIR-DS, not only on isolated proteins, but also in vivo.

In a first study the photoactivation mechanism of the Orange Carotenoid Protein (OCP), a water soluble protein found in cyanobacteria implicated in photoprotection was investigated [2]. TR-FTIR spectra of Wild-type and mutants OCPs show that an intermediate state in the OCP photocycle is present at early times of illumination. By using specific mutants this intermediate can be characterized by FTIR-DS [3]. Spectra recorded in H2O and D2O suggest an implication of internal water molecules in the photoactivation mechanism.

In a second study, we studied the photoprotective mechanism of diatoms in vivo. In this case in was possible, on a second time scale, to follow by TR-FTIR-DS the response of diatoms to strong light, implying a xantophyll cycle. We could follow different chemical events (chemical epoxydation/de-epoxydation of carotenoids; plastoquinone pool reduction; localized pH changes; energy dissipation mechanisms; reorganization of the membrane structure) and calculate the kinetics for each of these processes [4].

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[3] Mezzetti, Alexandre, Wilson, Thurotte, Gwizdala, Kirilovsky, J Phys Chem B (2019) 123, 3259–3266
[4] Mezzetti, Alexandre, Buchel, Robert in preparation

Institution: Sorbonne Université

CONTRIBUTED TALKS

Code: SOLFuel_T1

Presenter: Tianyou Peng (CHN)

Abstract Title: SrCO3-modified Brookite/Anatase TiO2 Heterophase Junctions with Enhanced Activity and Selectivity of CO2 Reduction to CH4

Co-Author(s): Jingpeng Jin, Shengtao Chen, Chun Wu

Abstract: Utilizing the abundant solar energy to chemically convert CO2 into high-energy chemical fuels such as CO, CH4 or CH3OH offers a way to address the serious concerns about the increasing atmospheric CO2 levels and the depletion of fossil fuels.1-3 Herein, a series of SrCO3-modified TiO2 composites have been synthesized by adding SrCl2 into a TiCl4 hydrothermal reaction solution. It is found that brookite TiO2 quasi nanocubes with high phase purity (denoted as pristine TiO2) can be derived from the TiCl4 reaction solution, and the additive Sr2+ ions lead to the formation of SrCO3-modified TiO2 heterophase junctions (HPJs) containing brookite nanorods and anatase nanoparticles. When used the SrCO3-modified TiO2 HPJs (hereafter denoted as SrCO3/HPJs) as photocatalyst for CO2 photoreduction, significantly enhanced activity and selectivity for CO2 photoreduction to CH4 can be achieved as compared to the pristine TiO2. Especially, 1.0% SrCO3/HPJs composite shows CH4/CO production activities of 19.66/2.64 □mol g-1 h-1 with an overall photoactivity of 162.6 □mol g-1 h-1, which is 12.3 times of the pristine TiO2 that shows an overall photoactivity of 13.2 □mol g-1 h-1 with CH4/CO production activities of 0.79/3.46 □mol g-1 h-1. The brookite/anatase TiO2 HPJs can effectively promote the photogenerated charge separation and restrain the interfacial charge recombination, and the SrCO3 species on the TiO2 HPJs can act as an efficient synergistic catalyst to improve the CO2 adsorption and activation abilities, and thus cause the enhanced activity and selectivity for CO2 photoreduction to CH4. This work represents the first example of coupling TiO2 HPJs with alkaline earth metal carbonates for efficient CO2 photoreduction.

Institution: College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, P. R. China

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Code: SOLFuel_T2

Presenter: Mohamad S Kodaimati (USA)

Abstract Title: Energy Transfer-enhanced Photocatalytic Reduction of Protons within Quantum Dot Light-Harvesting–Catalyst Assemblies

Co-Author(s): Shichen Lian, Emily A Weiss, George C Schatz

Abstract: A feature of natural photosynthetic systems is their ability to operate with the low photon flux of sunlight, where the absorption of light and transport of photochemical potential to the catalytic centers is efficiency-limiting. Natural systems overcome this limitation through energy transfer (EnT), where quanta of energy are gathered by many weakly coupled light-absorbing centers that pass the energy among themselves to funnel it to a single catalytic reaction center. Prior to this report, this type of energy migration-based approach has not been employed in artificial photocatalytic systems. This paper describes the use of electrostatically assembled CdSe quantum dot (QD) aggregates as artificial light harvesting-reaction center units for the photocatalytic reduction of H+ to H2, where excitons are funneled through EnT from sensitizer QDs (sQDs) to catalyst QDs (cQDs). Upon increasing the sensitizer-to-catalyst ratio in the aggregates from 1:2 to 20:1, the number of excitons delivered to each cQD (via EnT) per excitation of the system increases by a factor of nine. A kinetic model supports the proposed exciton funneling mechanism for enhancement of the catalytic activity. This work demonstrates the viability of energy-transfer–based sensitization in colloidal photocatalytic assemblies and provides a framework for its incorporation into scalable solar energy conversion systems.

Kodaimati, M.; Lian, S.; Jiang, Y.; Schatz, G.C.; Weiss, E.A. Energy-Transfer Enhanced Photocatalytic Reduction of Protons within Quantum Dot Light Harvesting–Catalyst Assemblies, Proc. Natl. Acad. Sci., 115, 8290-8295 (2018).

Institution: Northwestern University

Code: SOLFuel_T3

Presenter: Tai-Chu Lau (HKG)

Co-Author(s): Nil

Abstract Title: Photocatalytic CO2 Reduction Based on Earth-abundant Metal Complexes

Abstract: The search for green and economical renewable energy sources is one of the most important challenges facing scientists in the 21st century. One of the most promising sources of carbon neutral and renewable energy comes from the reduction of CO2 to generate various fuels, including CO, methanol or light hydrocarbons. Since CO2 is a stable molecule, in order for this process to occur at reasonable rates with low over-potentials, an efficient catalyst is required. Ideally, the energy required for CO2 reduction should be obtained from solar energy, since more solar energy strikes the earth in one hour than can be consumed by the whole planet in one year. Sunlight can also be first converted to electricity in photovoltaic cells, which can then be used for electrocatalytic CO2 reduction in the presence of a catalyst.

In this presentation, we will describe our work on the design of highly active and robust homogeneous CO2 reduction photocatalysts based on molecular transition metal complexes. In order to be economically viable, the complexes should be made from earth-abundant metals, such as Mn, Fe, Co, Ni and Cu.

We are interested in molecular catalysts because their structures are more well-defined and in general they have higher catalytic activity which can be readily tuned by systematic variation of the ligands.

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Institution: City University of Hong Kong

Code: SOLFuel_T4

Presenter: Jiangyun Wang (CHN)

Co-Author(s): Xiaohong Liu

Abstract Title: A Genetically Encoded Photosensitizer Protein Facilitates the Rational Design of a Miniature Photocatalytic CO2 Reducing Enzyme

Abstract: Photosensitizers, which harness light energy to upgrade weak reductants to strong reductants, are pivotal components of the natural and artificial photosynthesis machineries. However, it has proved difficult to enhance and expand their functions through genetic engineering. Here we report a genetically encoded, 27 kDa photosensitizer protein (PSP), which facilitates the rational design of miniature photocatalytic CO2-reducing enzymes. Visible light drives PSP efficiently into a long-lived triplet excited state (PSP*), which reacts rapidly with reduced nicotinamide adenine dinucleotide to generate a super-reducing radical (PSP•), which is strong enough to reduce many CO2-reducing catalysts. We determined the three-dimensional structure of PSP• at 1.8 Å resolution by X-ray crystallography. Genetic engineering enabled the site-specific attachment of a nickel-terpyridine complex and the modular optimization of the photochemical properties of PSP, the chromophore/catalytic centre distance and the catalytic centre microenvironment, which culminated in a miniature photocatalytic CO2-reducing enzyme that has a CO2/CO conversion quantum efficiency of 2.6%.

Recently, we have made significant progress in the further optimization of mPCE, and the conversion on non-photosynthetic organism (such as E coli.) to artificial photosynthetic cells, which has dramatically enhanced the ability of these biological cell factory to synthesize high-value chemicals and materials.

Citations:

1.Xiaohong Liu, … Jiangyun Wang* A genetically encoded photosensitizer protein facilitates the rational design of a miniature photocatalytic CO2 reducing enzyme Nat. Chem. 10, (2018), 1201-1206

2.Fang Yang,… Jinpeng Sun*, Jiangyun Wang* Allosteric mechanisms underlie GPCR signaling to SH3-domain proteins 2 through arrestin Nat. Chem. Bio. 14, (2018), 876-886.

Institution: Institute of Biophysics, Chinese Academy of Sciences

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Code: SOLFuel_T5

Presenter: Stefan Ilic (USA)

Abstract Title: Toward Metal-free Catalysis: Designing Organic Hydrides for Fuel-forming Reductions

Co-Author(s): Ksenija D. Glusac

Abstract: The apparent advantages of metal-based catalysts in energy conversion catalysis are overshadowed by their often-low selectivity, poor sustainability, and high toxicity. Organic hydrides are emerging as promising cost-effective replacements for selective CO2 reduction, where the selectivity is achieved via sequence of hydride transfers. Their utilization in catalytic processes, however, is significantly affected by the ease of hydride regeneration. In this work, we explore the hydride regeneration mechanisms for several biomimetic NADH analogs from their NAD+ correspondents using electrochemical methods. Previous efforts on the topic have been hindered by the large overpotentials and rapid dimerization of organic radicals produced as the first intermediates of these electrochemical transformations. Here, we achieve quantitative hydride regeneration by improving the stability of acridine-based radicals and by facilitating the protonation of benzimidazole-based radicals. This work provides the groundwork for effective use of organic hydrides as potential catalysts in energy conversion processes.

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S. Ilic; A. Alherz; C. Musgrave; K. D. Glusac; Importance of Proton Coupled Electron Transfers in Organic Hydride Regenerations, Chem. Comm., 2019, submitted
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S. Ilic; U. Pandey Kadel; Y. Basdogan; J. A. Keith; K. D. Glusac; Thermodynamic Hydricities of Biomimetic Organic Hydride Donors, J. Am. Chem. Soc., 2018, 140(13), 4569-4579

Institution: University of Illinois at Chicago; Argonne National Laboratory

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Code: SOLFuel_T6

Presenter: Gongxuan Lu (CHN)

Abstract Title: The Inhibition of Hydrogen and Oxygen Recombination by Halogen Atoms and Its Effect on Overall Water Splitting Over Pt-TiO2

Co-Author(s): No

Abstract: Semiconductor photocatalysts for overall water splitting into H2 and O2 require metal cocatalyst, such as Pt, to catalyze H2 evolution efficiently. However, these metal cocatalysts can also catalyze hydrogen and oxygen recombination to form water. In this work, we found that the pre-adsorbed halogen atom catalyst could inhibit the reverse reaction of water formation from H2 and O2 due to the decrease of adsorption energies of H2 and O2 on Pt. The adsorption energy decrease of H2 and O2 followed the order of F/Pt □ Cl/Pt □ I/Pt □ Br/Pt. H2-TPD results exhibited similar dependence. This inhibition was achieved via the occupation of halogen atom on the Pt surface sites, and thereby the adsorption and activation of hydrogen and oxygen molecules were decreased. The occupation difference of halogen atoms are determined by radius of halogen ions, which further leads the different activity for H2 and O2 recombination. By inhibition of water formation reverse reaction, the over-all water splitting over various TiO2 photocatalysts has been achieved. Isotope experiments with D2O and H218O confirmed the over-all water splitting to H2 and O2. This study may help scientist to develop high-efficient photocatalyst for overall water splitting.

Institution: Lanzhou Institute of Chemical Physics, CAS

Code: SOLFuel_T7

Presenter: Linda Nhon (USA)

Abstract Title: Donor-Acceptor-Donor Organic Chromophores for Photocathodic Applications

Co-Author(s): , Bing Shan, Aaron Taggart, M. Kyle Brennaman, Taylor Moot, James F. Cahoon, Kirk S. Schanze, Thomas J. Meyer, John R. Reynolds

Abstract: Significant progress has been made on the development of the dye sensitized photoelectrosynthesis cell (DSPEC). Development of the photoanode (site of water oxidation) has advanced greatly, however less attention has been placed on the photocathode (site of CO2/H+ reduction) a quintessential component for the tandem DSPEC. The photocathode knowledge gap arises from a lack of chromophores and p-type semiconductors available to study the charge transfer processes at the photocathode. Here, we introduce a design strategy for synthesizing organic chromophores for charge injection at the photocathode. The dyes synthesized were tailored to the p-type semiconductors, PbTiO3 and NiO. Their structures were inspired by the donor-acceptor-donor (D-A-D) design approach, where a thiophene-3-carboxylic acid donor was kept consistent throughout the family and the acceptor varied or where the anchoring group position was altered on the D-A-D scaffold. The dyes' structure-property relationships were studied using UV-vis absorption, fluorescence spectroscopy, electrochemistry, and density functional theory calculations. The electron affinity values were systematically tuned ranging between 2.83 eV to 1.94 eV while maintaining their ionization potential at ~6.0 eV. The dyes were adsorbed onto PbTiO3 and studied for hole injection processes using linear sweep voltammetry. Photocathodic measurements were observed, -4 μA•cm-2 for the dye, 4,10- benzobis(thiadiazole)-bis(thiophene-3-carboxylic acid)). Co-loaded with a hydrogen producing catalyst on NiO, the dye (5,5'-(benzothiadiazole-4,7-diyl)bis(thiophene-3-carboxylic acid) generated photocathodic current of -30 μA•cm-2 at an applied bias of -0.1 V vs NHE, which is indicative of both charge transfer to the catalyst and hole injection into the metal-oxide substrate.

Institution: Georgia Institute of Technology

Code: SOLFuel_T8

Presenter: Feng Xin (CHN)

Abstract Title: Photocatalytic Reduction of CO2 Over Nano Copper Oxide Deposited Cubic NaTaO3

Co-Author(s): Tianyu Xiang

Abstract: A photocatalyst composed of patchy CuO evenly planted on cubic NaTaO3 was synthetized for reducing CO2 in isopropanol. About 15 nm of the nano patches of CuO were dispersed on the surface of NaTaO3 via a phase-transfer protocol before a solvothermal synthesis. A 5 wt% CuO deposited NaTaO3 showed the highest methanol yield of 1302.22 μmol/(g. h). XRD, SEM, TEM, EDX, XPS, UV–Vis and PL were used to characterize its crystalline phase, morphology, composition, optical absorption and charge separation. Its performance in photocatalytic reduction of CO2 confirmed the CuO deposited NaTaO3 possessing better ability to separate charge carriers and selectively reduce CO2 to methanol than those of CuO loaded NaTaO3 via the conventional liquid phase reduction procedure.

Institution: Tianjin University

Code: SOLFuel_T9

Presenter: Chern-Hooi Lim (USA)

Abstract Title: Visible-light-driven Conversion of CO2 to CH4 with an Organic Sensitizer and an Iron Porphyrin Catalyst

Co-Author(s): Garret Miyake, Marc Robert

Abstract: Using a phenoxazine-based organic photosensitizer and an iron porphyrin molecular catalyst, we demonstrated photochemical reduction of CO2 to CO and CH4 with turnover numbers (TONs) of 149 and 29, respectively, under visible-light irradiation (λ > 435 nm) with a tertiary amine as sacrificial electron donor. This work is the first example of a molecular system using an earth abundant metal catalyst and an organic dye to effect complete 8e−/8H+ reduction of CO2 to CH4, as opposed to typical 2e−/2H+ products of CO or formic acid. The catalytic system continuously produced methane even after prolonged irradiation up to 4 days. Using CO as the feedstock, the same reactive system was able to produce CH4 with 85% selectivity, 80 TON and a quantum yield of 0.47%. The redox properties of the organic photosensitizer and acidity of the proton source were shown to play a key role in driving the 8e−/8H+ processes.

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Institution: Colorado State University, New Iridium LLC

Code: SOLFuel_T10

Presenter: Akihiko Kudo (JPN)

Abstract Title: Photocatalytic CO2 Reduction using Water as an Electron Donor

Co-Author(s): Syunya Yoshino, Haruka Nakanishi, Kosuke Iizuka, Tomoaki Takayama, Akihide Iwase

Abstract: Photocatalytic CO2 fixation is a challenging reaction as artificial photosynthesis, because light energy is converted to chemical energy. It is indispensable to use water as an electron donor without any sacrificial reagents. In the present paper, I introduce various metal oxide and sulfide photocatalysts and photoelectrochemical cells for the CO2 reduction. Ag cocatalyst-loaded ALa4Ti4O15 (A = Ca, Sr, and Ba) and tantalates photocatalysts such as NaTaO3:Ba with 3.79–4.1 eV of band gaps showed activities for CO2 reduction to form CO and HCOOH in an aqueous medium without any sacrificial reagents. CO is the main reduction product rather than H2 even in an aqueous medium. Especially, the Ag/NaTaO3:Ba photocatalyst gave ca. 90% of the selectivity for the CO2 reduction. The carbon source of produced CO was confirmed to be dissolved CO2 molecules using 13CO2. Thus, an uphill reaction of CO2 reduction accompanied with water oxidation was achieved using the Ag-loaded metal oxide photocatalysts. However, these metal oxide photocatalysts respond to only UV because of their wide band gaps. So, it is challenging to develop photocatalysts with visible light response for CO2 reduction. We constructed a Z-scheme system consisting of metal sulfide photocatalysts of a CO2-reducing photocatalyst with BiVO4 of an O2-evolving photocatalyst for the CO2 reduction. The Z-scheme system gave H2, O2, and CO simultaneously under visible light irradiation.

Institution: Tokyo University of Science

Code: SOLFuel_T11

Presenter: Minjung Son (USA)

Abstract Title: Controlling the Dynamics of Energy Flow in Plants with Near-native Model Membrane

Co-Author(s): Alberta Pinnola, Samuel C. Gordon, Roberto Bassi, Gabriela S. Schlau-Cohen

Abstract: The photosynthetic machinery of plants has evolved a capability of reacting sensitively to fluctuating light conditions. In low light, it serves its primary light-harvesting role by efficiently capturing and rapidly funneling sunlight towards the reaction center. In excess light, however, it switches on a photoprotective mechanism where the deleterious excess energy is dissipated as heat. While conformational changes in the antenna complexes have been proposed to control the balance between these two functions, identifying these changes has been challenging because studies have been performed in far-from-native environments, introducing non-native conformational changes to the antennae.

Here, we revisit the balance between light-harvesting and photoprotective photophysics of plants using light-harvesting complex II (LHCII), the major antenna complex in plants, incorporated in a near-native model membrane. Using ultrabroadband two-dimensional electronic spectroscopy, we map out the energy flow in LHCII across the visible, and investigate how the dynamics differ between the non-native detergent and near-native membrane environments.

The data reveal an enhancement of dissipative pathways and suppression of the competing energy transfer steps in the membrane via two mechanisms involving the short-lived dark state of the carotenoids, the accessory light-harvesting pigments. Moreover, we identify the two peripheral pigment clusters that undergo conformational changes in the membrane that leads to the enhanced dissipation of energy. Our observations highlight the central role of the membrane environment in regulating the balance between light harvesting and photoprotection in plants, which provides the fine tuning in the pigment structures needed for the flexibility to survive against sudden solar fluctuations.

Institution: Massachusetts Institute of Technology

Code: SOLFuel_T12

Presenter: Arkaprabha Konar (USA)

Abstract Title: Multispectral Two Dimensional Spectroscopy as a Probe of Excitonic and Vibronic Structure in Bacterial Reaction Centers

Co-Author(s): Riley Sechrist, Veronica R. Policht, Yin Song, Jennifer P. Ogilvie

Abstract: The bacterial reaction center (BRC) is a unique photosynthetic apparatus that converts solar energy to chemical potential by generating long-lived charge separated states with near unity efficiency. We perform two dimensional electronic spectroscopy (2DES) on the M250V mutant of purple bacteria Rhodobacter capsulatus. Broadband pump pulses covering the Qy absorption region of the BRC and white light continuum probe spanning the visible and near-IR frequencies are employed in a pulse-shaper-based 2D experiment. Cross-peaks in broadband 2DES data provide insight into the excitonic coupling throughout the BRC and the ultrafast relaxation processes. Through the observation of coherent dynamics we gain insight into the vibronic structure of the BRC. The interpretation of coherent dynamics in 2DES experiments and their implications for efficient energy transfer and charge separation in photosynthetic systems has been a subject of immense interest over the last decade, and has been investigated in photosynthetic antennae [1] and reaction centers, including the BRC [2]. While it is now understood that the majority of the observed coherent signals arise from pigment vibrations, several studies have proposed that the coherences also reflect resonances between vibrations and electronic energy gaps that may have functional importance[3]. Here we use multi-spectral 2DES to resolve the excitation and detection wavelength dependence of the coherent signals, providing insight into the physical origin of the coherence and the vibronic structure of the BRC.

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(2) Westenhoff, S. et al. JACS, 2012, 134(40), 16484–16487.
(3) Jonas, D. M. Ann Rev Phys Chem, 2018, 69, 327-352.

Institution: University of Michigan

Code: SOLFuel_T13

Presenter: Thomas Favet (CAN)

Abstract Title: Photoelectrochemical Improvement Under Sunlight Brought By Pulsed Laser Deposition of CoO and NiO Nanoparticles on TiO2 Nanotube

Co-Author(s): Thomas Cottineau, Valérie Keller, My Ali El Khakani

Abstract: The decoration of TiO2 nanotubes (NTs) with co-catalysts to form highly effective photoanodes (PAs) constitutes a very promising approach for photo-electrochemical (PEC) reactions where the oxygen evolution reaction plays a key role [1]. In this context, we report on the successful use of pulsed laser deposition (PLD) technique to decorate TiO2-NTs with Cobalt and Nickel nanoparticles (NPs). By varying the number of laser ablation pulses (NLP), the size and the surface density (catalyst load) of the NPs was varied. The PLD decoration process was performed under an O2 background atmosphere, allowing direct oxidation of NPs in CoO and NiO as confirmed by XPS analyses. Dependence of PEC activity with the chemical nature of those co-catalysts was systematically studied under sunlight (AM1.5) and visible solar light. While the PEC activity is directly influenced by the used NLP, chemical nature of the deposited NPs also displays a different effect. Indeed, the highest PEC response under sunlight was found to be tripled for TiO2/CoO or TiO2/NiO in comparison with bare TiO2 NTs. However, under visible solar light, the highest PEC efficiency of TiO2/CoO PAs was almost twice better than TiO2/NiO. Our results point out a PEC improvement under solar irradiation arising from a catalytic effect of CoO and NiO NPs, and a beneficial photocatalytic effect brought by CoO NPs. Finally, our results indicate a clear correlation between catalyst loading of the CoO and NiO decorated TiO2-NTs and their PEC activity.

[1]M. Tahir et al., Nano Energy, vol. 37, pp. 136–157, Jul. 2017.

Institution: ICPEES (Strasbourg,France) / INRS-EMT(Varennes, Canada)

Code: SOLFuel_T14

Presenter: Sven Rau (DEU)

Abstract Title: Towards an Artificial Chloroplast

Co-Author(s): Alexander Mengele, Dominik Weixler and Gerd Seibold

Abstract: Chloroplasts in green plants consist of the functional architecture of the photosynthetic apparatus which is embedded in the thylakoid membrane. Light driven electron transfer and redox catalysis within this architecture lead to the formation of O2 and NADH2+ together with a transmembranal proton gradient. This in turn fuels ATP synthesis. We will present results towards the utilization of a Ru(II)-Rh (III) photocatalysts able to generate NADH2+. (1-3) Once integrated into biological membranes containing elements of the respiratory chain (4) concomitant formation of NADH2+ and ATP driven by the artificial photosynthetic complex are observed. Thus, important functions of the chloroplast are fulfilled by this synthetic hybrid system.

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2) Mengele, A. K.; Rau, S. Inorganics (2017), 5(2), 35/1-35/23.
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4) Crauwels P.; Schafer L., Weixler D., Riedel C. U; Seibold G. M; Bar N. S; Diep D. B Frontiers in microbiology (2018), 9, 3038

Institution: Institute of Inorganic Chemistry 1, University of Ulm, Germany

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Code: SOLFuel_T15

Presenter: Wenxing Yang (USA)

Abstract Title: “Abnormal” Ligand Length Dependent ET Transfer Behavior in Mediator-based CdS Nanorod/Hydrogenases Assemblies for H2 Production

Co-Author(s): Greg Vansuch, Yawei Liu, Jin tao, Aimin Ge, Monica Sanchez, R. Brian Dye,Tim Lian

Abstract: In this study, we investigate a recently developed nanorod and NiFe hydrogenase (H2ase) assemblies which utilize a redox-mediated approach to shuttle the electron transfer between the nanorods and the H2ase enzymes with an impressive H2 production quantum yield up to 77 %.1 We study the impact of alkyl chain lengths of a common type of capping ligand for nanocrystals, mercaptoalkylcarboxylate, on the H2 production quantum yield of the system and elaborate the ligand’s impact on the underlying ET transfer between NRs and the electron acceptors. We observed the existence of an abrupt decrease of the quantum yield for H2 production of the system when increasing the alkyl chain length of the ligands from n= 7 to 10 (35 % and 12 %, respectively), wheras only a minor performance decrease is observed when n is below 7 (35 % and 42 % for n=7 and 2, respectively). These results are further shown in good agreement with the sudden decrease of the yield of the reduced mediator, propyl-bridged 2-2’-bipyridinium (PDQ2+), during the steady-state photoreduction experiments, suggesting that generation efficiency of the redox equivalents control the overall efficiency of the current redox-mediated systems. Further transient spectroscopic measurements revealed that the intrinsic ET transfer rates from the NR to the mediator PDQ are all on the order of 108 s-1 regardless of the length of the capping ligands. Instead, the amount of the average surface attached PDQ2+ molecules decreases dramatically when increasing the length of n above 7, with a saturated surface coverage of σ=40 to σ =0.5 for n=2 and n= 7, respectively. These results cannot be explained by the commonly perceived ligand length dependent ET transfer by tunneling through a barrier. Instead, these results are rationalized by the accessibility of CdS surface to electron acceptors, probably due to the change of the ligand configuration from the disordered to ordered phases. These results characterize quantitively the efficiency limiting step in the mediator based CdS nanorod/Hydrogenases assemblies, demonstrate impact of configurational arrangements of ligands on NR surface on its ET behavior, and therefore are important for the design of biotic and abiotic systems for various applications.

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Institution: Emory University

Code: SOLFuel_T16

Presenter: Bryant Chica (USA)

Abstract Title: Electron Transfer in Nanoparticle-Nitrogenase Hybrids

Co-Author(s): Hayden Kallas, Jesse Ruzicka, Kate Brown, David Mulder, Lance Seefeldt, John Peters, Gordon Dukovic, Paul King

Abstract: Molybdenum Iron Nitrogenase (MoFe) catalyzes the reduction of nitrogen to ammonia in biological systems. Electron transfer to MoFe in biological systems is exclusively carried out by the Fe protein with an obligatory coupling to ATP hydrolysis. We have described a system where productive photochemical electron transfer to MoFe is achieved by photo-excitation of mpa-capped cadmium sulfide nanoparticles (CdS NP). We investigate the mechanism of photoinduced electron transfer in CdS-MoFe complexes using a combination of physical and kinetic measurements. We use EPR spectroscopy to probe how the redox states of electron transfer mediating P clusters and catalytic M clusters of MoFe change as a function of photo excitation of CdS NCs as well as how this affected by poising the MoFe clusters in particular redox states prior to illumination. These results provide powerful insight into the mechanism of charge transfer in MoFe:NC hybrids. Photo-induced redox transitions observed at the M cluster are accompanied by P cluster redox changes, this is suggestive that transitions of the P cluster are obligatory for catalysis. Furthermore our results implicate the P cluster is the immediate point of entry of photo-excited electrons into the MoFe protein. Transient absorption spectroscopy was used to probe the kinetics of ET from CdS NC’s to the P cluster. Future directions for characterizing the MoFe catalytic mechanism are also discussed.

Institution: National Renewable Energy Lab

Code: SOLFuel_T17

Presenter: Asad Ali (CHN)

Abstract Title: Ultrathin MoS2 Nanosheets for High-performance Photoelectrochemical Applications via Plasmonic Coupling with Au Nanocrystals

Co-Author(s): Farhana Akbar Mangrio, Xiaolin Chen, Yiwen Dai, Kui Chen, Xiaoliang Xu, Ruixiang Xia and Lixin Zhu

Abstract: In this work, we prepared ultrathin MoS2 nanosheets with exposed active edge sites and high electric conductivity that can sufficiently absorb light in the visible region to enable solar energy conversion. The gold nanocrystal–decorated MoS2 nanosheets facilitate sufficiently enhanced photoelectrochemical water splitting in the UV–visible region. Different Au nanostructures, such as Au nanoparticles and nanorods, were modified on the surface of MoS2 nanosheets to promote photoelectrochemical water decomposition. By spin-coating a synthetic gold–modified MoS2 hybrid photoanode on a FTO substrate, the efficiency of photoelectrochemical water oxidation was significantly enhanced, by 2 times (nanorods) and 3.5 times (nanoparticles) in the visible–infrared region; furthermore, the average optical resistance was reduced by a factor of two compared to the MoS2 photoanode without Au, and the photocurrent increases exponentially when the system bias was greater than 0.7 volts. The Au–MoS2 metal–semiconductor interface plays an important role in studying the surface plasmon interactions, charge transfer mechanism, and electric field amplification. This rational design for such a unique hybrid nanostructure explains the plasmon-enhanced photoelectrochemical water splitting. This current contribution provides a new path for using the plasmonic metal/semiconductor heterostructure to effectively harvest UV– visible light for solar fuel generation.

Institution: Department of Surgery & Central Laboratory, The First Affiliated Hospital of Anhui Medical University, Hefei 230022, PR China.

Code: SOLFuel_T18

Presenter: Saurav Sorcar (KOR)

Abstract Title: Photocatalytic Reduction of CO2 to Higher Grade Hydrocarbon Products: A Peak Sunlight to Fuel Conversion Efficiency of 3.3%

Co-Author(s): Su-Il In

Abstract: The global atmospheric CO2 concentration is increasing at an alarming rate. With nearly one million species on the verge of extinction, immediate steps are required if we wish to sustain our terrestrial ecosphere. Photocatalytic reduction of CO2, in combination with water and sunlight into hydrocarbon fuels can be perceived as an ideal pathway to counter global warming. In spite of numerous works being done, such technology has not been viable due to the vanishingly small CO2-to-fuel photoconversion efficiencies of known photocatalysts. In the current work, we report a photocatalyst composed of reduced blue-titania deposited with Cu-Pt bimetallic nanoparticles, that over 6 h and 1 sun condition (AM1.5) generates a substantial amount of methane (3.0 mmolg-1) and ethane (0.15 mmolg-1) by CO2 photoreduction. The photocatalytic activity showcases a sustained Joule (sunlight) to Joule (fuel) photoconversion efficiency of 1% with a quantum efficiency of ϕ = 86%. A peak efficiency of 3.3% is reached over 0.5 h intervals. Mechanistic investigations and isotopic tracer experiments were carried out, and proves the photocatalytic CO2 reduction to be entirely based upon proton coupled multiple electron transfer (PCET) process.

Institution: Daegu Gyeongbuk Institute of Science and Technology (DGIST), South Korea

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Code: SOLFuel_T19

Presenter: Hanqing Pan (USA)

Abstract Title: Photons to Formate: Semiconductor Photocatalyzed Reduction of Bicarbonate to Solar Fuels

Co-Author(s): Michael D. Heagy

Abstract: Rising levels of anthropogenic carbon dioxide and the rapid depletion of fossil fuels are raising concerns about the environment and the future of our energy supply. One potential approach towards generating renewable fuels is to use solar energy to directly reduce atmospheric or locally produced CO2 to liquid fuels. This approach, referred to as “chemical carbon mitigation” can lead to methanol as an end product, a useful solar fuel. The concept of “The Methanol Economy”, championed by Chemistry Nobel laureate George Olah, highlights methanol as an alternative to hydrogen as a renewable and readily transportable fuel.

This talk will focus on the photocatalytic reduction of bicarbonate to value-added formate. Specifically, it aims to achieve this reduction by utilizing earth-abundant, non-toxic, and low-cost semiconductors. Three semiconductors (Cu2O, ZnO, Fe2O3) were evaluated in detail by characterizing their size, morphology, band gap, and crystal structure. To improve semiconductor efficiency, plasmonic noble-metal nanoparticles (gold, silver) and robust organic dyes were used as photosensitizers to extend optical absorption into the visible wavelengths. A gold nanoparticle-TiO2 nanocomposite (Au/TiO2) was synthesized and tested for bicarbonate reduction under solar irradiation and 365 nm irradiation. Formate production was significantly enhanced with the addition of gold nanoparticles under solar irradiation. To date, significant achievements have been made in the field of photocatalysis with respect to CO2 reduction. However, the photoconversion efficiency is still fairly low and selectivity for desired products is still difficult. More focus needs to be placed on light harvesting, charge generation, separation, and transportation.

Institution: University of Nevada, Reno

Code: SOLFuel_T20

Presenter: Su-Il In (KOR)

Abstract Title: Highly Smart and Efficient Photocatalytic Materials for CO2 Conversion into Hydrocarbon Fuels

Co-Author(s): n/a

Abstract: Photocatalytic reduction of CO2 to fuel offers an exciting opportunity for helping to solve current energy and global warming problems. Hereby, we will be discussing a visible-light responsive, highly efficient and stable photocatalyst, blue-colored reduced titania nanoparticles sensitized with platinum nanoparticles, for the photoconversion of CO2 to methane [1]. The photocatalyst has showcased a recorded methane generation at a rate of 80.35 mmolg-1h-1with an apparent quantum yield of 12.40%. Further moving ahead, we will be discussing the shifting of CO2 reduction products selectivity to higher-order hydrocarbon products. The photocatalyst synthesized is composed of Pt-sensitized graphene-wrapped blue-titania, that produces a record high combined photocatalytic yield of ethane and methane [2]. For the first time, a systematic ultraviolet photoelectron spectroscopy and transient absorption spectroscopy study on the mechanism underlying ethane formation indicates that the process is dependent upon upward band bending at the reduced blue-titania/graphene interface, due to holes migration into graphene sheets, a phenomenon contradicting prior assumptions that graphene acts as an electron extractor. In the final work we would be describing about a photocatalyst named Cu-Pt deposited blue titania nanoparticles, which has achieved a sustained Joule (sunlight) to Joule (fuel) photoconversion efficiency of 1%, with an apparent quantum efficiency of ϕ = 86% [3]. The time-dependent photoconversion efficiency over 0.5 h intervals yields a maximum value of 3.3% (ϕ = 92%).

1. Materials Today, 2017, 20, 507-515
2. Energy & Environmental Science, 2018, 11, 3183-3193
3. Energy & Environmental Science, 2019, Accepted, In press

Institution: DGIST

Code: SOLFuel_T21

Presenter: Qi Hu (DEU)

Abstract Title: Mechanistic Studies of Solar Energy Harvesting with N-Heterocyclic Frameworks

Co-Author(s): V. S. Vyas, G. Savasci, B. V. Lotsch, E. Riedle

Abstract: Triazine-based covalent organic frameworks (COFs) have been proven to be a new generation of photoactive materials for light-induced hydrogen evolution. The efficiency of hydrogen evolution increases significantly building blocks of the COFs with a larger number of N atoms are used. This provides strong evidence for a crucial role of heterocyclic N-atoms in the photocatalytic water-splitting. Detailed knowledge of the influence of the nitrogen content on the activity of the photocatalyst would benefit the design of new materials.

We present a spectroscopical investigation of the building blocks 2,4,6-tri-p-tolyl-benzene with a varying number of N atoms in the central ring (Nx-Me, x=0,1,2,3) of the COFs. All the Nx-Me show an absorption band below 350 nm. The fluorescence spectra do not form a mirror image of the corresponding absorption band and show a large Stokes shift particular for x=0 and 3. The form of the emission spectrum of N1-Me and N2-Me is dependent on the excitation wavelength, which indicates that different fluorescing species exist. By TA measurements we observe that the lifetime of the singlet excited state drops dramatically with the increase of the nitrogen content, from 16 ns to 53 ps. We also find that the triplet quantum yield rises from 40 to 93% with the increase of nitrogen content. Since the triplet is likely important as the active excited state in the electron transfer process, this study discloses the reason for the observed increase of the efficiency of hydrogen evolution with the nitrogen content of the heterocycles in COFs.

Institution: LS für BioMolekulare Optik, Faculty of Physics, LMU Munich

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Code: SOLFuel_T22

Presenter: Yu Wang (USA)

Abstract Title: Hot Electron-driven Photoelectrochemical Water Splitting by Plasmonic-metal Grating Nanostructures

Co-Author(s): Yu Wang, Lang Shen, George N. Gibson, Ernest Guignon, Nathaniel C. Cady, William D. Page, Arturo Pilar, Stephen B. Cronin

Abstract: In the work presented here, we explore photoexcited hot electrons generated by different metal-based plasmon grating nanostructures in water splitting reactions. The grating nanostructures consist of 100nm Au or Ag film deposited on corrugated silicon substrates with 500nm pitch. Depending on the applied bias, photoexcited hot electrons and holes participate in the hydrogen evolution reaction (HER) or oxygen evolution reaction (OER). The polarization of the incident light can be changed simply by rotating a half waveplate without alternating any other parameters of the experiment, which provides a more accurate basis for comparing resonant and non-resonant excitation. Additionally, grating nanostructures attached to a rotational motor are tuned at different light incident angles to further explore the incident angle dependence. Under light polarized perpendicular to the grating lines (p-polarization), the hot electron-generated photocurrent shows an enhancement of 2.3X for Au metal gratings in OER and 7X for Ag metal gratings in HER at resonant incident light angles. The angle dependence of the photoreflectance of these gratings also shows very sharp dips at their resonant angles, corresponding to conditions under which there is wavevector matching between the incident light and grating plasmon modes. Finite difference time domain (FDTD) simulations of s and p-polarized light at various incident angles confirmed the existence of enhanced electric fields under resonant excitation for both Au and Ag grating nanostructures.

Wang, Yi, et al. "Hot electron-driven photocatalysis and transient absorption spectroscopy in plasmon resonant grating structures." Faraday Discussions (2019).

Shen, Lang, et al. "Plasmon resonant amplification of hot electron-driven photocatalysis." Applied Physics Letters113.11 (2018): 113104.

Institution: University of Southern California

Code: SOLFuel_T23

Presenter: Cody R. Carr (USA)

Abstract Title: Bridging the Divide Between Molecular and Heterogeneous Electrocatalysis: Fast HER Mediated by [Co13C2(CO)24]4-

Co-Author(s): Atefeh Taheri, Louise A. Berben

Abstract: In many examples, reactions mediated by homogenous electrocatalysts are rate limited by proton transfer (PT) steps. A common approach to speeding up PT is manipulation of the secondary coordination sphere with proton relays and these drastically enhance PT rates and overall reaction rates. Heterogenous electrocatalysts have band structures that promote facile PT concerted with electron transfer (ET) which is known as the Volmer mechanism. In this presentation I will discuss electrocatalytic hydrogen evolution by a cobalt carbonyl cluster with formula [Co13C2(CO)24]4-. At -0.86 V vs. SCE (overpotential 650 mV), H2 evolution is catalyzed by [Co13C2(CO)24]4- with observed rate of 4 x 109 s-1. Characterization of [Co13C2(CO)24]4- in the presence and absence of protons reveals electron transfer kinetics and diffusion behavior similar to nanomaterials, formation of protonated [H-Co13C2(CO)24]3-, and sufficient stability to probe ET and PT mechanisms. Kinetic isotope effects associated with the first ET event of the catalytic cycle revealed both facile PT transfer chemistry and facile hydride migration on the cluster surface. We attribute the fast PT kinetics and the low potential for reduction of [Co13C2(CO)24]4- to the delocalized electronic structure which lowers overall Marcus reorganization energies associated with ET.

Institution: UC Davis

POSTERS

Code: SOLFuel_P1

Presenter: Xiaohong Yin (CHN)

Abstract Title: Enhanced Photocatalytic Reduction of CO2 to Methanol by ZnO Nanoparticles Decorated ZnSe Nanosheet

Co-Author(s): Shuangfang Zhang

Abstract: the ZnO/ZnSe composites were successfully synthesized via a solvothermal method and characterized with a serious of experiments to investigate into the effects of their compositions and microstructures on the activities of photocatalytically reducing CO2. The sample of ZnO/ZnSe performed the best photocatalytic activity up 1581.82 μmol/gcat/h compared to bare ZnO and ZnSe under irradiation. ZnO/ZnSe composites were performed a novel morphology with ZnO nanoparticles decorated ZnSe nanosheets which is mainly contributed to the transfer of carriers and the separation of electrons-holes in the presence of ZnSe nanosheets. In addition, a type Ⅱ heterojunction between ZnO and ZnSe was constructed to restrain recombination of photo-generated electron and hole. These are likely to improve the photocatalytic reduction activity as for the sample of ZnO/ZnSe.

Institution: Tianjin University of Technology

Code: SOLFuel_P2

Presenter: Monica Sanchez (USA)

Abstract Title: Nanorod-enzyme Conjugates for Photoinduced Turnover of [FeFe] Hydrogenase

Co-Author(s): Constanze Sommer, James Birrell, Ed Reijerse, Wolfgang Lubitz

Abstract: Hydrogen has been proposed as the ideal fuel to meet the worlds energetic requirements, but a scalable hydrogen production system is currently unavailable.1 Hydrogenases (H2ase), and in particular [FeFe] H2ases, provide a tantalizing model for efficient H2 producing catalysts.2 Despite considerable effort devoted to unraveling the mechanistic details of the [FeFe] H2ase catalytic cycle, there remains several open questions in the field, highlighting the need for a novel approach to studying this enzyme.2 We hypothesized that a hybrid system composed of a nanorod, electron shuttle and enzyme, would allow us to rapidly initiate turnover by photoinduced reduction of the enzyme. By illuminating a sample of this biohybrid system, we can “jump” the solution potential triggering turnover as h2ase is reduced. With this system we have utilized time resolved spectroscopic techniques for the observation of catalytically relevant intermediates on the nanosecond to millisecond timescale. Time resolved IR and visible spectroscopies allowed us to measure the rate at which known intermediate states form, yielding unprecedented insight into the catalytic mechanism of this enzyme. By taking advantage of the light sensitivity of nanorods and the versatility of the mediators, we have developed a system for giving us precise control over enzyme activity and can for the first time observe catalytically active states of [FeFe] H2ase under sub-turnover conditions.

Institution: Emory University

Code: SOLFuel_P3

Presenter: Dr. Kelly L. Materna (SWE)

Abstract Title: Photocathodes for Photocatalytic Hydrogen Generation using Molecular Cobalt Catalysts and a Push-Pull Dye

Co-Author(s): Reiner Lomoth, Anders Thapper, Sascha Ott, Haining Tian, and Leif Hammarström

Abstract: Due to the world´s excessive use of fossil fuels, global warming and climate change have become a concern. To mitigate this, alternative energy sources must be employed to generate renewable fuels. Solar energy is an abundant option and can be harvested and converted into renewable fuels, like H2, using water-splitting dye-sensitized photoelectrochemical cells (WS-DSPECs).(1) In WS-DSPECs, the photocathode performs photocatalytic hydrogen generation using light harvesting dye molecules and molecular proton reduction catalysts covalently bound to semiconductor electrode surfaces.(2) Here, photocathodes were assembled using a push-pull dye, PB6,(3) as the light harvester and a variety of molecular cobalt-oxime catalysts covalently bound to NiO electrodes. Photocathodes were analyzed by spectroscopic techniques, photoelectrochemical measurements, and hydrogen evolution experiments to probe their performance and understand how molecular changes in catalyst structure effect the overall photocathode efficiency.

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Institution: Uppsala University

Code: SOLFuel_P4

Presenter: Kazushi Iwamura (JPN)

Abstract Title: Efficient H2O2 Generation from Water and Oxygen using BiVO4 Photocatalyst under Visible Light

Co-Author(s): Kojiro Fuku, Kazuhiro Sayama, Naoki Ikenaga

Abstract: Hydrogen peroxide (H2O2) is a clean oxidant and is used as an oxidant in bleaching, sterilization, and organic synthesis. Recently, it has been reported that Au-supported BiVO4 (Au-BiVO4) photocatalyst exhibits high performance for the H2O2 generation by two-electrons reduction of oxygen (O2) 1). We have reported that Au co-catalyst prepared at pH 7.2 by photo-assisted deposition on BiVO4 showed high activity for the reductive H2O2 generation in the presence of methanol as a hole scavenger. However, almost of oxidative reaction on BiVO4 is the O2 generation by water splitting or the oxidation of the hole scavenger. Combining the reductive and oxidative H2O2 production from O2 and H2O can be one of promising processes from the view point of practical applications. On the other hand, it was reported on the oxidative H2O2 generation in hydrogen carbonate (HCO3-) solution using electrochemical reaction 2). In this reaction, oxidized HCO3- on anode electrode acts as a co-catalyst for the H2O2 generation from H2O. In this study, we focused on the oxidative reaction on Au-BiVO4 exhibited high performance and the effective utilization of oxidative reaction on BiVO4. We investigated the effect of HCO3- on photocatalytic H2O2 generation activity. It should be noted that the H2O2 generation with HCO3- exhibited about 2.7 times higher than that with only water. Therefore, we succeeded the efficiency improvement of photocatalytic H2O2 generation from H2O and O2.
1) H. Hirakawa, et al., ACS Catal., 2016, 6, 4976.
2) D. E. Richardson, et al., J. Am. Chem. Soc., 2000, 122, 1729.

Institution: Graduate School of Science and Engineering, Kansai University

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Code: SOLFuel_P5

Presenter: Daiki Fujimoto (JPN)

Abstract Title: Development of Pd-introduced WO3 Photocatalyst for Efficient Hydrogen Peroxide Production

Co-Author(s): Kojiro Fuku, Naoki Ikenaga

Abstract: Almost of hydrogen peroxide (H2O2) generation using photocatalytic reaction have been focused on two-electrons reduction of oxygen (O2), and gold (Au) nanoparticle has been widely utilized as an effective co-catalyst1). In our laboratory, the effects of various metallic co-catalyst species on the H2O2 generation were investigated. As a result, it has been found that 1.0 wt% Pd-supported WO3 prepared using the impregnation method (IMP) exhibited high performance for the H2O2 generation and accumulation as compared with other WO3 introduced co-catalysts. In this study, we investigated the effects of supporting method and introducing amount of Pd using Pd-introduced WO3. It was achieved that Pd-introduced WO3 using the photo-assisted deposition (PAD) capable of selectively supporting Pd co-catalyst only on the reductive site of WO3 exhibited excellent the H2O2 production activity. Furthermore, it was found that supporting 0.1 wt% Pd using the PAD exhibited the highest H2O2 production activity in tried amounts. It should be noted that enhanced performance of about 3.6 times was achieved by using the 0.1 wt% Pd-WO3 (PAD) compared with reported 1.0 wt% Pd-WO3 (IMP). In addition, the particle sizes of Pd on WO3 were measured using CO-pulse adsorption method. The average particle size of Pd were 28.2 nm (0.1 wt% PAD) and 73.0 nm (1.0 wt% PAD), respectively. These results suggest that Pd nanoparticle possessing smaller size supported on reduction site acts as effective co-catalyst for the photocatalytic H2O2 production from O2.
1) M. Teranishi, et al., J. Phys. Chem. C, 120（2016）1083

Institution: Graduate School of Science and Engineering, Kansai University

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Code: SOLFuel_P6

Presenter: Nataliia Vereshchuk (ESP)

Abstract Title: Designing New Efficient Ru Based Molecular Water Oxidation Catalysts

Co-Author(s): R. Matheu, J. Benet-Buchholz, M. Pipelier, J. Lebreton, D. Dubreuil, A. Tessier, C. Gimbert-Suriñach, M. Z. Ertem, A. Llobet

Abstract:

Designing New Efficient Ru Based Molecular Water Oxidation Catalysts
Nataliia Vereshchuk a,b, Roc Matheu a,b, Jordi Benet-Buchholz a, Muriel Pipelier c, Jacques Lebreton c, Didier Dubreuil c, Arnaud Tessier c, Carolina Gimbert-Suriñach a, Mehmed Z. Ertem d and Antoni Llobet a,e

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Developing a sustainable global energy currency is considered one of the major challenge facing researchers today. Future sustainable energetic schemes rely on technologies that store energy into chemical bonds. The resulting solar fuels are produced from abundant substrates such as water, carbon dioxide, or nitrogen.1,2
There are still a lot of investigation to be done in this field, before the efficient commercially viable solution will be realized. Our group has been at the forefront of this area of research for many years and particular attention is being paid to the water oxidation, which is a bottleneck process in solar fuel technologies. The most efficient WOCs known today are based on the Flexible Adaptative Multidentate Equatorial ligands containing polypyridyl carboxylate groups such as H2tda and H2bda.3,4
A new re-design Ru catalyst has been prepared and characterized by spectroscopic and electrochemical methods. Comparative studies of the catalytic activities for a different kind of ligand design has provided a better understanding of the mechanisms for water oxidation as well as catalyst degradation. Further, we show that these new Ru based complexes can achieve water oxidation catalysis driven chemically, electrochemically or photochemically.

1.Matheu, R., Ertem, M. Z., Gimbert-Suriñach, C., Sala, X., Llobet, A., Chem. Rev., 2019, 119, 3453–3471
2.Garrido-Barros, P., Gimbert-Suriñach, C., Matheu, R., Sala, X., Llobet, A., Chem. Soc. Rev., 2017,46, 6088-6098
3.Matheu, R., Ertem, M. Z., Benet-Buchholz, J., Coronado, E., Batista, S. V., Sala, X., Llobet, A., J. Am. Chem. Soc., 2015, 137 , 10786–10795
4.Richmond, C. J.; Matheu, R.; Poater, A.; Falivene, L.; Benet-Buchholz, J.; Sala, X.; Cavallo, L.; Llobet, A., Chem. - A Eur. J. 2014, 20, 17282–17286

Institution: Institute of Chemical Research of Catalonia (ICIQ), Spain

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Code: SOLFuel_P7

Presenter: Raymundo Moya (USA)

Abstract Title: Single-molecule Ultrafast Spectroscopy to Investigate Heterogeniety in Energy Transfer Rates

Co-Author(s): Toru Kondo, Audrey Norris, Gabriela Schlau-Cohen

Abstract:

Photosynthesis begins with the absorption and migration of energy through a protein network to the reaction center with near-unity quantum efficiency. Despite its prevalence and connection to most life on Earth, the molecular mechanisms of photosynthesis remain not fully understood. While various energy transfer steps of photosynthesis have been thoroughly investigated with ensemble ultrafast techniques, these energy-transfer rates represent the average over a heterogeneous sample. While the heterogeneous excited state manifold available to light-harvesting complexes can be investigated through single-molecule fluorescence experiments, these techniques are inherently limited to the nanosecond dynamics of fluorescence. A new technique, single-molecule ultrafast spectroscopy (smUS), utilizes a pump-probe like excitation into a confocal microscope to report femto to picosecond dynamics into the fluorescence emission of single molecules. We have successfully built a new smUS apparatus that spans the visible wavelengths to investigate how energy transfer rates vary in a noisy, fluctuating environment. Herein, we detail results on allophycocyanin, a robust and well characterized light-harvesting complex present in cyanobacteria. By correlating energy transfer rates with lifetime and intensity information, we investigate how the molecular machinery is optimized to transfer energy despite thermal fluctuations.

Institution: Massachusetts Institute of Technology

Code: SOLFuel_P8

Presenter: Katherine Brown (USA)

Abstract Title: The NAD(P)H-dependent Oxygen Reduction Reaction Catalyzed by Synechocystis 6803 Flavodiiron-3

Co-Author(s): Z. Guo, M. Tokmina-Lukaszewska, L. W. Scott, C. E. Lubner, S. Smolinski, D. W. Mulder, B. Bothner, and P. W. King

Abstract: The reduction of excess O2 without the formation of reactive oxygen species (ROS) is an essential reaction for photosynthetic organisms. In higher plants this reaction is accomplished by the Mehler reaction, where O2 is reduced to peroxide and then to water by antioxidants. Photosynthetic bacteria perform O2 reduction to water via a single catalytic reaction driven by the non-heme diiron flavoprotein flavodiiron (Flv). In cyanobacteria soluble Flvs are known to be essential for managing photosynthetic electron flow and protection against oxidative damage to PSI during periods of high and fluctuating light. The biochemical and kinetic basis for these functions and the mechanism of the 4 electron reduction of O2 that minimizes ROS formation are only partially understood. Here we begin the characterization of the biochemistry and mechanism of the soluble Synechocystis 6803 flavodiiron 3 (Flv3). Flv3 forms homodimers with flavin and FeFe-cofactor arrangements that support direct oxidation of pyridines and inter-monomer electron transfer. Flv3 catalyzes O2 reduction using either NADH or NADPH with kinetics consistent with cooperativity. These properties tune Flv3 reactivity for dynamic levels of O2 and reduced pyridine nucleotides during photosynthetic growth. Reduction of the flavin cofactors show formation of 2-electron reduced states with no semiquinone observed at steady-state, suggesting Flv3 may be tuned to minimize the stability of one electron flavin states that can react with O2 and form ROS. Reduction of Flv3 with NAD(P)H shows a Fe(II)Fe(III) redox state signal similar to other non-heme iron and flavodiiron proteins which is fully reduced in dithionite. These redox properties suggest that Flv3 cofactor potentials are tuned to favor the 4-electron reduction of O2 to water to minimize ROS formation and to cycle reducing equivalents during photosynthesis.

Institution: National Renewable Energy Lab

Code: SOLFuel_P9

Presenter: Sarah Narehood (USA)

Abstract Title: Development and Optimization of CdSe Nanoparticles for Photocatalysis

Co-Author(s): Monica L.K. Snachez, Dr. R. Brian Dyer

Abstract: Harvesting the sun's energy and direct conversion to a fuel source has been the goal of researchers for decades, as our other energy resources are in decline. This light energy can be harnessed and converted into high energy chemical bonds with photocatalytic systems composed of a photosensitizer and catalyst. Success with this approach has been observed with the use of hybrid systems composed of nanoparticles, a redox mediator, and hydrogenase as the catalytic hydrogen produce. With systems of this class, dot-in-rod (DIR) type materials are often used, however, optimization of photosensitizer properties such as elongating the “dot” core into a more rod like structure to allow for a broader range for light excitation. The wider range of excitation sources which can be utilized makes this nanoparticle-mediator system to allow us to study and drive catalysis with of a larger variety of biological systems, such as [FeFe] hydrogenase or NADP+ reductase. Steady-state photo-reduction experiments have allowed us to quantify the efficiency of both redox partner and enzyme reduction utilizing 532 nm light with this other class of particles. Also, important to broadening and adapting this methodology is an understanding of the principles influencing electron transfer efficiency such as pH, photosensitizer physical characteristics and band gap energies. Improvements to the photocatalytic system components described above and others will lead to more effective methods for harvesting light energy and yield a powerful tool for studying biological systems.
i.Energy Environ. Sci., 2017, 10, 2245
ii.J. Am. Chem. Soc. 2000, 122, 51, 12700-12706

Institution: Emory University

Code: SOLFuel_P10

Presenter: Gregory E. Vansuch (USA)

Abstract Title: Gating Proton-coupled Electron Transfer at the Active Site of a [NiFe] Hydrogenase: The Roles of the First and Second Coordinati

Co-Author(s): Bryant C. Chica; Brandon L. Greene; Chang-Hao Wu; Dominik K. Haja; Michael W.W. Adams; and R. Brian Dyer

Abstract: The [NiFe]-H2ases utilize facile proton-coupled electron transfer within a minimal potential range near the H2/H+ couple. This has sparked broad interest to utilize the enzymatic structural and electronic framework to design the inner and outer coordination spheres of biomimetic and bioinspired systems. Despite a fundamental understanding of the elementary steps necessary for efficient [NiFe]-H2ase turnover, the roles of the first and second coordination spheres remain poorly understood. We have thus studied the intrinsic hydride photochemistry of a native and variant enzyme that allowed us to further understand the role of a terminal thiolate of the (CN)2 (CO)FeII(μ-Cys)2Ni(Cys)2 catalytic core during proton migration from the active site. Furthermore, we have utilized photoreduction with enzyme variants to understand the role(s) of guanidinium and carboxylic acid functionalities in the second coordination sphere. Excitation of a CdSe/CdS dot-in-rod in solution with a variant enzyme allowed for rapid reduction of a redox mediator that acted as an external electron shuttle. This perturbed the reduction potential of the solution, which caused the enzyme to reduce protons in order to relax to the new reduction potential of the solution. Because of this relaxation, the CO stretching frequency of the active site changed from the initial conditions, which has allowed to understand structural and electronic aspects that are critical for efficient [NiFe]-H2ase catalysis.

Institution: Emory University

Code: SOLFuel_P11

Presenter: Abdulaziz Alherz (USA)

Abstract Title: Organic Hydrides for the Photoelectrochemical Catalytic Reduction of CO2

Co-Author(s): Stefan Ilic, Chern-Hooi Lim, Ksenija Glusac, Charles Musgrave

Abstract: Increasing atmospheric CO2 concentration and dwindling fossil fuel supply necessitate the search for efficient methods for CO2 conversion to fuels. Assorted studies have shown pyridine and its derivatives capable of photoelectrochemically reducing CO2 to methanol, and some mechanistic interpretations have been proposed. We analyze the thermodynamic and kinetic aspects of the efficacy of pyridines as well as benzimidazoles as hydride-donating catalytic reagents that transfer hydrides via their hydridic form. We investigate both the effects of functionalizing catalysts with electron-donating and electron-withdrawing groups on hydride-transfer catalyst strength, assessed via their hydricity (thermodynamic ability) and nucleophilicity (kinetic ability), and catalyst recyclability, assessed via their reduction potential. We find that catalysts substituted with electron-donating groups have stronger hydride-donating ability (having lower hydricity and larger nucleophilicity values) but are less efficiently recycled (having more negative reduction potentials). In contrast, catalysts substituted with electron-withdrawing groups are more efficiently recycled but are weaker hydride donors. Functional group modification favorably tunes hydride strength or efficiency, but not both. We attribute this problematic coupling between the strength and recyclability of such hydrides to their aromatic nature. Proton-coupled electron transfers can be utilized at appropriate conditions to mitigate the costs of catalyst recovery.

Institution: University of Colorado - Boulder

Code: SOLFuel_P12

Presenter: Paula Enciso (URY)

Abstract Title: Evaluation of Dyes Obtained from Antarctic Red Algae in DSSC

Co-Author(s): María Fernanda Cerdá

Abstract: Dye sensitized solar cells (DSSC) are photoelectrochemical devices that resemble natural photosynthesis because they use an organic dye to absorb light and produce a flow of electrons [1]. Today, many types of research are conducting around the search for the best dye in order to improve energy efficiency conversion. The use of natural dyes is an attractive alternative due to the low cost of fabrication and the environmental benefits related to their employment. More particularly, the search for clean sources of energy is relevant in the Antarctic area. DSSC constitute an alternative to partially solve the energy needs in this area, especially if we use dyes from red algae, that are in great abundance in South Seas. [2]

In this work, we study the extraction of dyes with different solvents, absolute ethanol and water. After that, we carried out spectroscopic and voltammetry studies in order to identify the dyes we extract and also to characterize and evaluate the potential use of them as sensitizers for DSSC.

Finally, the cells were assembled with the different pigments obtained, evaluating its performance through electrochemical techniques as IV profiles and electrochemical impedance spectroscopy.

These studies allowed us to obtain and compare the efficiency values of the energy conversion and the fill factor of the different cells.

[1] O´Regan, B. & Grätzel, M. 1991. Nature, 353, 737-740.
[2] Enciso, P., Woerner, M., & Cerdá, M. 2018. MRS Advances, 3 (61), 3557-3562.

Institution: Laboratorio de Biomateriales, Facultad de Ciencias, UdelaR, Montevideo, Uruguay.

Code: SOLFuel_P13

Presenter: Jesse Ruzicka (USA)

Abstract Title: Electron-transfer Kinetics in Complexes of CdS Nanocrystals and Nitrogenase Enzyme

Co-Author(s): Gordana Dukovic, Paul King, Kate Brown, Bryant Chica, Lance Seefeldt, Hayden Kallas

Abstract: Complexing semiconductor nanocrystals (NCs) with redox enzymes has recently emerged as a strategy for creating photocatalytic and photosynthetic systems. Such systems combine the tunable optical and surface properties of NCs and the catalytic selectivity of redox enzymes to efficiently drive a variety of reactions using light. One such system of interest couples CdS NCs with MoFe protein of the nitrogenase enzyme. This system was able to catalyze the reduction of N2 to NH3 using light as the energy source. Photoinduced electron transfer (ET) is in direct competition with nonproductive decay pathways within the NC. This competition determines the quantum efficiency of ET, which in turn defines the upper limit on the quantum yield of product generation. Thus, gaining a detailed understanding of the ET kinetics in this system is crucial for controlling the overall photocatalytic cycle. To understand the complex photophysical processes taking place, transient absorption spectroscopy (TAS) was used to measure the rate constant and efficiency of ET from CdS to MoFe as well as FeMo-co, the active site for substrate binding and catalysis within nitrogenase. The results of these experiments give insight into a key step of the photocatalytic cycle that is not probed during product detection experiments and can provide information of how the system can be improved. In this presentation, we discuss the measurement and determination of the rate constant for ET, as well as the quantum efficiency of ET, and their implications for catalysis.

Institution: University of Colorado Boulder

The 29th International Conference on Photochemistry
Boulder, Colorado
July 21 – 26, 2019

SPECTROSCOPY AT THE NANOSCALE (SPECNano)
ABSTRACTS

INVITED TALKS

Code: SpecNano_I1

Presenter: Xiaoyang Zhu (USA)

Abstract Title: Mott Transition of Interlayer Excitons at 2D Van der Waals Heterojunctions

Co-Author(s): J. Wang, J. Ardelean, Y. Bai, X. Xu, M. Kira, J. Hone

Abstract: Controlling charge density in two-dimensional (2D) materials is a powerful approach for engineering new electronic phases and properties. Such control is traditionally realized by electrostatic gating. Here, we report an optical approach for generation of high carrier densities utilizing transition metal dichalcogenide hetero-bilayers, WSe2/MoSe2, with type-II band alignment. By tuning the optical excitation density above the Mott threshold, we realize the phase transition from interlayer excitons to charge-separated electron/hole plasmas, where photoexcited electrons and holes are localized to individual layers. Remarkably, high carrier densities up to 4x10^14 cm^-2 can be sustained under both pulsed and continuous wave excitation conditions. These findings open the door to optical control of electronic phases in 2D hetero-bilayers.

Institution: Columbia University

Code: SpecNano_I2

Presenter: Natalie Banerji (CHE)

Abstract Title: Terahertz Spectroscopy of Organic Solar Cell Materials with Controlled Phase Morphology

Co-Author(s): Philipp Krauspe,a Demetra Tsokkou,a Martina Causa',a Ester Buchaca-Domingo,b Zhuping Fei,b Martin Heeney,b Natalie Stinge

Abstract: The phase morphology of organic solar cell materials, in particular the nanoscale arrangement of the donor and acceptor, plays a defining role in the efficient functioning of such devices. It affects amongst others the nanoscale mobility of the photogenerated electrons and holes, which can be investigated by terahertz (THz spectroscopy). While transient absorption (TA) spectroscopy gives information about the population of photogenerated excitons and charges, both the population and short-range mobility of charge carriers determines the photoconductivity dynamics in optical-pump-THz-probe (OPTP) measurements. By combining both techniques, the evolution of only the mobility at different times after photoexcitation can be extracted. This is then further substantiated by the mobility and localization parameters obtained from analyzing the real and imaginary parts of the complex photoconductivity spectra at selected time delays with an appropriate model. Here, we have undertaken such a study with different polymer:fullerene and polymer: non-fullerene blends, where the phase morphology was carefully controlled. We can thus follow changes in the short-range mobility as the charges evolve between different neat and intermixed regions of the blend. Moreover, ways to improve the THz setup to deal with the very small signals of organic semiconductors will be presented.

Institution: University of Bern

Code: SpecNano_I3

Presenter: Margaret Murnane (USA)

Abstract Title: Mapping Hidden Phases and Electron-Phonon Coupling in Materials using High Harmonic Sources

Co-Author(s): X. Shi, W. You, Y. Zhang, H. Kapteyn

Abstract: In recent work, we developed a new technique called ultrafast electron calorimetry, which allows us to sensitively measure the dynamic electron temperature in laser excited materials.[1-3] Because the heat capacity of the electrons is much less than that of the lattice, any change in state or couplings in a material manifests itself as an abrupt change in the electron temperature. In the case of laser excited quasi-2D materials, the timescales for subsequently exciting the different phonon baths is different. In quasi-2D materials, this allows us to drive a material in to new metastable phases, or to tune the electron-phonon coupling - essentially by using a laser to induce unique periodic lattice distortions that cannot be accessed using static pressure/doping. In magnetic materials, we can directly transfer spin-polarization in materials using light, on femtosecond-to-attosecond timescales.[2, 4] This talk will also discuss new capabilities for tuning the polarization, spin and orbital angular momentum of HHG beams by sculpting the driving laser beams.[5,6]

[1] X. Shi et al., Science Advances 5, eaav4449 (2019).
[2] P. Tengdin et al., Science Advances 4, 9744 (2018).
[3] X. Shi et al., submitted (2019).
[4] P. Tengdin et al., submitted (2019).
[5] L. Rego et al., Science, in press (2019).
[6] K. Dorney et al., Nature Photonics 13, 123 (2019).

Institution: JILA, University of Colorado and NIST, Boulder CO

Code: SpecNano_I4

Presenter: Ye Yang (CHN)

Abstract Title: Ultrafast Interfacial Charge Transfer of Si Surface Carriers

Co-Author(s): Matthew Beard

Abstract: Silicon (Si) is the most important semiconductor for which modern electronic technology relies. Beside the electronics industry, the solar cell market is also dominated by Si panels. The expanding demand for solar electricity has reduced the price of Si wafers for photovoltaic applications due to economies of scale, which provides a unique opportunity to integrate Si into photoelectrochemical (PEC) systems in order to achieve cost-effective solar fuel production. Interfacial charge transfer from Si to various metal contacts plays a key role in silicon-based electronics and optoelectronics. Surprisingly, a direct probe of this interfacial charge transfer process has not been developed. Here we exploit transient reflection spectroscopy to interrogate charge transfer from Si to platinum. We find that the charge transfer velocity from Si to Pt reaches 10^7 cmS^-1, which surprisingly is the same order of magnitude as the carrier thermal velocity in Si. We also show that the charge transfer velocity can be controllably reduced and eventually brought to zero by inserting silica spacing layers between the Si and platinum interface.

Institution: Xiamen University

Code: SpecNano_I5

Presenter: Martin Zanni (USA)

Abstract Title: Spatial Mapping of Slip-stacked Structures in Singlet Fission Microcrystals using 2D White-Light and Broadband TA Microscopies

Co-Author(s): Andrew Jones

Abstract: This talk will present data showing a previously unresolved eigenstate in TIPS-pentacene microcrystals that is created by a non-equilibrium packed geometry. The eigenstate was identified via cross peaks in 2D White-Light spectra and the population of the molecular geometry mapped using broadband transient absorption microscopy. Modeling is consistent with strong charge transfer couplings in slip-stacked geometries that create a low energy eigenstate. The technological developments that make possible these measurements will be described and the impact of this eigenstate on triplet populations discussed.

Institution: University of Wisconsin-Madison

CONTRIBUTED TALKS

Code: SPECNano_T1

Presenter: Thilo Glatzel (CHE)

Abstract Title: Force Spectroscopy of a Donor-Acceptor Molecule under Illumination

Co-Author(s): Tobias Meier, Rémy Pawlak, Alexis Baratoff, Yan Geng, Xunshan Liu, Silvio Decurtins, Shi-Xia Liu and Ernst Meyer

Abstract: We investigated by atomic force microscopy and scanning tunneling microscopy a prototypical system consisting of a π-conjugated tetrathiafulvalene-fused dipyridophenazine molecule (TTF-dppz) adsorbed on a thin NaCl film on Cu(111) as presented. Depending on the adsorption site and the interaction with the underlying NaCl ions, the molecule was found either in a bound state forming a chelate complex with a single Na+ alkali cation or in a nearly undisturbed free state [1]. Upon optical excitation the lateral dipole moment of the TTF-dppz molecule in the gas phase is expected to change from 0.9D in the ground state to 5.9D in the excited state caused by the internal redistribution of charges. Since the local charge distribution of single molecules can be accessed by Kelvin probe spectroscopy experiments, a clear difference in the measured local contact potential difference (LCPD) is expected under illumination. We performed such LCPD measurements of single TTF-dppz molecules on NaCl thin films and observed a clear change of the charge distribution of the molecule upon photo-excitation. However, the influence of the molecule-substrate interaction to this process as well as tip sample interactions might disturb the measured signal and will be discussed in the presentation. Finally, also atom and molecule manipulations have been performed to study the influence of various structural conformations on the local charge distribution.

[1] Meier, T. et al. Donor-acceptor properties of a single-molecule altered by on-surface complex formation. ACS Nano 11, 8413–8420 (2017).

Institution: Department of Physics, University of Basel, Klingelbergstr. 82, 4056 Basel, Switzerland

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Code: SPECNano_T2

Presenter: Monica Ricci (BEL)

Abstract Title: Silver Nanowire Endoscopy for Single-Cell Investigation

Co-Author(s): Beatrice Fortuni, Susana Rocha, Tomoko Inose and Hiroshi Uji-i

Abstract: Surface Enhanced Raman Scattering (SERS) is considered to be among the most promising tools for intracellular studies thanks to its sensitivity and fingerprinting capabilities.

To date, SERS-based measurements in living cells have mainly been demonstrated by delivering metal nanoparticles (NPs) into the intracellular environment via endocytosis.[1] This approach, however, is highly invasive and lacks spatial and temporal control.

Silver nanowire - (AgNW-) mediated endoscopy holds great potential as alternative non-invasive technique thanks to the thin diameter of AgNWs and the possibility to insert the endoscopy probes into living cells with both spatial and temporal control.

In this contribution, we further improved the SERS performances of our endoscopy probes [2] and demonstrated their site-specificity by staining different cellular compartments and obtaining highly resolved fingerprints of labels used. Furthermore, we successfully applied our technique to investigate the intracellular distribution of Doxorubicin, a widely employed anticancer drug. The choice for this system is motivated by the fact that the detection of Doxorubicin inside the nucleus with conventional fluorescence microscopy is challenging, as once intercalated into the host DNA, its fluorescence signal is drastically reduced. [3]

In conclusion, we present an alternative approach for SERS-based measurements which enables the specific detection of species with high sensitivity and spatio-temporal control. Our method holds great potential for studying chemical and structural dynamics of distinct biomolecules in single living cells.

[1] H. Yuan, et al. Anal. Bioanal. Chem.405, 6165-6180 (2013)
[2] G. Lu, et al. Adv. Mater. 26, 5124-5128 (2014)
[3] Gołunski, et al. Biochimie,123, 95-102 (2016)

Institution: KU Leuven, Belgium

Code: SPECNano_T3

Presenter: Andrey Krayev (USA)

Abstract Title: Correlated SPM–TERS Imaging: Revealing Unexpected Nanoscale Heterogeneities in 2D Semiconductors

Co-Author(s): _

Abstract: In this presentation we'll discuss the application of scanning probe microscopy (SPM) cross-correlated with tip enhanced Raman scattering (TERS) and photoluminescence (TEPL) imaging for detection of unexpected nanoscale heterogeneities in TMDs.
It will be demonstrated that few-layer flakes of WSe2 exfoliated to gold or silver may possess doping heterogeneity with domains within 30-300nm range. These domains identified by Kelvin probe imaging showed different TERS response and generated photocurrent of opposite polarity.
We'll further discuss how scanning capacitance microscopy can identify the grain boundaries (GB) in CVD-grown MoSe2 crystals, while TERS characterization of such crystals transferred to gold reveals possible etching of MoSe2 along GB during the transfer, an effect beneficial for photocatalytic activity.
3-rd example of the use of cross-correlated SPM and TERS/TEPL imaging of 2D semiconductors is a discovery of the nature of strong PL of WS2 and WSe2 transferred to gold via heat-assisted exfoliation. Through TERS/TEPL it was identified that PL is coming from nanoscale bubbles formed in TMD layers. Exciton funneling towards the bubbles was also discovered, which resulted in strong enhancement of Raman/PL response from the bubbles, and in significant suppression of TERS/TEPL signal in adjacent area.

Institution: HORIBA Scientific

Code: SPECNano_T4

Presenter: Martin Vacha (JPN)

Abstract Title: Stark Effect, Electroluminescence and Modulation of Photophysics in Single Halide Perovskite Nanocrystals

Co-Author(s): D. K. Sharma, S. Hirata, V. Biju

Abstract: Exceptional excitonic properties such as strong absorption and efficient narrow-band emission make lead halide perovskite nanocrystals (NCs) possible candidates for applications in light-emitting and sensing devices. Here, we report a simultaneous study of EL and PL of inorganic halide perovskite nanocrystals of CsPbBr3 on single particle level. We examined the influence of a surrounding matrix on their spectral properties and blinking behavior by dispersing the NCs in an inert matrix of PMMA and in a conductive matrix of PVK/PBD, both on the level of single NCs and aggregates of tens of NCs. Incorporation of the NCs in the conductive matrix increases blinking and causes appearance of frequent dim states. Similar effects are caused by externally applied electric field on the NCs dispersed in the insulating matrix. Further, the applied field induces a non-linear Stark shift, the extent of which differs from particle to particle. Based on the above characterization, we fabricated a single-particle light-emitting device by dispersing the NCs at very low concentrations in a PVK/PBD matrix as an emitting layer in an ITO/PEDOT:PSS/PVK/PBD/TPBi/LiF/Al device and studied the device by PL and EL single-particle spectroscopy. The same NC can exhibit dramatically different brightness and blinking behavior upon the different modes of excitations, pointing to the origin of the different quantum efficiencies of the PL and EL processes.

D. K. Sharma, S. Hirata, V. Biju and M. Vacha: Stark effect and environment induced modulation of emission in single halide perovskite nanocrystals. ACS Nano 2019, 13, 624-632

Institution: Tokyo Institute of Technology

Code: SPECNano_T5

Presenter: Dominik Wöll (DEU)

Abstract Title: Diarylethene photoswitches for localization-based superresolution imaging of polymer structures

Co-Author(s): Oleksii Nevskyi, Eric Siemes, Dmitry Sysoiev, Thomas Huhn

Abstract: Super-resolved fluorescence imaging has been frequently used for biological and biomedical applications.[1] Applying these methods to material science, and in particular to polymer systems, is a challenging task due to the need for appropriate dyes and labeling strategies for often non-aqueous and apolar systems. Many super-resolution imaging techniques are based on the switching of fluorophores between a fluorescent and a non-fluorescent state. The sulfone derivatives of diarylethenes[2] have been found to be suitable photoswitches with a strongly fluorescent closed form.[3] We demonstrated their power for resolving different polymer systems including block copolymer structures[4] with the different super-resolution techniques PALM (PhotoActivated Localization Microscopy), RESOLFT (REversible Switchable OpticaL Fluorescence Transition) and SOFI (Super-resolution Optical Fluctuation Imaging).[5] The successful story of diarylethene super-resolution imaging is continued for different scientific questions in polymer science such as the distribution of crosslinkers in various polymer networks.[6]

[1] S. W. Hell, Nature Methods 2009, 6, 24.
[2] M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, Chem. Rev. 2014, 114, 12174.
[3] K. Uno, H. Niikura, M. Morimoto, Y. Ishibashi, H. Miyasaka, M. Irie, J. Am. Chem. Soc. 2011, 133, 13558.
[4] O. Nevskyi, D. Sysoiev, A. Oppermann, T. Huhn, D. Wöll, Angew. Chem. Int. Ed. 2016, 55, 12698.
[5] O. Nevskyi, D. Sysoiev, J. Dreier, S. C. Stein, A. Oppermann, F. Lemken, T. Janke, J. Enderlein, I. Testa, T. Huhn, D. Wöll, Small 2018, 1703333.
[6] E. Siemes, O. Nevskyi, D. Sysoiev, S. K. Turnhoff, A. Oppermann, T. Huhn, W. Richtering, D. Wöll, Angew. Chem. Int. Ed. 2018, 57, 12280.

Institution: RWTH Aachen University

Code: SPECNano_T6

Presenter: Olivia F. Williams (USA)

Abstract Title: Spatially-Resolved Energy Transfer and Exciton Diffusion in Layered Perovskite Quantum Wells

Co-Author(s): Ninghao Zhou, Andrew M. Moran

Abstract: Layered perovskite quantum wells (QWs) have generated substantial interest due to their ambiguous photophysical behavior and impressive stability in devices. Recent ensemble measurements of such 2D perovskite films assign their ultrafast dynamics to Förster-type energy transfer, but this observation has not yet been combined with spatial resolution. For example, it is unknown how the inherent heterogeneity of the film affects the local rates of energy transfer and exciton diffusion. Additionally, the effect of quantum well size and the degree of exciton confinement on cooling processes remains unclear. Using wide-field diffractive optic-based transient absorption microscopy, we directly observe rapid energy transfer and diffusion at 41 different sub-micron spots on a 2D perovskite film. Despite quantum confinement and structural heterogeneity, excitons within even the smallest quantum wells diffuse over > 0.5 microns within 500 ps. Diffusion lengths nearly twice as long are measured for bulk-like components, indicating that excitons can transport over the full thickness of the film (~ 1 micron) before the populations equilibrate. Simultaneous energy transfer occurs on the 100 ps time scale, funneling excitations from small to large QWs. Focused ion beam milling experiments reveal that the bulkier QWs reside closest to the surface of the film, while smaller ones are embedded deep within. Such 2D perovskite films rapidly shuttle excitations from the interior of the film toward the surface through a downhill cascade of transport events. Although further investigation is required, these experiments suggest energy transfer as a possible explanation for the accelerated exciton movements within 2D perovskites.

Institution: University of North Carolina at Chapel Hill, Dept of Chemistry

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Code: SPECNano_T7

Presenter: Philipp Wilhelm (DEU)

Abstract Title: Asymmetrically End-capped Oligomers: A Molecular Excitonic Seesaw as a Polarization-to-wavelength Converter

Co-Author(s): Jakob Schedlbauer, Florian Hinderer, Daniel Hennen, Sigurd Höger, Jan Vogelsang, John M. Lupton

Abstract: To achieve high performance both in photosystems in nature as well as in organic photovoltaic devices an efficient charge separation is crucial. Excitation energy transfer (EET) therefore plays an important role. Unfortunately, the microscopic pathways of EET are hard to monitor. For this reason, we introduce model systems which consist of a π-conjugated donor oligomer of variable length and two different acceptor dyes. One of the units emits in the green and the other one in the red wavelength region [1]. By using these molecules with two competing EET pathways from the oligomer to the asymmetric endcaps, we can learn whether excitation energy migrates preferentially to the global minimum (i.e. the red dye) or if EET is fundamentally non-deterministic so that emission from both endcaps occurs. By employing single-molecule spectroscopy we examine photon correlations and polarization characteristics of single molecules, demonstrating spontaneous symmetry breaking in the excited state. By monitoring these properties over time, we can analyze the dynamics occurring in the model systems, for example how EET changes over time. By combining fluorescence correlation spectroscopy (FCS) and pulsed interleaved excitation (PIE) techniques, we also answer the question whether a dark state (e.g. a triplet state) on one of the bodipys impacts the intramolecular energy transfer pathway to the other acceptor. Finally, we demonstrate how the EET pathway can be influenced externally, by changing the polarization of the excitation laser. We find that these model systems can act as a single-molecule polarization-to-wavelength converter.

[1]P. Wilhelm et al., PNAS 2018, 115, E3626

Institution: University of Regensburg

Code: SPECNano_T8

Presenter: Wannes Peeters (BEL)

Abstract Title: Plasmonic Wave-guided Tip-enhanced Fluorescence Microscopy for Super Resolution Imaging

Co-Author(s): Peter Walke, Yasuhiko Fujita, Shuichi Toyouchi, Mathias Wolf, Johan Hofkens, Hiroshi Uji-i

Abstract: Near-field optical microscopy is a method to achieve true sub-diffraction images with full spectral information. This can be applied to several spectroscopic techniques and works by using a sharp metal probe to excite localized surface plasmons (LSPs) and locally enhance signals. For tip-enhanced Raman scattering (TERS) microscopy, a spatial resolution of several nanometers can be reliably achieved, however for tip-enhanced fluorescence (TEF) it is still typically limited to around 20nm. In TEF, the probe not only enhances fluorescence, but also quenches it due to energy transfer from the excited dye to the nearby metal, whilst high cross-sections generate strong far-field backgrounds and limit signal contrasts.

We have previously developed novel probes for TERS by attaching silver nanowires to AFM-cantilevers. Such probes deliver significant improvements in reproducibility, reliability and signal contrast compared to research standards.[1] We intend to extent these probes to TEF whilst maintaining this same unique performance. Using MoSe2/WSe2 monolayer heterostructures for their distinct photoluminescence, we have so far managed to reach resolutions of up to 100nm.

Moreover, we discuss how this can further be improved by using remote-excitation to decouple the excitation and detection focal spots. Here plasmons propagating along the tip body are used to excite LSPs at the apex, providing lower background signals that in turn will lead to higher resolutions. The remote excitation also minimizes photo damage. We hope the new strategies discussed herein shall allow TEF to reach its full analytical potential.

[1] Peter Walke et al ,Nanoscale, 2018, 10, 7556–7565

Institution: KU Leuven

Code: SPECNano_T9

Presenter: Shuichi Toyouchi (BEL)

Abstract Title: Nonlinear Optical Interactions between Dipole Antenna and Surface Plasmon Polaritons on Silver Nanowires

Co-Author(s): Yasuhiko Fujita, Hiroshi Uji-i

Abstract: Silver nanowires (AgNWs) have been proved to be promising nanostructures with excellent plasmonic waveguide properties to confine and transport the light on their one-dimensional structure with sub-diffraction limit. Our group has demonstrated remote surface-enhanced Raman scattering spectroscopy via propagating surface plasmon polaritons (SPPs) on AgNWs [1, 2]. Now we are aiming to expand the remote spectroscopic technique with AgNW plasmonic waveguide from linear into nonlinear regime.

In this study, we first investigated nonlinear optical responses, second harmonic generation (SHG) of AgNW under fs pulsed laser irradiation. SHG signals were observed when the fs laser was focused at ends of AgNW because SHG as 2nd order nonlinear effect requires a symmetry breaking point to be generated. Furthermore, SHG could be excited at the distal end remotely through propagating SPPs on AgNWs. These results suggest that remote excitation of nonlinear effect SHG is promising to a point light source for super-resolution optical imaging and spectroscopy.

Next, we investigated nonlinear interactions on AgNWs between propagating SPPs and a fluorescence dye as a dipole antenna by measuring two-photon fluorescence excitation spectra with remote excitation. Our results demonstrated that dipole antenna was excited via two-photon absorption at the body of AgNWs, while, at the ends of AgNW, the dipole antenna was excited via “quasi” two-photon process, that is, absorbing a single photon of SHG generated at the ends. We will provide more detail results and discuss the “quasi” two-photon absorption in the presentation.

1, Nano Lett., 2009, 9, 995-1001
2, Adv. Mater., 2014, 26, 5124-5128

Institution: Katholieke Universiteit Leuven

Code: SPECNano_T10

Presenter: Philipp Krauspe (CHE)

Abstract Title: Investigating the Ultrafast THz-Conductivity in Polymer:Non-Fullerene Heterojunctions

Co-Author(s): Yufei Zhong, Natalie Banerji

Abstract: In search of efficient material systems to harvest solar energy, polymer:fullerene bulk heterojunctions have been overtaken in power conversion efficiency by polymer:non-fullerene (NFA) systems. Here we investigate the charge generation and subsequent short range mobility of carriers in J61:mITIC blends. With optical pump THz probe spectroscopy (OPTP), we concentrate on the high frequency mobility on the nano scale. Applying the THz probing field for just around a picosecond allows to probe the charge carrier on length scales <5 nm. This way grain boundaries in the blend or inter-chain transfer effects that are dominating lower frequency conductivity measurements are avoided. Although this THz conductivity does not directly translate into the final DC device conductivity, it still contributes important information on the charge generation mechanisms, since it is also understood as an important factor in the step from coulombically relatively bound (CT states) to free charges. Investigating this charge generation mechanism in a low driving force system helps to understand the superior device performance in this class of materials used in organic photovoltaics.

Institution: University of Bern

Code: SPECNano_T11

Presenter: R. Colby Evans (USA)

Co-Author(s): Austin Ellingworth, Christina J. Cashen, C. R. Weinberger , Justin B. Sambur

Institution: Colorado State University

Abstract Title: Influence of Particle-dependent Electrochromic Dynamics on the Durability and Speed of Smart Windows

Abstract: Nanomaterials have tremendous potential to increase electrochromic smart window tinting rates and cycling stability, but it is unknown whether single nanoparticles tint with the same rate and magnitude across a large area window to achieve uniform appearance. Here we use single nanoparticle-level optical absorbance imaging to study how particle-particle interactions impact tinting dynamics and reversibility as tungsten oxide nanorod building blocks are assembled into a thin film. Single nanorods exhibit a particle-dependent waiting time for tinting (from 100 ms to 10 s) due to Li-ion insertion at optically inactive surface sites. Longer nanorods tint darker than shorter nanorods because long nanorods develop a Li-ion gradient that increases from the nanorod ends to the middle. Single particles tint 4x faster and cycle 20x more reversibly than thin films made of the same particles. These findings allow us to propose a nanostructured electrode architecture that optimizes optical modulation rates and reversibility across large area smart windows.

Code: SPECNano_T12

Presenter: Hyun Suk Kang (USA)

Co-Author(s): Thomas J. Sisto, Samuel Peurifoy, Dylan H. Arias, Obadiah G. Reid, Boyuan Zhang, Colin Nuckolls, Jeffrey L. Blackburn

Institution: National Renewable Energy Laboratory

Abstract Title: Long-Lived Charge Carriers at Heterojunctions between Single-Walled Carbon Nanotubes and Perylene Diimide Electron Acceptors

Abstract: To understand the fundamental aspects of photoinduced charge generation processes at donor/acceptor heterojunctions with semiconducting single-walled carbon nanotubes (s-SWCNTs), fullerene-based electron acceptors have been paired with s-SWCNTs in previous studies. However, nonfullerene acceptors have been rarely used for these types of studies, and the molecular effects such as geometries and aggregation on photoinduced charge generation processes have not been systematically studied. Herein, we investigated the photophysical nature of these processes for the heterojunctions between two singly chiral s-SWCNTs ((6,5) and (7,5)) and two different perylene diimide (PDI)-based acceptors (hPDI2-pyr-hPDI2 and Trip-hPDI2).

Transient absorption (TA) and time-resolved microwave conductivity (TRMC) studies reveal the efficient photoinduced hole/electron transfer at the s-SWCNT/PDI acceptor heterojunctions with the separated charges living more than 1.5 μs. The charge carriers at hPDI2-pyr-hPDI2 heterojunctions live longer than those at Trip-hPDI2 ones due to aggregated phases of hPDI2-pyr-hPDI2 that facilitate charge extraction out of the heterojunction interfaces. Moreover, the charge recombination kinetics for these heterojunctions from TA and TRMC studies are well-matched, indicating that most of the generated charge carriers are free, not trapped. This may be attributed to the high carrier mobility and good charge delocalization in both s-SWCNTs and PDI-based acceptors.

These photophysical studies provide the fundamental understandings of how different electron acceptor materials and wrapping polymers can impact the charge generation processes at s-SWCNT heterojunctions with respect to the heterojunction energetics and molecular orientations.

*Kang, H. S. et al. J. Phys. Chem. C 2018, 122, 14150-14161.

Code: SPECNano_T13

Presenter: Lin Guo (CHN)

Co-Author(s): Xiaotian Wang

Institution: School of Chemistry, Beihang University, 100191 Beijing, P. R. China

Abstract Title: Remarkable Surface-enhanced Raman Scattering (SERS) Effect of Amorphous Nanomaterials

Abstract: Enhancement of substrate–molecule interaction, especially promoting the efficient photo-induced charge transfer (PICT), is pivotal to the performance of nonmetal surface-enhanced Raman scattering (SERS) technology. Recently, our group have found the remarkable SERS activity of amorphous nanomaterials, including amorphous ZnO nanocages [1], 2D amorphous TiO2 nanosheets [2] and amorphous RhS microbowls [3]. Our results show that the numerous metastable electronic states of amorphous semiconductor nanostructures could serve as an intermediate level in the band gap, which benefited the interfacial charge transfer. Moreover, the relatively small band gap and high DOS of amorphous materials enable the strong vibronic coupling to occur in the substrate–molecule system. Our studies clearly provide a deep insight of the nonmetal SERS effect and open a new frontier for developing highly sensitive and stable SERS technology.

[1] Xiaotian Wang, Lin Guo* et al., “Remarkable SERS Activity Observed from Amorphous ZnO Nanocages” Angew. Chem. Int. Ed., 2017, 33, 9983-9987.
[2] Xiaotian Wang, Lin Guo* et al., “Two-Dimensional Amorphous TiO2 Nanosheets Enabling High-Efficiency Photoinduced Charge Transfer for Excellent SERS Activity” J. Am. Chem. Soc., 2019, 141, 5856-5862.
[3] Anran Li, Xiaotian Wang*, Lin Guo* et al., “Surface-Enhanced Raman Spectroscopy on Amorphous Semiconducting Rhodium Sulfide Microbowl Substrates” iScience, 2018. 10, 1-10.

Code: SPECNano_T14

Presenter: Johan Hofkens (BEL)

Abstract Title: Single Particle Microscopy & Spectroscopy of Morphology and Size Controlled Perovskite crystals

Co-Author(s): E. Debroye, H. Yuan, J. Steele, M. Keshavarz, M. Roeffaers

Abstract: After seminal reports of their interesting physical properties (published in 2009 and 2012, [1–3]), an explosion of scientific interest into metal halide perovskites (MHPs) in the past decade has seen this family of materials emerge as the most exciting avenue for next-generation solar cells. The strong promise for MHP materials arise of course from their fundamental physics; from high absorption coefficients at visible wavelengths, long carrier diffusion lengths and small exciton binding energies, to its simple solution-based processing. Justifiably, an early surge of research activity was inspired by an empirical race to produce photovoltaic devices with ever-higher photo-conversion efficiencies. Consequently, early research saw perovskite engineering significantly outpace the understanding of their physical properties. In response, the focus of researchers is steadily shifting toward the intrinsic properties of perovskites, as these will ultimately define their performance in any photonic application. In this light, recent research in my laboratory aims at connecting the microstructure of perovskite crystals with their physical properties, by addressing three overarching goals: (1) Development of systematic experimental protocols for controlled and reproducible synthesis of a variety of highly crystalline, monodisperse and defect-poor perovskite crystals with well-defined morphology, with sizes covering a few nanometres over microns to millimetres. (2) In-depth investigation on these materials using an arsenal of single particle microscopy and spectroscopy techniques. Specifically, complementary information obtained from such experiments will provide true understanding of how perovskite composition and grain morphology influence the fate of the photo-generated charge carriers, and this structure-property relationship can be used to develop better perovskite materials. (3) Finally, the knowledge base generated will be applied to the development of better-performing photonic devices. In this contribution, I will report recent progress in perovskite synthesis[4] and single particle spectroscopy. [5–8]
[1] A. Kojima et al., J. Am. Chem. Soc. 2009, 131, 6050–6051. [2] H.-S. Kim et al., Sci. Rep. 2012, 2, srep00591. [3] M. M. Lee et al., Science 2012, 338, 643–647. [4] E. Debroye et al., ChemNanoMat 2017, 3, 223–227. [5] H. Yuan et al., ACS Omega 2016, 1, 148–159. [6] H. Yuan et al., J. Phys. Chem. Lett. 2016, 7, 561–566. [7] H. Yuan et al., Adv. Mater. 2018, 10.1002/adma.201705494. [8] A. Merdasa et al., ACS Nano 2017, 11, 5391–5404.

Institution: Department of Chemistry, KULeuven

Code: SPECNano_T15

Presenter: Geoffrey Geberth (USA)

Abstract Title: Fluorescence Microscopy of Single Perylene Diimide Aggregates

Co-Author(s): David Vanden Bout

Abstract: Perylene diimides (PDIs) have emerged as an important class of materials for solar energy applications given both their inherent photostability and their capacity for one photon to two electron conversion via singlet exciton fission (SF). Despite the potential of these materials to usher in a new generation of high efficiency solar cells, the mechanism of SF is not completely understood, despite nearly 60 years of study. By examining the excited states of these PDI systems in isolated aggregates, we can gain insights into the SF process that are unattainable in larger scale crystals with the aim of understanding how to better tune and design systems to maximize triplet yield from the bottom up. After producing single PDI aggregates via solvent vapor annealing, we utilize a combination of single molecule fluorescence spectroscopy and fluorescence time traces in varying environmental conditions in order to gain a better understanding of the excited states. In this research, we take advantage of the natural triplet-quenching abilities of oxygen to observe the dramatic differences in the excited state behavior of PDI aggregates when exposed to an atmosphere of air as opposed to controlled nitrogen.

Institution: The University of Texas at Austin

Code: SPECNano_T16

Presenter: Dr. Riya Bose (USA)

Abstract Title: Engineering Multilayered Optically Active Nanocrystal Solids by Surface Passivation using Metal Oxides for Photonic Applications

Co-Author(s): Yangzi Zheng, Tianle Guo, Yuri Garstein, Anton V. Malko

Abstract: Colloidal semiconductor nanocrystal quantum dots (NQDs) provide a powerful platform for optoelectronic applications with their tunable properties and inexpensive synthesis techniques. However, a major drawback for NQDs applications is the strong dependence of NQD optical properties such as PLQY on their surface chemistry, i.e., the ligands on their surface, which tend to be damaged under environmental/light exposure or several device processing, eventually leading to permanent photobleaching. Another bottleneck for fabrication of multilayer NQD films remains the use of solution phase deposition methods, where the solvent in subsequent step of deposition dissolves the initial layer, until each layer is rendered insoluble by means of any surface passivation technique. An attractive approach to protect NQD's integrity during and after deposition has been to overcoat them with various metal oxides grown using atomic layer deposition (ALD), in which self-limiting surface reactions of the precursors allows conformal growth of the metal oxide layer with precise thickness control. This process, though prevents the deterioration of NQDs, is observed to decrease their PLQY significantly. To mitigate this issue, we develop an alternate gas phase deposition technique where a pulsed co-deposition of both metal and oxidant precursors at room temperature is able to deposit uniform metal oxide (AlOx) films, originating from gas-phase reactions in the immediate vicinity of the NQD layer. Unlike conventional ALD, this method preserves the optical properties of NQD film and paves the way for controlled assembly of optically active multilayered NQDs for efficient photonic devices.
Reference:
ACS Appl. Nano Mater., 2018, 1, 6782

Institution: Post-Doctoral Research Associate

Code: SPECNano_T17

Presenter: Quynh L. Nguyen (USA)

Abstract Title: Time-Resolved Strong-Field Photoemission Dynamics of Isolated, Ligand-free Nanoparticles using UV, Visible and Mid-Infrared Lasers

Co-Author(s): K. Dorney, J. Ellis, N. Brooks, D. Hickstein, A. Grennell, G. Dukovic, E. Campbell, H. Kapteyn, M. Murnane

Abstract: Nanomaterials have advanced from fundamental science to having a presence in our daily lives, due to emergent phenomena associated with their spatial scales. They are being used in a wide range of applications, including biofuels, biomedical technology, quantum and energy science. There is great interest in the photophysical properties of nanomaterials due to broad tunability in composition, size, or geometry. However, a complete understanding of these properties is lacking due to the complex environments surrounding these nanomaterials. Here, we simplify the situation by studying the photophysical properties of isolated, ligand-free nanoparticles in vacuum, thereby avoiding any effects from the surrounding environment. We accomplish this by combining a magnetron-sputtering nanoparticle source with a velocity map imaging photoelectron spectrometer. Using this novel technique, we drive strong-field effects—above-threshold-ionization and channel-closings—in nanoparticles at much lower intensities compared to atomic and molecular systems. Additionally, we conduct femtosecond time-resolved photoelectron measurements on isolated, ligand-free nanoparticles, thereby probing isolated nanoparticle photophysics. We disentangle the contribution of different ionization mechanisms, each with a distinctive timescale ranging from femtoseconds to picoseconds. The transition between mechanisms depends upon the nanoparticle composition, which can be influenced by varying the intensities of the pump or probe pulse to access different regions in the band structure. Moreover, this approach can be extended to extreme-ultraviolet probes of excited state dynamics and orbitals. Our unique apparatus extends the methods from strong-field physics and attosecond science to study nanoparticles, enabling ultrafast imaging of nanoscale potentials, state-resolved photoionization measurements, and surface plasmon dynamics/control.

Institution: JILA - Department of Physics, University of Colorado and NIST, Boulder, Colorado, 80309, USA

Code: SPECNano_T18

Presenter: Geoffrey Diederich (USA)

Abstract Title: Exciton many-body and relaxation dynamics in perovskite films

Co-Author(s): Mark Siemens, Sean Shaheen

Abstract: Multidimensional coherent spectroscopy (MDCS) is an ultrafast spectroscopy technique that spreads information about the coherent dynamics of a complex system across multiple dimensions, resolving features that overlap in one-dimensional measurements. For example, homogeneous and inhomogeneous broadenings act in orthogonal directions in MDCS spectra, allowing straightforward separation of these mechanisms. Both coherent and incoherent transport, relaxation, and spectral diffusion can all be separated and clearly measured. Additionally, the phase sensitivity of MDCS measurements allow visualization of the full complex signal field, enabling identification of first-order and higher-order excitations in the spectra. These attributes make MDCS ideal for studying complex material systems like lead halide perovskites, where cation mixing, ion migration, and inhomogeneous grain conditions can make spectra difficult to interpret.

Here, we present phase-modulated MDCS (PM-MDCS) spectra from thin films of a mixed cation perovskite at low temperature. The spectra show inhomogeneously broadened free and defect-bound excitons with a homogeneous dephasing time on the order of 1 ps, contrary to reports that claim that the exciton is homogeneously broadened. The excitons undergo spectral diffusion and relaxation on a much more rapid timescale than has been measured in GaAs quantum wells, increasing the homogeneous dephasing rate by a factor of ~3 over one picosecond. Additionally, the phase reveals the presence of strong many-body effects, suggesting the presence of higher order excitations leading to a biexciton or doubly excited state.

Institution: University of Denver

POSTERS

Code: SPECNano_P1

Presenter: Shunpei Oikawa (JPN)

Abstract Title: Spectroscopic Evaluation of Ultimate Confined Light Energy Field Prepared by Electrochemical Method

Co-Author(s): Hiro Minamimoto, Quan Sun, Kosei Ueno, Hiroaki Misawa, and Kei Murakoshi

Abstract: The optical property of metal nanodimer structure strongly depends on its shape and gap distance. Especially for the gap distance of less than 1 nm, the light energy can be highly confined at the gap. However, the valuable techniques to precisely control the gap distance in sub-nanometer scales have not been established yet. In this study, we have tried to propose a new method for fine tuning of the optical property of Au nanodimer structures via electrochemical method. The changes in the optical properties of nanodimers associated with the progress of the electrochemical reactions have been examined by in-situ dark-field microscopy. For further discussion about the light confinement, photoemission electron microscopic (PEEM) measurement was conducted. Well-defined Au nanodimer structures were fabricated on a conductive glass substrate. From SEM images which obtained before and after electrochemical measurements, we have confirmed the formation of the quite small gap at the center. From scattering spectra collected during dissolution, the excitation of the higher order plasmon modes was observed. Furthermore, through PEEM measurements, it was confirmed that the photoemission rate of the Au dimers after gap formation is several ten times higher than that of the structure before dissolution. Based on these results, this optical property changes could be assigned to the plasmon mode change from charge transfer mode to gap plasmon modes. Therefore, it can be said that our method would become a useful tool for controlling the gap distance in a single nanometer scales.

Institution: Graduate School of Chemical Sciences and Engineering, Hokkaido University

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Code: SPECNano_P2

Presenter: Marcelo H. Gehlen (BRA)

Co-Author(s): João Henrique de Souza

Abstract Title: Time-resolved Emission Spectroscopy and Confocal Microscopy of Graphene Oxide in Poly-lysine Thin Films

Abstract: The time-resolved emission spectroscopy and confocal microscopy of modified graphene oxide (GO) and reduced rGO are studied in solution and thin films containing poly-lysine over a glass surface. In general GO and rGO are efficient quenchers of fluorescent dyes due to the presence of low electronic energy trap that deactivate the single-excited state of the added dyes. In solution, the quenching is mainly static due to the concomitant association of the cationic dye with the peripheral carboxylic acid and with the hydrophobic surface of GO. However, when GO and rGO are placed onto poly-lysine, their weak emission increase toward the visible region. Such effect may be ascribed to an exciplex type formation due to close contact of the aromatic moieties of GO with free amino groups of the poly-lysine chain. The recorded position average decay times of a GO microplate were 192 ps, 1309 ps, and 4477 ps. Addition of aniline or dimethylaniline to the poly-lysine thin films seems to enhance the local exciplex formation and the observed decay components become shorter (60 ps, 789 ps and 3375 ps). The long lived component in the range of 3 – 5 ns contrast with the usual components of GO fluorescence decay and it is ascribed to the GO//NH2-R excimer type contribution. The results showed that emission and photochemical properties of modified GO and rGO may be somewhat shaped by donor-acceptor interaction and intramolecular charge-transfer (ICT) dynamics.

Financial support: FAPESP 22159-5/2018 and CNPq 303997/2017-6

Institution: Institute of Chemistry of São Carlos - University of São Paulo

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Code: SPECNano_P3

Presenter: Jie Lu (JPN)

Co-Author(s): Kayo Fujiwara, Shoji Tatsuya, Yasuyuki Tsuboi

Abstract Title: Microspectroscopic Analysis of a Single Microdroplet of Various Thermoresponsive Polymers Trapped by Optical Tweezer

Abstract: Poly(N-isopropylacrylamide) (PNIPAM) and Poly(2-(2-ethoxy)ethoxyethyl vinyl ether)(PEOEOVE) are thermo-responsive polymers which exhibit coil-to-globule transition above a lower critical solution temperature (LCST), leading to the formation of polymer-rich microdroplets by aggregation of the polymer chains. To understand such phase separation mechanism, it is necessary to analyze hydration structures in a polymer microdroplet. However, it is difficult to selectively analyze a single microdroplet because of continuous fluctuation in dilute solutions.

In such backgrounds, we have developed confocal Raman microspectroscopy combined with optical tweezers to analyze hydration structures in polymer droplets [1]. In this study, we investigated polymer concentration of a PEOEOVE microdroplet. Focusing a near-infrared laser beam (λ = 1064 nm) into a dilute polymer solution, a single polymer-rich droplet was formed at the focal point because of the optical force and photothermal effect. We estimated the optical force exerted on the polymer chains by means of Abbe Refractometer and Lorentz-Lorentz equation.

Furthermore, we determined polymer concentration of a single droplet by the Raman intensity ratio between the C-H band from polymer and O-H band from water. We found that a PEOEOVE microdroplet hold abundant water molecules in comparison with a PNIPAM microdroplet.

[1] T. Shoji, Y. Tsuboi et al., Anal. Chem. Acta., 2015, 854, 118–121

Institution: Osaka City University

Code: SPECNano_P4

Presenter: Linrui Jin (USA)

Co-Author(s): Ti Wang, Libai Huang

Abstract Title: The Role of Grain Boundary in Hot Carrier Transport in Hybrid Perovskite

Abstract: One method to improve power conversion efficiency (PCE) of single-junction solar cells beyond the Shockley-Queisser limit is to capture hot carriers - the carriers excited above the semiconductor bandgap. We have demonstrated long-range hot-carrier transport in an organic-inorganic MAPbI3 thin film. However, grain boundaries and invisible subgrains widely exist in polycrystalline films, potentially limiting the overall hot carriers transport distance. In this work, we investigate MAPbI3 single crystalline nanowires to unravel the role of crystal boundaries in hot carrier cooling and transport process. A home-built transient absorption microscopy (TAM) is employed to directly map carrier generation and transport within the MAPbI3 nanowires with 50 nm spatial precision and 300 fs temporal resolution. Carrier diffusion constant is measured to be ~ 1 cm2s-1 in these crystals. Hot carrier transport is extremely rapid along the wire and is enhanced over polycrystalline thin films, which confirms MAPbI3's potential in hot carrier devices. In comparison, shortened hot carrier lifetime and transport distance is observed at the edge of the wire compare to along the wire. Results indicate that the existence of grain boundaries is detrimental for hot carrier diffusion.

Institution: Chemistry Department, Purdue University

Code: SPECNano_P5

Presenter: Daedu Lee (KOR)

Abstract Title: Metal-enhanced Fluorescence of Dyes on Homogeneous Silver Colloidal Surfaces

Co-Author(s): Jaebeom Lee, Junghyun Song, Yoonsoo Pang

Abstract: Metal-enhanced fluorescence (MEF) has attracted much attention in many disciplines due to significant increases in fluorescence intensity and photostability of dyes. MEF has been understood as originating from the local electric field effect and plasmon-coupled emission by the excitation of surface plasmon resonance (SPR) on metal nanoparticles. Recently, we observed the strong enhancements in the fluorescence intensity of dyes by the ultrafast energy transfer between the dyes and silver island surfaces, but the inhomogeneity of the surfaces has limited further studies. In this study, homogeneous silver colloidal films (SCFs) with a specific particle diameter from ~70 to 200 nm, were synthesized by a seeded growth method. The particle-size-dependent fluorescence enhancements and excited state dynamics of DCM and Rh700 with SCFs were thoroughly investigated by time-resolved fluorescence spectroscopy. The fluorescence enhancements of both DCM and Rh700 were strongly increased when the dipolar SPR bands of the SCFs overlap with the emission bands or are located between the absorption and emission bands of dyes. The excitation and emission enhancements, which are correlated with the electric field effect and plasmon-coupled emission, respectively, were estimated by combining the results from time-resolved fluorescence measurements and finite-difference time-domain simulations. The fluorescence enhancements of dyes with each SCF are predominantly attributed to the electric field effect, but the particle-size-dependence in the enhancements originates mainly from the plasmon-coupled emission.

Institution: Gwangju Institute of Science and Technology

Code: SPECNano_P6

Presenter: Damianos Agathangelou (USA)

Abstract Title: Acquisition of LH2 Linear Excitation Spectra using a Rapid-Scanning Phase-Modulation Fluorescence-detected Method

Co-Author(s): Y. A. Matutes, V. Tiwari, A. Javed, D. Agathangelou, A. T. Gardiner, R. J. Cogdell and J. P. Ogilvie

Abstract: The type of peripheral light-harvesting complexes (LH2) assembled in purple photosynthetic bacteria varies depending on the light intensity conditions under which the cells are grown [1]. Different LH2 composition in bacterial samples grown under Low-Light (LL) and High-Light (HL) conditions yield different spectroscopic signatures for the two cases. The spatial heterogeneity present in the samples is highly pronounced in their linear absorption spectra as indicated by the ratio between the two peaks at 800nm and 850nm [2]. In this work, by performing spatially resolved measurements, we record the linear excitation spectra of LH2 as they are presented in colonies and isolated cells of photosynthetic bacteria Rps palustris. For this purpose we adopt a phase-modulation fluorescence-detected method as was recently described by Tiwari et.al for the collection of spatially-resolved fluorescence-detected two dimensional electronic spectra (SF-2DES) [3]. The use of a microscope objective and lock-in detection, provides simultaneous sub-micron spatial resolution and high detection sensitivity enabled by the fluorescence detection scheme. Here we modify the previous SF-2DES approach to enable rapid scanning and the collection of linear excitation spectra with an acquisition time of ~2s. This approach, which dramatically reduces the acquisition time, minimizes photo-bleaching effects and will be beneficial for both spatially-resolved linear excitation and SF-2DES measurements.

[1] Brotosudarmo, T H. P. et al. The light intensity under which cells are grown controls the type of peripheral light-harvesting complexes that are assembled in a purple photosynthetic bacterium. Biochem. J. 440, 51–61 (2011).
[2] Scholes,G.D. et al. Lessons from nature about solar light harvesting. Nat Chem. 3, 763-774 (2011)
[3] Tiwari, V. et al. Spatially-resolved fluorescence-detected two-dimensional electronic spectroscopy probes varying excitonic structure in photosynthetic bacteria. Nat Comm. 9, 4219 (2018)

Institution: Department of Physics, University of Michigan, Ann Arbor, Michigan 48109, USA

Code: SPECNano_P7

Presenter: Haipeng Lu (USA)

Abstract Title: Sensitizing Singlet Fission with Perovskite Nanocrystals

Co-Author(s): Xihan Chen, John E. Anthony, Justin Johnson, Matt Beard

Abstract: The marriage of colloidal semiconductor nanocrystals and functional organic molecules has brought unique opportunities in emerging photonic and optoelectronic applications. Traditional semiconductor nanocrystals have been widely demonstrated to initiate efficient triplet energy transfer at the nanocrystal−acene interface. Herein, we report that unlike conventional semiconductor nanocrystals, lead halide perovskite nanocrystals promote an efficient Dexter-like singlet energy transfer to surface-anchored pentacene molecules rather than triplet energy transfer. Subsequently, molecular pentacene triplets are efficiently generated via singlet fission on the nanocrystal surface. Our demonstrated strategy not only unveils the obscure energy dynamics between perovskite nanocrystal and acenes, but also brings important perspectives of utilizing singlet fission throughout the solar spectrum.

Institution: NREL

Code: SPECNano_P8

Presenter: Zhiting Chen (USA)

Abstract Title: Electron Transfer at the Nanoscale: Imaging Redox Reactions in Blended Polymer Films

Co-Author(s): Enrico Daviddi, Brooke Massani, Jonathan Harris, Cameron L. Bentley, Patrick R. Unwin, and Erin L. Ratcliff

Abstract: Electron transfer is a fundamental process in energy conversion and storage devices and as such, understanding the underlying structure-function properties is critical to new technological development. Inspired by the ability to tune the opto-electronic properties of conductive polymers and the prospect of highly controlled photoelectrochemical processes, this work undertakes a proof-of-principle study to evaluate the charge transport-charge transfer mechanism in conductive polymer/electrolyte interfaces at the micron to nanometer length scale. Both charge transport and charge transfer will follow paths of least resistance, hypothesized to be due to local percolation pathways and intermolecular spacings. The vision to develop a collective characterization tool suite that allows for imaging of distributions in nanoscale properties, which will enable identification of key structure-function relationships, and finally, leveraging these known nanoscale properties to increase photon-to-electron-to-molecule conversions.

As a model system, amorphous insulating polymethylmethacrylate (PMMA) was blended with conductive poly(3-hexylthiophene) (P3HT). The enthalpy and entropy of mixing are such that the materials phase segregate, creating an ideal spatial heterogeneity to investigate connections between macroscale and nanoscale electrochemistry approaches. Using scanning electrochemical cell microscopy, the spatially-dependent electron-transfer kinetics associated with a rapid electron transfer process is mapped at the nanoscale. We combine the kinetic insight with complementary conductive AFM to understand the underlying electrical charge transport properties. A new technique - synchrotron infrared nanoscale spectroscopy (SINS) - is used to image local chemical structure and evaluate composition of buried interfaces. Finally, using finite analysis, we demonstrate the limitations of macroscale electrochemical approaches to assess rate constants due to uncompensated resistances.

Institution: The University of Arizona

Code: SPECNano_P9

Presenter: Miyako Iida (JPN)

Abstract Title: Fluorescence Microspectroscopic Study on a Molecular Release Process of a Single Drug Delivery Microcapsule by Optical Tweezers

Co-Author(s): Tatsuya Shoji, Yasuyuki Tsuboi

Abstract: Poly(lactic-co-glycolic acid) (PLGA) has received great interests as a micron-sized carrier of drug delivery system because of its biodegradability, biocompatibility, and so on. Drug molecules are released from PLGA microcapsules via gradual decomposition of PLGA in our human body. The drug release mechanism should be influenced by several factors such as size, surface morphology, and molecular weight. In order to understand details of drug release mechanisms, it is important to investigate a drug release rate of a single microcapsule. However, it has been difficult to access each microcapsule due to Brownian motion.

For addressing the issue, we focused on optical tweezers (OT) combined with microspectroscopy [1]. In the present study, using this method, we demonstrated a real-time monitoring of a reagent release from a single PLGA microcapsule.

We succeeded in stable optical trapping of a single PLGA microcapsule for a long time (> 15 min). Furthermore, in order to get insights into a reagent release process, we carried out fluorescence microspectroscopy for the trapped microcapsule. We observed time profiles of the fluorescence intensities. Since the fluorescence decay curves were well fitted with a single exponential function, we determined the time constant of the reagent release. We found that the time constant depended on the size of a PLGA microcapsule. Our optical manipulation technique will be a powerful analytical tool for real-time monitoring of release process from drug microcapsules of drug delivery.

[1] H. Yan et al., Soft Matter, 14 (2018) 8090.

Institution: Osaka City University

Code: SPECNano_P10

Presenter: Daria Blach (USA)

Abstract Title: Ultrafast Imaging of Energy Transport in CdSe/CdS Lateral Heterostructures

Co-Author(s): Libai Huang

Abstract: Two-dimensional semiconducting heterostructures are a promising platform for a wide range of optoelectronic applications including solar cells and photodetectors. The quantum confinement is maintained in one direction, while charge and exciton transport can occur over other two dimensions, making them attractive for achieving directional transport. However, there is a lack of fundamental understanding of the mechanisms behind energy transport and charge separation across interfaces in lateral heterostructures. Here, we investigate energy transport at the interfaces of CdSe/CdS lateral nanoplatelet heterostructures by directly mapping the exciton population using ultrafast transient absorption microscopy. Due to a type-I band alignment, upon excitation, the electron and hole transfer from CdS to CdSe. Both ultrafast photoluminescence and transient absorption measurements indicate energy transfer instead of charge separation dominating at the interface. We employ transient absorption microscopy to directly visualize exciton transport across the type-I interfaces, demonstrating efficient energy flow from CdS to CdSe. We have developed a kinetic model to describe the spatial and temporal dependence of exciton population and transfer. Our study highlights the unique capability of transient absorption microscopy in investigating interfacial energy transfer in two-dimensional lateral heterostructures.

Institution: Purdue University

Code: SPECNano_P11

Presenter: Dominik Wöll (DEU)

Abstract Title: 4D Microgel PAINT – nanoscopic polarity imaging of thermoresponsive microgels

Co-Author(s): Ashvini Purohit, Silvia P. Centeno, Sarah K. Wypysek, Eric Siemes, Walter Richtering

Abstract:

Nanoscopic investigation of polymer structures is essential for a detailed understanding of the function of nano-devices for their ongoing miniaturization. Beyond structural details, the local environmental conditions in polymer structures play an important role. Especially for (thermo-)responsive polymers, local changes in polarity control their adaptive behavior. Microgels are a prominent example of a (soft) polymer system with a multitude of applications.

We present a super-resolution Point Accumulation for Imaging in Nanoscale Topography (PAINT) approach for the study of the 3D structure and the point-wise polarity of thermo-responsive microgel systems. The polarity information is gained by the application of a solvatochromic dye and splitting their fluorescence signal into two different wavelengths channels. With this "4-dimensional" 4D PAINT approach, significant structural and polarity changes were elucidated as a function of temperature. A comparison between a simple poly(N-isopropylacrylamide) (PNIPAM) microgel and a complex core-shell microgel (core: PNIPAM; shell: PNIPMAM (poly(N-isopropylmethacrylamide))) was drawn and showed us the surprising way how the structural restrictions opposed by polymer networks control the local environment inside microgels.

Our results demonstrate that accessing spectral information in localization-based super-resolution microscopy can give unprecedented insights into local (nano-)environments that are not accessible by any other experimental technique.

Institution: RWTH Aachen University

The 29th International Conference on Photochemistry
Boulder, Colorado
July 21 – 26, 2019

ULTRAFAST PHOTOCHEMISTRY (ULTPhoto)
ABSTRACTS

INVITED TALKS

Code: ULTPhoto_I1

Presenter: Lin X. Chen (USA)

Abstract Title: Probing Excited State Pathways by Coherent Vibrational Motions in Light Conversion Model Pt Dimer Complexes Using Femtosecond Op

Co-Author(s): Pyosang Kim, Denis Leshchev, Subhangi Roy, Andrew Valentine, Antonio A. Lopez, Felix N. Castellano, Xiaosong Li

Abstract: Many photochemical events, such as bond breaking, intersystem crossing and electron/energy transfer, can occur well before excited state vibrational relaxation. Using fs broadband transient spectroscopy and fs X-ray solution scattering, events of light-matter interactions in molecular systems, such as coherent vibrational wavepacket motions can be readily examined. From the time evolution of key vibrational modes, particularly the Pt-Pt stretching mode, we mapped out excited state trajectories on potential energy surfaces of model Pt-dimer complexes for light conversion, including coherent nuclear motions. These studies were carried out in a series of model platinum dimer complexes in solution featuring rich photochemistry and a set of intricate excited state potential energy surfaces on time scale previously unattainable. The combined molecular design, experimental and theoretical approaches enabled quantitative evaluation of the excited state trajectories of a series of Pt-dimer complexes in terms of actual nuclear motions via the Pt-Pt stretch as well as the energetic variations associated with these motions. This study was also extended to supramolecular systems featuring both Pt-dimer electron donor and NDI acceptors. Extensive studies have been carried out to map out how electronic coupling and coherent vibrational wavepacket evolution are used to probe the excited state dynamics including intersystem crossing, internal conversion and electron transfer photochemistry with a time resolution <50 fs. The studies also suggest specific nuclear motions are critical for steering light induced electron transfer, ultimately controlling reaction directionality.

Institution: Argonne National Lab./Northwestern U.

Code: ULTPhoto_I2

Presenter: Erik T. J. Nibbering (DEU)

Abstract Title: Ultrafast Proton Transport along Solvent Bridges: Transport as Excess Proton vs. Proton Defect

Co-Author(s): Maria Ekimova, Felix Hoffmann, Gül Bekçioğlu-Neff, Aidan Rafferty, Oleg Kornilov, Daniel Sebastiani

Abstract: Aqueous proton transport plays a key role in acid-base neutralization, and energy transport through biological membranes and hydrogen fuel cells. Extensive experimental and theoretical studies have resulted in a highly detailed elucidation of one of the underlying microscopic mechanisms for aqueous excess proton transport, known as the von Grotthuss mechanism, involving different hydrated proton configurations with associated high fluxional structural dynamics. Hydroxide transport, with approximately two-fold lower bulk diffusion rates than those of excess protons, has received much less attention. We present femtosecond UV/IR pump-probe experiments and ab initio molecular dynamics simulations of different proton transport pathways of the bifunctional photoacid 7-hydroxyquinoline (7HQ) in water-methanol mixtures. For 7HQ solvent-dependent photoacidity, free energy-reactivity correlation behaviour and QM/MM trajectories point to a dominant OH-/CH3O- transport pathway, for all water-methanol mixing ratios investigated. This provides conclusive evidence for the hydrolysis/methanolysis acid-base neutralization pathway formulated by Manfred Eigen half a century ago. Our findings on the distinctly different acid-base reactivities for aromatic hydroxyl and aromatic nitrogen functionalities suggest the usefulness of further exploration of these free energy reactivity correlations as a function of solvent polarity. Ultimately the determination of solvent-dependent acidities will contribute to a better understanding of proton transport mechanisms at weakly polar surfaces, and near polar or ionic regions in transmembrane proton pump proteins or hydrogen fuel cell materials.

Institution: Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Berlin, Germany

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Code: ULTPhoto_I3

Presenter: Libai Huang (USA)

Abstract Title: Ultrafast Dynamic Microscopy of Exciton and Charge Transport

Co-Author(s): Long Yuan, Tong Zhu

Abstract: The frontier in solar energy research now lies in learning how to integrate functional entities across multiple length scales to create optimal devices. Advancing the field requires transformative experimental tools that probe energy transfer processes from the nano to the meso lengthscales. To address this challenge, we aim to understand multi-scale energy transport across both multiple length and time scales, coupling simultaneous high spatial, structural, and temporal resolution. In my talk, I will focus on our recent progress on visualization of exciton and charge transport in solar energy harvesting materials from the nano to mesoscale employing ultrafast optical nanoscopy.

With approaches that combine spatial and temporal resolutions, we have recently revealed a new singlet-mediated triplet transport mechanism in certain singlet fission materials. This work demonstrates a new triplet exciton transport mechanism leading to favorable long-range triplet exciton diffusion on the picosecond and nanosecond timescales for solar cell applications.

We have also visualized of hot carrier migration in CH3NH3PbI3 thin films by ultrafast transient absorption microscopy, demonstrating three distinct transport regimes. Quasi-ballistic transport was observed to correlate with excess kinetic energy; resulting in up to 230 nanometers transport distance in 300 fs that could overcome grain boundaries. The nonequilibrium transport persisted over tens of picoseconds and ~ 600 nanometers before reaching the diffusive transport limit. These results suggest potential applications of hot carrier devices based on hybrid perovskites.

Institution: Purdue University

Code: ULTPhoto_I4

Presenter: Tahei Tahara (JPN)

Abstract Title: Tracking Ultrafast Photochemical Processes with Observing Excited-state Coherent Nuclear Motion

Co-Author(s): NONE

Abstract: A large number of fundamental processes in photochemistry proceed in the femtosecond time region, and hence the elucidation of such primary processes is essential. A uniqueness of the femtosecond time region is that it is the time scale of nuclear motion of the molecules. Thus, using ultrashort optical pulses as short as 10 fs, we can investigate primary photochemical processes with observing coherent nuclear motion of the reacting excited states [1]. In fact, femtosecond time-resolved absorption/fluorescence spectroscopy utilizing two ultrashort pulses enables us to detect the coherent motion of the excited state that is triggered by photoexcitation itself, whereas femtosecond time-resolved impulsive stimulated Raman spectroscopy using three ultrafast pulses allows us to track chemical processes with inducing the coherent nuclear motion at an optional delay time. In this presentation, I discuss our recent studies on ultrafast photochemical processes of complex molecular systems such as photoresponsive proteins and molecular assemblies, in which observation of the characteristic coherent nuclear motion of the reacting excited-state was essential. Indeed, they were the keys to clarify their reaction mechanism [3, 4].

[1] S. Takeuchi and T. Tahara, In Advances in Multi-Photon Processes and Spectroscopy, Vol. 22, pp111-162 (2014); [2] T. Fujisawa, H. Kuramochi, H. Hosoi, S. Takeuchi and T. Tahara, J. Am. Chem. Soc. 138, 3942 (2016); [3] H. Kuramochi, S. Takeuchi, K. Yonezawa, H. Kamikubo, M. Kataoka and T. Tahara, Nat. Chem. 9, 660 (2017); [4] H. Kuramochi, S. Takeuchi, M. Iwamura, K. Nozaki and T. Tahara, in preparation.

Institution: RIKEN

Code: ULTPhoto_I5

Presenter: Irene Burghardt (DEU)

Abstract Title: Ultrafast Quantum Dynamics of Functional Organic Polymer Materials: Coherence, Confinement, and Disorder

Co-Author(s): Robert Binder, Wjatscheslaw Popp

Abstract: This talk addresses quantum dynamical studies of ultrafast photo-induced energy and charge transfer in functional organic materials, complementing time-resolved spectroscopic observations that underscore the coherent nature of the ultrafast elementary transfer events in these molecular aggregate systems. Our approach combines first-principles parametrized Hamiltonians [1], with accurate quantum dynamics simulations using the Multi-Configuration Time-Dependent Hartree (MCTDH) method [2], along with semiclassical approaches [3]. The talk will specifically focus on (i) exciton dissociation and free carrier generation in regioregular donor-acceptor assemblies [1,4], and (ii) the elementary mechanism of exciton migration [3,5,6] and creation of charge-transfer excitons [7] in polythiophene type materials. Special emphasis is placed on the influence of structural and dynamic disorder and molecular packing, which can act as a determining factor in transfer efficiencies.

[1] M. Polkehn, P. Eisenbrandt, H. Tamura, I. Burghardt, Int. J. Quantum Chem. 118:e25502. (2018).
[2] G. A. Worth, H.-D. Meyer, H. Koeppel, L. S. Cederbaum, I. Burghardt, Int. Rev. Phys. Chem. 27, 569 (2008).
[3] R. Liang, S. J. Cotton, R. Binder, I. Burghardt, W. H. Miller, J. Chem. Phys. 149, 044101 (2018).
[4] M. Polkehn, H. Tamura, I. Burghardt, J. Phys. B: At. Mol. Opt. Phys. 51, 014003 (2018).
[5] R. Binder, D. Lauvergnat, I. Burghardt, Phys. Rev. Lett., 120, 227401 (2018).
[6] R. Binder, I. Burghardt, Faraday Discuss., in press (2019).
[7] W. Popp, M. Polkehn, R. Binder, I. Burghardt, J. Phys. Chem. Lett., https://doi.org/10.1021/acs.jpclett.9b01105 (2019).

Institution: Goethe University Frankfurt, Germany

Code: ULTPhoto_I6

Presenter: Edward G. Hohenstein (USA)

Abstract Title: First Principles Simulation of Excited-State Proton Transfer

Co-Author(s): Edward G. Hohenstein

Abstract: Excited-state proton transfer reactions are among the most fundamental photochemical processes. Two general types of these reactions are possible: intermolecular and intramolecular excited-state proton transfer. Molecules that undergo intermolecular proton transfer are known as photoacids; these molecules are weak acids in their ground electronic state, but become strong acids in their excited state after absorbing light. Intramolecular proton transfer processes are important to many natural and synthetic sunscreens and photostabilizers. These reactions are well suited to this application due to the remarkable rate of these reactions (often occuring within tens of femtoseconds after photoexcitation) and ease of reversibility. I will discuss my group’s recent efforts to understand inter- and intramolecular excited-state proton transfer processes from first principles computation. We have performed a series of quantum dynamics simulations to understand the mechanistic details of proton transfer in aqueous methyl viologen (the first example of a Lewis photoacid) as well as several prototypical examples of intramolecular proton transfer. I will also discuss the recent theoretical and algorithmic advances that make it possible, for the first time, to directly simulate the nonadiabatic dynamics of these processes.

Institution: SLAC National Accelerator Laboratory

Code: ULTPhoto_I7

Presenter: Cathy Y. Wong (USA)

Abstract Title: In Situ Transient Absorption Spectroscopy during Molecular Aggregation

Co-Author(s): Kelly S. Wilson, Madelyn N. Scott

Abstract: The electronic structure and exciton dynamics of the molecules and polymers that form the active layer in organic electronic devices can change dramatically during solution deposition. As solvent vaporizes, molecules aggregate and become electronically coupled, sometimes dramatically changing the exciton dynamics and thus the suitability of the material for electronic devices. The exciton dynamics of molecules in solution and and in films of aggregates can be measured using transient absorption spectroscopy. However, the progression of exciton dynamics during film formation is unknown since measurements typically cannot be performed quickly enough to collect accurate transient absorption spectra of these species. The exciton dynamics of evolving material systems can be measured by increasing the speed of data collection. A novel implementation of transient absorption spectroscopy is introduced that can measure transient spectra with up to a 60 ps pump-probe time delay in one shot. The exciton dynamics of intermediate aggregation states are revealed during the formation of an organic film. The information gained using this technique can be used to modify environmental parameters during the film formation process to kinetically trap aggregates with exciton dynamics tailored for particular types of electronic devices.

Institution: University of Oregon

Code: ULTPhoto_I8

Presenter: J. Olof Johansson (GBR)

Abstract Title: Vibrational Coherences in Manganese Single-molecule Magnets after Ultrafast Photoexcitation

Co-Author(s): Florian Liedy, Robbie McNab, Julien Eng, Ross Inglis, Tom J. Penfold, Euan K. Brechin

Abstract: Single-Molecule Magnets (SMMs) are metal complexes with two degenerate magnetic ground states arising from a non-zero spin ground state and a zero-field splitting. SMMs are promising for future applications in data storage, however, to date the ability to manipulate the spins using optical excitation is lacking. Here, we have explored the ultrafast dynamics occurring after photoexcitation of two structurally related Mn(III)-based SMMs, whose magnetic anisotropy is closely related to the Jahn-Teller distortion, and demonstrate coherent modulation of the axial anisotropy on a femtosecond timescale.

We have performed ultrafast transient absorption (TA) spectroscopy in solution of two SMMs of gradual complexity, namely Mn3 ([Mn(III)3O(Et-sao)3(b-pic)3(ClO4)]) and Mn6 ([Mn(III)6O2(Et-sao)6(O2CPh(Me)2)2(EtOH)6]), with Et-sao = ethyl-salicylaldoxime, Ph = phenyl, b-pic = beta-picoline [1]. After excitation at 400 nm, we observed two excited-state absorption (ESA) bands around 345 nm and 430 nm in the TA spectra. We found oscillations superimposed on the decay traces with corresponding energies of around 200 cm-1. The wavenumbers coincide with strong Raman peaks observed in the ground state, which are assigned to a vibrational mode along the Jahn-Teller axis based on DFT calculations. We therefore attribute the oscillations to a coherent vibrational wavepacket along the JT axis upon photoexcitation [1].

Our results provide a non-thermal, coherent mechanism to dynamically control the magnetisation in SMMs and open up new molecular design challenges to enhance the change in anisotropy in the excited state, which is essential for future ultrafast magneto-optical data storage devices.

[1] F. Liedy et al., ChemRxiv, 2019, https://doi.org/10.26434/chemrxiv.7485011.v1

Institution: University of Edinburgh

Code: ULTPhoto_I9

Presenter: Christopher G. Elles (USA)

Abstract Title: Probing and Controlling Reaction Dynamics of Photochromic Molecules in Higher-Lying Electronically Excited States

Co-Author(s): Timothy J. Quincy, Matthew S. Barclay, Marco Caricato

Abstract: Probing the dynamics of molecules in higher-lying electronically excited states (i.e. states above S1) presents many experimental and theoretical challenges. While ultrafast techniques routinely measure the dynamics of molecules in the ground and first-excited states, probing the dynamics in higher-lying states requires new approaches to overcome the very short lifetimes and poorly resolved electronic transitions. Beyond scientific curiosity, higher-lying states present an opportunity for controlling the outcomes of photochemical reactions by opening new reaction channels. For example, recent experiments have shown that sequential excitation to higher-lying states offers a new level of control over chemical reactions by accessing new regions of the higher-lying potential energy surfaces that are not accessible directly from the equilibrium geometry of the ground state. This contribution examines the dynamics for sequential excitation of a photochromic molecular switch, and shows that the outcome of a cycloreversion (ring-opening) reaction can be selectively controlled based on secondary excitation to a higher-lying state that favors the reaction coordinate. In addition to direct (pump-repump-probe) measurements, we use femtosecond stimulated Raman scattering (FSRS) measurements to probe the ultrafast dynamics immediately following the secondary excitation. The excited-state resonance Raman measurements probe the potential energy surfaces of the upper states and reveal different nuclear motions following re-excitation at different wavelengths. The combination of techniques provides unique insight on the dynamics of higher-lying excited states, which is an important frontier in reaction dynamics.

Institution: University of Kansas

CONTRIBUTED TALKS

Code: ULTPhoto_T1

Presenter: Ruibin Liang (USA)

Abstract Title: Nonadiabatic photodynamics of the retinal protonated Schiff base in channelrhodopsin 2

Co-Author(s): Fang Liu, Todd J. Martinez

Abstract: Channelrhodopsin 2 (ChR2) is a light-gated ion channel and an important tool in optogenetics. Photoisomerization of retinal protonated Schiff base (RPSB) in ChR2 triggers channel activation. Despite the importance of ChR2 in optogenetics, the detailed mechanism for photoisomerization and channel activation is still not fully understood. Here, we report on computer simulations to investigate the photoisomerization mechanism and its effect on the activation of ChR2. Nonadiabatic dynamics simulation of ChR2 was carried out using the ab initio multiple spawning (AIMS) method and quantum mechanics/molecular mechanics (QM/MM) with a restricted ensemble Kohn–Sham (REKS) treatment of the QM region. Our results agree well with spectroscopic measurements and reveal that the RPSB isomerization is highly specific around the C13=C14 bond and follows the “aborted bicycle-pedal” mechanism. In addition, RPSB photoisomerization facilitates its deprotonation and partially increases the hydration level in the channel, which could trigger subsequent channel opening and ion conduction.

Institution: Stanford University

Code: ULTPhoto_T2

Presenter: I-Chia Chen (TWN)

Abstract Title: Rapid Relaxation Pathway of the Excited State of Linear-merocyanines in Solutions

Co-Author(s): Shao-An Wang, Wei-Hao Chen, Ming-Lun, Syue, Kui-Thong Tan

Abstract: Excited state relaxation of linear merocyanine dyes in solution are investigated using time-resolved spectroscopy techniques. The merocyanine L-Mero4 and phenyl substituted P-L-Mero4 have S-trans and S-cis structure, respectively consisting of indole moiety as the donor, indandione as the acceptor, and the tetramethine as the bridge. The time-correlated single photon counting (TCSPC) measurements after excitation at wavelength 515 nm to the pp* state yield emission curves with a short component t1 in the range 27-160 ps, and the second component t2 200-780 ps for L-Mero4. In P-L-Mero4, t1 lies in the range 18-150 ps, and t2 220-520 ps. The subfemtosecond transient absorption measurements yield a short component around 0.4-1.4 ps and the second/third components are similar to those in the TCPSC measurements. The analysis on the experimental data displays that the ground state recovery exhibits biexponential rise and is rapid indicating that the conversion back to the electronic ground state provides a fast non-radiative pathway. We identify the excited states and the relaxation path along the twist of the center double bonds in tetramethine that might be the non-radiative pathway. The C=C double bond is weakened in the pp* state. The phenyl substitution in the conjugated double bond further weakens this C=C bond and lowers the isomerization barrier. In polar solvents, the energy of the perpendicular conformer along the trans-cis isomerization path is raised to have less coupling to the ground state surface. Because of the small barrier to the trans form these two conformers establish an equilibrium condition.

Institution: Department of Chemistry, National Tsing Hua University

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Code: ULTPhoto_T3

Presenter: Krishnapriya KC (IND)

Abstract Title: Spin Density Encodes Intramolecular Singlet Exciton Fission in Pentacene Dimers

Co-Author(s): Krishnapriya KC, Roy P, Puttaraju B, Salzner U, Musser AJ, Jain M, Dasgupta J, Patil S.

Abstract: Singlet exciton fission (SEF) is the process of evolution of a photoexcited singlet exciton into two individual triplet excitons located on different chromophores, thereby producing two excitons at the expense of one photon. In the present contribution we provide compelling evidence on the significance of electronic spin density distribution in facilitating efficient intramolecular singlet exciton fission (iSEF) in π-bridged pentacene dimers. We synthetically modulated the spin density distribution in a novel series of pentacene dimers using phenyl-, thienyl- and selenyl- flanked diketopyrrolopyrrole (DPP) derivatives as π-bridges. Remarkably we find that efficient iSEF is only observed for the phenyl-derivative while absent in other two dimers. Electronic structure calculations reveal that phenyl-DPP bridge localizes α- and β-spin densities on distinct terminal pentacenes. Upon photoexcitation, a novel spin exchange mechanism enables iSEF from a singlet state which has an innate triplet pair character. Our new perspective based on spin density distribution of the frontier molecular orbitals offers important insight into ultrafast iSEF process and reveals a critical aspect to rationally design new materials.
Reference : Krishnapriya, KC; Roy, P.; Puttaraju, B.; Salzner, U.; Musser, A. J.; Jain, M.; Dasgupta, J.; Patil, Spin density encodes intramolecular singlet exciton fission in pentacene dimers Nat. Comm. 2019, 10, 1-8

Institution: Solid state and structural chemistry Unit, Indian Institute of Science, Bangalore

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Code: ULTPhoto_T4

Presenter: Pauline Gosset (FRA)

Abstract Title: Excited-State Proton Transfer of the Oxyluciferin and its Analogues

Co-Author(s): Grégory Taupier, Jérémie Léonard, Johanna Brazard, Kokou-Dodzi Dorkenoo, Pascal Didier

Abstract: Bioluminescence is a natural phenomenon during which living organisms convert chemical energy into light1. One of the most characterized reaction involves the firefly luciferase that catalyses the oxidation of the luciferin producing oxyluciferin in its first excited state. While relaxing to the ground state, oxyluciferin emits visible light with an emission maximum that can vary from green to red1. The oxyluciferin photophysics has been widely studied and it was shown that it can exist under six different chemical forms resulting from the keto/enol tautomerization and the deprotonation of the phenol/enol moieties2. The optical properties of each chemical form has been recently characterized by using oxyluciferin derivatives with steady state and nanosecond time-resolved spectroscopy. In particular, it evidenced the role played by excited state proton transfer (ESPT) reactions but its characterization remains elusive due to the limited temporal resolution (50 ps).

In this work, femtosecond pump-probe spectroscopy was used to characterize the ESPT dynamics of the oxyluciferin and its different derivatives in aqueous buffer as a function of pH. With the help of global analysis, it was possible to obtain the transient species' spectra together with the characteristic time associated to the ESPT. We also evidenced that transient absorption spectra of oxyluciferin's analogues can be used to model the complex excited state dynamics of the natural emitter.

References:
1.Seliger, H. H et al. Proc. Natl. Acad. Sci USA, 1964, 52, p75.
2.Ghose, A. et al. The Journal of Physical Chemistry B, 2014 119, p2638.

Institution: Université de Strasbourg

Code: ULTPhoto_T5

Presenter: Muhammad Shafiq Bin Mohd Yusof (SGP)

Abstract Title: Ultrafast Dynamics of Ionized Biomolecules in Aqueous Solution via Few-Femtosecond Transient Absorption Spectroscopy

Co-Author(s): Tushar Debnath, Yong Liang Lim, Zhi-Heng Loh

Abstract: Few-femtosecond optical transient absorption spectroscopy elucidates the ionization-induced vibrational coherences and ultrafast dynamics of small biomolecules in aqueous solution. Strong-field ionization of tryptophan (Trp) and tyrosine (Tyr) in basic medium by intense, few-cycle (~5-fs) laser pulses yields the tryptophan radical (Trp•) and tyrosine radical (Tyr•) respectively, and the accompanying hydrated electron. The expected absorption of tryptophan radical at ~580-nm is concealed by the strong and broad absorption of the hydrated electron in the visible region. On the other hand, the tyrosine radical appears in the ultraviolet region at ~410-nm. The absorption band observed produces pronounced amplitude and energy modulations in the time domain, which furnishes the vibrational frequencies coupled to the ionization process. These frequencies are assigned with the aid of density functional theory (DFT) calculations, where we modelled a micro-hydrated radical species in aqueous solution to account for the interaction of the radical with the surrounding solvent . In addition, the amplitude, dephasing time and phases of each vibrational frequencies observed will be furnished. The ultrafast dynamics and vibrational coherences of the ionized tryptophan and tyrosine in aqueous solution will be presented.

Institution: Nanyang Technological University

Code: ULTPhoto_T6

Presenter: Kajari Bera (USA)

Abstract Title: Exploring Structural Dynamics during Singlet Fission using Femtosecond Stimulated Raman Spectroscopy

Co-Author(s): Renee R. Frontiera

Abstract: The efficiency of solar energy conversion in single-junction photovoltaic devices limited by the Shockley-Queisser limit to values of ~34% can be improved to ~45% through singlet fission (SF). SF is a process where an excited state chromophore couples with a ground state chromophore, generating a correlated triplet pair, which eventually separates into two triplets. Thus, SF generates a pair of charge carriers from the absorption of a single photon, thereby increasing the energy conversion efficiency of photovoltaic devices. Understanding the molecular structural dynamics during the SF process will help to fabricate materials with optimal charge separation and transport properties for highly efficient organic photovoltaics. Here, I use femtosecond stimulated Raman spectroscopy (FSRS) to provide new insights to the structural evolution during the SF and triplet separation processes in rubrene and structurally similar derivatives. FSRS is an ultrafast vibrational technique capable of probing the nuclear dynamics within a system on a femtosecond timescale, thus providing information about the real time structural changes that the system undergoes after photoexcitation. In crystalline rubrene, we proved that the separation of the correlated triplet pair is associated with the loss of electron density from the tetracene backbone in rubrene. I will discuss how deliberately functionalizing the molecular structure to promote decrease ground state electron density in the tetracene core affects the SF dynamics. Additionally, I will discuss a pulse shaping and automated data analysis approach to minimize vibronic background features in crystalline FSRS experiments to extract valuable information on excited state dynamics.

Institution: Department of Chemistry, University of Minnesota

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Code: ULTPhoto_T7

Presenter: Stephen Meech (GBR)

Abstract Title: Ultrafast Excited State Dynamics in Unidirectional Molecular Motors

Co-Author(s): Palas Roy, Andy Sardjan, Wesley Browne, Ben Feringa

Abstract: Unidirectional molecular motors can convert optical radiation into directional rotational motion, and thus have the potential to power nanomolecular machines. The mechanism involves sequential excited state isomerization and ground state thermal helix inversion steps. In this presentation we describe studies of the primary photochemical isomerization reaction in these photomotors, through studies of their ultrafast fluorescence decay with 50 fs time resolution.[1] The behavior of two distinct molecular structures – the first- and second-generation molecular motors[2] – are compared. Remarkable differences in both the population decay and coherent vibrational dynamics are noted.[1,3] For example, the effect of solvent viscosity on their radiationless rate coefficients are quite different, suggesting a variation in the pathway leading to excited state decay. The roles of solvent polarity, excited state barrier crossing and solvent viscosity are investigated and discussed.

References.

1. Conyard et al. Nat. Chem. 2012, 4, 547
2. Kassem et al. Chem. Soc. Rev., 2017, 46, 2592
3. Sardjan et al. In preparation

Institution: University of East Anglia

Code: ULTPhoto_T8

Presenter: Luis Miaja-Avila (USA)

Abstract Title: Table-top Ultrafast X-ray Spectroscopies using a Laser Plasma X-ray Source and Microcalorimeter Sensors

Co-Author(s): Galen O'Neil, Young Joe, Daniel Swetz, Ralph Jimenez, and Joel Ullom

Abstract: We present successful demonstrations of table-top Time-Resolved X-ray Absorption Spectroscopy (TR-XAS) and Emission Spectroscopy (TR-XES) using a laser plasma x-ray source and a microcalorimeter array detector. Using TR-XAS, we studied the photoreduction of ferrioxalate, a reaction that has been the subject of a long-running debate in the literature, including contradictory x-ray measurements. Our results strongly support a picture in which reduction of the central iron is complete by 100 ps and contradict a theory in which the photoreduction occurs on much longer timescales. Using TR-XES, we studied spin cross-over in photoexcited iron tris-bipyridine and accurately measured the lifetime of the quintet state from simultaneous observations of the iron Kα and Kβ features. We also determined the time resolution of our apparatus to be better than 6 ps. Better time resolution in TR-XES has only been demonstrated at x-ray free electron lasers. These results are the first laboratory-scale demonstration of ultrafast TR-XES. They were enabled by a multi-institution collaboration and by the unique combination of spectral resolution and collecting efficiency provided by microcalorimeter sensors. The collecting efficiency of these devices allowed the quintet lifetime to be measured using 100-1,000× fewer x-rays delivered to the sample than comparable work performed at a synchrotron.

Finally, we present a study of the valence-to-core emission lines for different titanium compounds using microcalorimeters. We measured the Kβ2,5 features of six titanium compounds with an energy resolution of approximately 4 eV and compared our results to previously published synchrotron data and to DFT theory.

Institution: NIST

Code: ULTPhoto_T9

Presenter: Alexander Aster (CHE)

Abstract Title: Tuning Symmetry Breaking Charge Separation of Perylene Bichromophores by Conformational Control

Co-Author(s): Giuseppe Licari, Francesco Zinna, Elodie Brun, Tatu Kumpulainen, Emad Tajkhorshid, Jerome Lacour and Eric Vauthey

Abstract: The structure-property relationship in multichromophoric systems is crucial to establish design principles in organic electronics as well as fully comprehend how nature converts sunlight to energy. Bichromophores, consisting of two identical chromophores linked in a controlled geometry, are the model of choice to study how inter-chromophore conformation, can be used to tune the photophysical properties of a material.

In this communication, we will present a series of bichromophores consisting of two perylene heads, linked to different crownether backbones, which upon complexation of a cation change geometry and thereby the inter-chromophore conformation.

Transient absorption from femtosecond to microsecond and from UV to NIR as well as broadband fluorescence upconversion are paired with molecular dynamics simulation. This allows to link the intermolecular geometry with the adiabatic dimer states formed in close proximity and the dynamics in which they are populated.

We will show that controlling the conformational restrictions can turn on and off symmetry breaking charge separation (SB-CS), allow for excimer formation, and even tune the SB-CS rate over 2 orders of magnitude.

Institution: Department of Physical Chemistry, University of Geneva, CH-1211 Geneva, Switzerland.

Code: ULTPhoto_T10

Presenter: Tatu Kumpulainen (CHE)

Abstract Title: How Does Solvent Control Excited-state Proton Transfer?

Co-Author(s): Bogdan Dereka, Arnulf Rosspeintner, Eric Vauthey

Abstract:

The choice of a solvent can have a dramatic effect on the outcome of a chemical reaction. In addition to specific solvent interactions such as hydrogen bonding, the solvent environment can greatly influence chemical equilibrium, reaction rate and driving force by differing stabilization of the reactants, transition states or products, especially with reactions involving charged or strongly dipolar species.[1] If the rate of such a reaction is faster or comparable to the dynamics of the solvent, the reaction becomes solvent controlled. In this case, both the rate and the yield of the reaction are controlled by solvent relaxation in a non-equilibrium fashion.

In our communication, we demonstrate how a combination of ultrafast spectroscopic techniques allows us to address the influence of solvent relaxation on the rate and yield of excited-state proton transfer (ESPT) to solvent. In particular, femtosecond broadband fluorescence up-conversion enables real-time monitoring of both the solvent relaxation and reaction kinetics simultaneously.[2] Our data shows that ESPT from a 1,8-naphthalimide-based “super” photoacid to protic solvents and DMSO is indeed solvent controlled. Interestingly, the overall yield of the anionic species is significantly higher in DMSO although the ESPT process itself is more efficient in protic solvents. The reasons for this behavior are discussed.

[1] Christian Reichardt, Thomas Welton (2010) Solvents and Solvent Effects in Organic Chemistry, Wiley-VCH, Weinheim, Germany, pp. 107–357.
[2] T. Kumpulainen, A. Rosspeintner, B. Dereka, E. Vauthey, J. Phys. Chem. Lett. 2017, 8, 4516–4521.

Institution: Department of Physical Chemistry, University of Geneva, 30 Quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland

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Code: ULTPhoto_T11

Presenter: Jasper J. van Thor (GBR)

Abstract Title: Optical Control of Protein Structural Dynamics by Ultrafast TR-SFX

Co-Author(s): n.a.

Abstract:

The new ability to perform ultrafast time resolved X-ray crystallography in pump-probe mode [1] raises a number of fundamental questions regarding the assignment, control and analysis of light-induced differences that are measured [2][3][4][5][6]. I will discuss methods of analysis and experimental design that allow quantification and control of non-linear photochemical reactions under typical conditions of femtosecond time resolved TR-SFX[1][4]. This analysis has now also been extended to retrieve the explicit orientation-dependence of transient populations by crystal optics calculations [3]. The high peak power required for successful pump-probe TR-SFX experiments also provide an opportunity, to measure and control low frequency ground state and excited state vibrational coherence[2][3]. Future high repetition rate XFEL instruments such as LCLS-II may advance the technique to the practical application of the X-ray crystallographic equivalent of an impulse time-domain Raman measurement of vibrational coherence at high frequencies [3]. In addition, I will present a first experimental demonstration of optical control of protein structural dynamics using femtosecond TR-SFX at near-atomic resolution.

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Institution: Imperial College London

Code: ULTPhoto_T12

Presenter: Dennis Bank (DEU)

Abstract Title: E → Z Photoisomerization Studies of an Alternating Linear Main-chain Azobenzene–trisiloxane Polymer with 45 Weight-% Chromophor

Co-Author(s): Mathias Schulz-Senft, Jan Strueben, David Presa Soto, Frank D. Sönnichsen, Falk Renth, Friedrich Temps, Anne Staubitz

Abstract: The photoswitching properties of a light-responsive main-chain polymer with an alternating sequence of azobenzenes (AB) as photochromic switching units and trisiloxane linkers were investigated by diffusion-ordered NMR in chloroform, tetrahydrofuran and n-hexane as solvents. The polymer was synthesized via step-growth polycondensation and exhibits an effective high chromophore load of 45 wt-%. By irradiation to the photostationary state (λ = 365 nm) in chloroform and tetrahydrofuran, a molar fraction of 67 % of the Z-ABs could be obtained. The photoisomerization is accompanied by a decrease of the hydrodynamic volume of the solvated polymer coils by ≈ 20 %. In n-hexane, a light-triggered collapse of the polymer led to a globular non-solvated form with ≈ 70 % drop in hydrodynamic volume. The collapsed polymer exhibits a fraction of 50 % Z-isomers in the respective PSS365. Femtosecond electronic absorption spectroscopy in n-hexane showed an ultrafast deactivation of the initially excited S2 state of the AB chromophores within τ1 ≈ 150 fs. The conversion to the S1 state leads to a sequential relaxation, whereby the polymer causes only a slight slow-down of the deactivation time to τ2 = 1.0 ps and τ3 = 8.3 ps compared to the monomeric reference compound (τ2 = 0.6 ps and τ3 = 5.3 ps). These results highlight a nearly unimpeded switching of the azobenzene moieties in the polymer, in contrast to previous results of an azobenzene cross-linked into a polybutylmethacrylate polymer [1].

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Institution: Christian-Albrechts University Kiel

Code: ULTPhoto_T13

Presenter: Michela Gazzetto (CHE)

Abstract Title: Anti-Kasha Photophysics and Photochemistry in Pt-dithiolene Complexes Investigated with Ultrafast Transient Absorption

Co-Author(s): F. Artizzu, S. Attar, L. Marchio`, L. Pilia, E. Rohwer, T. Feurer, P. Deplano, A. Cannizzo

Abstract: Metal-dithiolene complexes with d8-square planar structure and non-innocent ligands show outstanding hyperpolarizability and non-linear optical behavior due to highly delocalized frontier electrons, making them interesting for photovoltaics, visual and sensing technologies. They can potentially act as charge transfer (CT) relays for artificial photocatalyzers, controllable by external stimuli as light, temperature, solvent polarity, etc. For instance complexes containing quinoxdt ligands show proton-switchable properties in acidic solutions

Surprisingly, quinoxdt complexes have additionally a photophysical response that markedly dependents on the excitation wavelength (anti-Kasha behavior). Systems with such an uncommon behavior have raised more and more interest because of the possibility to conceive multi-response molecular devices or to explore novel photochemical routes. Such a behavior originates from a competition between the functional process in the upper photo-excited state and internal conversion (IC) towards the lowest excited state. Therefore femtosecond transient absorption is ideal to characterize the anti-Kasha process with the perspective to optimize its performance.

We elucidated the origin of the anti-Kasha behavior both in homoleptic and heteroleptic quinoxdt complexes, which stems from a neat spatial separation between the molecular orbitals of the excited states localized on the quinoxdt moiety. This electronic arrangement gives a CT character to the IC slowing down the process.

We also discuss the role of such an unusually long lifetime of the photo-excited higher state on the functional processes characterizing the two investigated complexes, namely photocatalytic H2 production and photo-induced chemiluminescence, respectively.

Institution: Institute of Applied Physics, University of Bern, Sidlerstrasse 5, 3012 Bern (Switzerland)

Code: ULTPhoto_T14

Presenter: Giordano Amoruso (GBR)

Abstract Title: Tracking the Ultrafast Dynamics of an Intermolecular Excited State Proton Transfer Reaction between Coumarin and Methylimidazole

Co-Author(s): Victoria C.A. Taylor, Marta Duchi, Emma Goodband and Thomas A.A. Oliver

Abstract: Excited state proton transfer (ESPT) reactions are an important class of photoinduced reactions responsible for driving chemical transformations spanning tautomerization, isomerization, and the generation of fluorescent anions in GFP. Due to the complexity and challenges that ESPT pose to both experimentalists and theoreticians, the detailed investigation of readily modifiable reduced biomimetic model systems is imperative. We have studied the ultrafast dynamics of an inter-molecular excited state proton transfer (ESPT) reaction between the photoacid 7-hydroxy-4-(trifluoromethyl)-1-coumarin (CouOH) hydrogen bonded to 1-methylimidazole (MI) in aprotic chloroform-d1 solution using transient absorption and time-resolved infrared spectroscopies. The excited state lifetime of the photoacid in solution is relatively short (50 ps) which at the millimolar concentrations used in our study precludes any diffusion-controlled bimolecular ESPT reactions with MI molecules. This allows the immediate ESPT reaction to be studied in isolation, and the dynamics to be unambiguously determined. Our time resolved studies reveal ultrafast ESPT from the CouOH moiety to hydrogen bonded MI molecules occurs within ~1 ps and tracked by unequivocal spectroscopic signatures of CouO–* photoproducts which are formed in tandem with HMI+. We infer that some of these photoproducts rearrange to minimize the attractive Coulombic forces between the oppositely charged aromatic molecules to form π-stacked exciplexes on a ~35 ps timescale. At the low concentrations of CouOH and MI used in our study (up to 8 mM), we saw no evidence for excited state tautomerization of coumarin anions.

Institution: School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK

Code: ULTPhoto_T15

Presenter: Siobhan Bradley (AUS)

Abstract Title: Ultrafast Photoexcitation Dynamics in a Series of Diketopyrrolopyrrole Derivatives

Co-Author(s): Ming Chi, Ken Ghiggino, Trevor Smith and Jonathan White

Abstract: Diketopyrrolopyrrole is a versatile chromophore with an abundance of desirable properties for optoelectronic applications. It has a strong absorption coefficient, high quantum yield, is chemically robust, inexpensive to make and easy to modify. It also fulfills the energetic requirements for singlet fission (SF) in that it has a triplet energy level that is less than half of its singlet energy level and has significant charge-transfer character – a feature which has been proposed to facilitate the SF process.

Dimeric forms of DPP derivatives show significant quenching compared to their monomer counterparts, indicating that a new non-radiative pathway is present associated with intramolecular excited state chromophore interactions. One possible quenching pathway – given the aforementioned properties of DPP is SF, forming two triplets with half the singlet energy.

In the study of DPP dimers with varying linkers, an excited state absorption appears at 640 nm which grows in at a rate that is solvent dependent. This state has a few curiosities – its rate of growth and decay are strongly solvent-dependent, and it decays rapidly in reprecipitation nanoparticles formed from all derivatives. It has been suggested that this excited state absorption indicates the formation of a charge separated state rather than a charge-transfer or triplet state. In this work we investigate this state and use transient absorption spectroscopy to resolve the relaxation pathways and electronic states involved following photo-excitation of monomeric material, the dimers, through to larger nanoscale structures.

Institution: ARC Centre of Excellence in Exciton Science, University of Melbourne, Australia

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Code: ULTPhoto_T16

Presenter: Victoria Taylor (GBR)

Abstract Title: Investigating the Role of the Organic Cation in Formamidinium Lead Iodide Perovskites using 2DIR Spectroscopy

Co-Author(s): Devendra Tiwari, Paul Donaldson, Thomas A.A. Oliver

Abstract: Hybrid organic-inorganic halide perovskites are remarkable materials with a plethora of unusual properties. High absorption coefficients, high carrier mobilities, and low charge recombination rates, despite low-cost solution-phase synthesis,[1] have led to intense research into these materials for photovoltaic applications. Hybrid organic-inorganic halide perovskites consist of organic cations caged within an inorganic lattice of metal and halogen atoms. Several studies have proposed that the organic cations play a pivotal role in the high charge separation efficiencies of these materials[2] by orientating within the inorganic lattice to form (anti) ferroelectric domains at room temperature.[3] These domains could then act to channel opposite charges away from one another, thereby reducing charge recombination. Ultrafast spectroscopy is an ideal tool to elucidate the dynamics of these organic cations as it enables monitoring of materials on timescales commensurate with that of molecular vibrations or rotations.

Two-dimensional infrared (2DIR) anisotropy measurements were used to interrogate the reorientation of formamidinium cations (FA+, NH2CHNH2+) in formamidinium lead iodide perovskite thin films. These rotational anisotropy measurements returned 470 ± 50 fs and 2.8 ± 0.5 ps time constants, meaning that any initial alignment of FA+ molecules is very short lived. Molecular dynamics simulations reveal FA+ cations agitate about an equilibrium position, with NH2 groups pointing at opposite faces of the inorganic lattice cube, undergoing 90° flips between cube faces on picosecond time scales. Our 2DIR results provide the first direct measurement of FA+ rotation inside thin perovskite films, and cast significant doubt on the presence of long-lived (anti)ferroelectric domains.[4]

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(4) Taylor, V. C. A.; Tiwari, D.; Duchi, M.; Donaldson, P. M.; Clark, I. P.; Fermin, D. J.; Oliver, T. A. A. J. Phys. Chem. Lett. 2018, 9, 895–901.

Institution: University of Bristol

Code: ULTPhoto_T17

Presenter: Björn Kriete (NLD)

Abstract Title: Shedding Light on Ultrafast Exciton Dynamics in Unwrapped Nanotubes

Co-Author(s): Julian Lüttig, Tobias Brixner, Maxim S. Pshenichnikov

Abstract: Inspired by the remarkable quantum efficiencies of natural light-harvesting complexes (LHCs), double-walled tubular aggregates have attracted considerable interest as artificial LHCs.[1] At the core of their efficient energy transfer is a dense array of thousands of strongly coupled molecules giving rise to highly delocalized and mobile excitons. Unravelling the nature of exciton delocalization as well as exciton diffusion is inevitable for potential applications, yet inherently challenging to measure due to congested spectroscopic signatures.

Here we employ a novel spectroscopic lab-on-a-chip approach to first simplify the supramolecular hierarchy of our model system, double-walled C8S3 nanotubes, and then directly probe multi-exciton interactions via 5th order 2D spectroscopy.[2] The outer layer is selectively removed in a microfluidic channel thereby opening a sufficient time window for 2D spectroscopy before the original double-walled structure is re-established. This allowed us to obtain an unobscured view on the exciton dynamics of the isolated subspecies and make an unambiguous assignment of the exciton delocalization and diffusion of the simplified as well as the complete system.

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Institution: Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

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Code: ULTPhoto_T18

Presenter: Kristjan Kunnus (USA)

Abstract Title: Controlling Photoinduced Electron Back-Transfer in Molecular Fe-based Photosensitizers

Co-Author(s): L. Li, M. Reinhard, K. Ledbetter, K. S. Kjaer, S. Koroidov1, K. Hong, E. Biasin, A. Cordones-Hahn, K. J. Gaffney

Abstract: We have investigated photoinduced intramolecular electron transfer relaxation dynamics following a metal-to-ligand charge-transfer (MLCT) excitation in [Fe(CN)4(2,2’-bipyridine)]2-, [Fe(CN)4(2,3-bis(2-pyridyl)pyrazine)]2- and [Fe(CN)4(2,2’-bipyrimidine)]2- complexes in various solvents. By tuning the lowest MLCT absorption band over a wide range of 1.3 to 2.1 eV we observe changes in electron transfer lifetimes from 44.8 ps to 180 fs with UV-visible pump-probe spectroscopy. The 44.8 ps MLCT lifetime corresponds to longest observed for either hetero- or homoleptic Fe polypyridine complexes. The driving forces governing the electron transfer lifetimes have been determined from combined analysis of UV-visible absorption and Fe 2p3d resonant inelastic X-ray scattering (RIXS) spectra. Using classical Marcus theory and the experimentally determined variations in the driving force for MLCT relaxation to a metal-centered triplet state (3MC) explain the MLCT lifetime variation for all by one system, [Fe(CN)4(2,2’-bipyrimidine)]2- in dimethyl sulfoxide. For this system, the anomalously short lifetime results from direct relaxation to the electronic ground state, rather than relaxation to a 3MC state. This distinct relaxation mechanism involves reorganization of an effective high-frequency accepting mode (ħω = 1600 cm-1) associated with a breathing mode of the 2,2’-bipyrimidine ligand.

Institution: Stanford University

Code: ULTPhoto_T19

Presenter: Yoonsoo Pang (KOR)

Abstract Title: Ultrafast Intramolecular Proton Transfer and Charge Transfer Probed by Time-resolved Raman Spectroscopy

Co-Author(s): Myungsam Jen, Sebok Lee, Kooknam Jeon

Abstract: Ultrafast photophysical processes in the excited states including intramolecular proton transfers and charge transfers are of fundamental importance in understanding chemical reactions and many applications. In this work, ultrafast intramolecular proton transfer of 1,2-dihydroxyanthraquinone (alizarin) and intramolecular charge transfer of DCM dye and 1-aminoanthraquinone (1AAQ) were studied by femtosecond stimulated Raman spectroscopy. From population and spectral changes of transient vibrational modes of the probe, structural changes of probe accompanying proton transfer or charge transfer can be obtained. Tautomerization of alizarin and twisted intramolecular charge transfer of DCM dye and 1AAQ will be discussed. We have also investigated the changes in the solvent vibrational modes of solvent DMSO during these ultrafast processes, where the v(S=O) and v(CSC) mode substantially increase especially in the sub-bands for “aggregated” species of DMSO, which clearly shows the dynamics of the intramolecular proton transfer of probe alizarin. We also noticed a substantial decrease in the v(S=O) mode especially in the sub-bands for “hydrogen-bonded” species of DMSO during the intramolecular charge transfer of 1AAQ. The instantaneous changes of these DMSO modes disappear with the vibrational relaxation and population dynamics of the probe in product states. In conclusion, we propose that the solvent vibrations of DMSO can be used as the measure of the chemical reaction dynamics of solute molecules and solvation dynamics accompanying the ultrafast photophysical processes.

Institution: Gwangju Institute of Science and Technology

Code: ULTPhoto_T20

Presenter: Hugo J. B. Marroux (USA)

Abstract Title: Attosecond Transient Absorption of Molecular Core-excited States: Lifetime Dependence on Orbital Alignment with Molecular Bond

Co-Author(s): Ashley P. Fidler; Yuki Kobayashi; Aryya Ghosh; Kirill Gokhberg; Alexander I. Kuleff; Daniel M. Neumark; Stephen R. Leone

Abstract: Core-excited states in atoms have lifetimes on the order of a few to tens of femtoseconds with decays leading to emission of Auger electrons. These lifetimes are often determined by lineshape analysis but this is difficult when investigating core-excitation in molecules as the additional degrees of freedom complicate the lineshape. Using attosecond transient absorption (ATAS), core-excited state lifetimes of iodine monochloride are retrieved, with additional detail about the alignment of the core excited state orbital relative to the bond direction.

Lifetimes measured from the ATAS spectrum following 6p<-4d excitation show a dramatic increase of core-excitation lifetime for core hole vacancies perpendicular to the covalent bond. Lifetimes of 3.4 ± 0.3 and 4.3 ± 0.3 fs are observed for states parallel to the bond (4d5/2 and 4d3/2 character, respectively) and 5.5 ± 0.4 and 6.5 ± 0.4 fs for states perpendicular (4d5/2 and 4d3/2 character, respectively).

All the excited state lifetimes measured are well below the 87 fs vibrational period of ICl, ensuring that excited state decay does not depend on the nuclear motion and that pure electronic dynamics is observed.

This is a direct time-resolved observation of molecular core-excited state decays. The observed state-specific dynamics is implicated in a broad range of topics, including pre-edge spectral simulation, where lifetime broadening is often assumed to be independent of the core-hole alignment, and interatomic Coulombic decay mechanisms in core-excited molecules.

Institution: UC Berkeley

Code: ULTPhoto_T21

Presenter: Robin Pierron (FRA)

Abstract Title: Two-Dimensional Electronic Spectroscopy to study the Ultrafast Photoisomerization of Biomimetic Molecules

Co-Author(s): Johanna Brazard, Damianos Agathangelou, Youssef El Khoury, Olivier Crégut, Jérémie Léonard

Abstract: The process of vision is triggered by the vibrationally coherent, cis-to-trans photo-isomerization of retinal in the rhodopsin protein (Rho) [1]. We demonstrated that a similar photo-isomerization mechanism can be reproduced in a model compound called “NAIP” [2]. Using very short laser pulses (<10 fs), it is possible to trigger the photoreaction synchronously in an ensemble of molecules in solution and to follow the spectroscopic signatures of their coherent vibrational motion along the course of the photoreaction [3]. This is called vibrational coherence spectroscopy (VCS). Applying VCS to the NAIP’s allowed us to demonstrate that a small initial twist (~15°) of the isomerizing C=C double bond, induced by a methyl substitution in the molecule, is necessary to observe a vibrationally coherent photo-isomerization in NAIP in solution. We now implement two-dimensional electronic spectroscopy (2DES) by upgrading our transient absorption spectrometer for VCS [3] with a “TWINS” device, which uses birefringent wedges to control the time delay between two co-propagating pump pulses [4]. Our goal is to use 2DES to unravel the influence of the excitation wavelength – i.e. of the initial excess vibrational energy - on the vibrationally coherent reactive motion in NAIP. Also the interaction with the environment is expected to tune the NAIP photoreactivity, which we investigate by varying the solvent polarity. Ultimately these investigations aim at unraveling the recipes for optimizing of the chemical structure of synthetic molecular systems to generate this type of vibrational coherence and, if possible, exploit it to control the photoreactivity, as Rho does with retinal.

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Institution: University of Strasbourg, CNRS, IPCMS

Code: ULTPhoto_T22

Presenter: Taiha Joo (KOR)

Abstract Title: Coherent Nuclear Wave Packets in the Product of Coherent Chemical Reactions

Co-Author(s): Wooseok Heo, Changmin Lee, Pyoungsik Shin, Jungsoo Ahn

Abstract: Oscillation of a signal by coherent nuclear wave packets is ubiquitous in time-resolved spectroscopies. For a coherent photochemical reaction occurring in an electronic excited state, molecular reaction dynamics can be studied by recording the nuclear wave packet motions in the reactant and product potential energy surfaces following photoexcitation to a Franck-Condon state. Wave packets in the product state may be formed by the initial photoexcitation or impulsive chemical reaction [1], and they may or may not be coupled with the chemical reaction. We developed a method based on molecular dynamics simulation to analyze the wave packet motion of each vibrational mode following photoexcitation. The method was applied to the excited state intramolecular proton transfer of 10-hydroxybenzo[h]quinoline (HBQ), and the results are consistent with the wave packet motions observed by time-resolved fluorescence including both amplitude and phase. The theory and experiement provided the shape of the potential energy surface and the role of low-frequency skeletal vibrations of HBQ. The intuitivepicture of barrierless proton transfer through the assistance of low frequency skeletal vibrations cannot be justfied. The vibrational mode at 248 cm−1, which was thought to promote the proton transfer by transporting the proton to the acceptor nitrogen is excited by the initial photoexcitation. High frequency modes that are copled strongly witht the proton transfer were identified.

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Institution: POSTECH

Code: ULTPhoto_T23

Presenter: Marcos Dantus (USA)

Abstract Title: Ultrafast Dynamics of a "Super" Photobase

Co-Author(s): W. Shang, M. Nairat, P. Pawlaczyk, E. Mroczka, B. Farris, E. Pines, J. Geiger, B. Borhan, and M. Dantus

Abstract: Acid-base equilibria drive most chemical reactions and are paramount for sustaining life processes. Stronger acids or bases are associated with a greater driving force, based on the greater Gibbs free energy of reaction. Unfortunately, the use of very strong acids or bases is limited because they are not compatible with the medium where the reaction takes place. For example, concentrated sulfuric acid reacts violently with most solvents. Interestingly, extreme acidity or basicity can be achieved by harnessing the energy of photons. A change of electronic configuration can bring about orders of magnitude greater acidity or basicity. This last statement will be illustrated by the characterization of the first super photobase. This compound, with pKa of 7 in the ground state has a pKa* of 21 in the excited state [Angew. Chem. Int. Ed. 57, 14742 (2018)].

Institution: Michigan State University

Code: ULTPhoto_T24

Presenter: Christopher C. Rich (USA)

Abstract Title: Coherent Control of Rapid Phonon Dynamics during Photoinduced Charge Transfer in Molecular Crystals

Co-Author(s): Renee R. Frontiera

Abstract: Photoinduced phase transitions in molecular crystals are intriguing processes to study for further developing our understanding of photophysics that extend beyond the Born-Oppenheimer approximation. Learning how the underlying interplay between nuclear and electronic motion in these materials will inform future rational design for efficient and inexpensive light-driven molecular photoswitch technology. In this work, we examine the spin-Peierls phase melting transition of potassium tetracyanoquinodimethane (KTCNQ) crystals driven by ultrafast light-driven charge transfer and show that we can influence this process through coherent control of excited state phonon modes. High time resolution measurements of excited state dynamics using the femtosecond stimulated Raman spectroscopy (FSRS) pulse sequence reveal two coherent phonons, corresponding to longitudinal and lateral intermolecular motion of the TCNQ anion monomers, that drive both the phase transition and the subsequent photocarrier recombination. Our study revealed large spectral shifts in both modes occurring within 1.5 ps suggesting rapid and massive molecular restructuring within the crystal following photoinduced charge transfer. Double pulse photoexcitation experiments emphasize the role of these modes on the underlying photochemistry of the photoinduced phase transition and our ability to amplify and suppress this process by selectively triggering these optical phonons. Our findings further contribute to the important role of coherent vibrations and phonons involved in photochemical and photophysical processes.

Institution: University of Minnesota

Code: ULTPhoto_T25

Presenter: Andreas Hugi (CHE)

Abstract Title: Spectroscopic Applications of Quantum Cascade Laser Frequency Combs

Co-Author(s): Horvath, R.; Mangold, M.; Geiser, M.; Strand, C. L.; Pinkowski, N. H.; Ding, Y.; Hanson, R. K.;Klocke, J. L.; Kottke, T.

Abstract: Fast infrared spectroscopy is an important tool for research and industrial applications, giving insight into chemical kinetics on many timescales, biological processes, as well as providing an important tool for routine process monitoring and quality control. Quantum cascade laser frequency comb infrared spectroscopy has recently emerged as a new method for obtaining fast continuous measurements, enabling the parallel acquisition of many mid-infrared wavelengths with microsecond time resolution. In addition, laser-based IR spectroscopy breaks the fundamental size vs resolution barrier that is a limiting factor for interferometric techniques, allowing for spectral resolutions of <1x10-4cm-1.

This contribution presents pump-probe experiments conducted on the transmembrane protein bacteriorhodopsin using a frequency comb spectrometer, which enables spectral information of three different light-activated states to be obtained after a single 10 ns excitation pulse, representing a total experimental time of 16 ms[1]. Combustion monitoring and chemical kinetics are other important applications where single-shot measurements are essential, as relatively variable reaction conditions complicate acquisition averaging. Preliminary results show the evolution of multiple species on a microsecond timescale in a gas-phase reaction at high temperature and pressure[2]. Frequency comb spectroscopy is unique in its ability to simultaneously detect and quantify these species on a single-shot basis in the mid-infrared spectral region.

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Institution: IRsweep AG

Code: ULTPhoto_T26

Presenter: Matthijs R. Panman (SWE)

Abstract Title: Observing Fundamental Reaction Events in the Dissociation of Diiodomethane with Ultrafast X-ray Scattering

Co-Author(s): E. Biasin, O. Berntsson, M. Hermann, M. M. Nielsen, J. Davidsson, J. Uhlig, K. Haldrup, J. S. Hub, S. Westenhoff

Abstract: The earliest events in chemical reactions are critical in determining their outcome. Short-lived reaction intermediates often include non-bonded species, such as radical pairs, but are typically difficult to characterize structurally. Femtosecond Time-Resolved Wide-Angle X-ray Scattering (TRWAXS) can potentially resolve the interatomic distances of structurally evolving species on chemically relevant time scales.

Here, we use TRWAXS to monitor the photodissociation of diiodomethane in cyclohexane, a reaction which involves both covalently bound and solvent separated species. The data reveal the trajectories and relative positions of all reaction fragments from femto- to nanoseconds. We observe real-time I-I bond scission, the flight of the resultant fragments and their collision with the solvent, determining that impulsive solvent-cage escape is negligible. Furthermore, contrary to established expectations, the diffusion of the products is strongly hindered and the radicals remain geminately confined to the same solvent cavity for up to 1 ns. Quantum chemical calculations indicate that this is due to dispersion forces between the fragments. We suggest that spin multiplicity is responsible for the biphasic recombination into the photoisomer.

Our experiment demonstrates how the solvent directs the course of a reaction during its earliest steps. The observation of the structural evolution of the laser-generated species prompt a revision of the reaction mechanism of the photodissociation of diiodomethane. Monitoring the interplay between solvent and solute is critical for deeper understanding of the course and rate of liquid-state chemical reactions.

Institution: University of Gothenburg

Code: ULTPhoto_T27

Presenter: Yogita Silori (IND)

Abstract Title: Unravelling the Role of Water in Ultrafast Excitation Energy Transfer within Nano-architectures of Chlorophyll a

Co-Author(s): Sakshi Chawla and Arijit K. De

Abstract: In natural light-harvesting complexes, organization of pigment assemblies leads to collecting and funneling light with nearly unit efficiency. Interaction between chlorophyll molecules (and also with its local environment) gives rise to formation of various architectures. With varying the ratio of acetonitrile (ACN) and water, chlorophyll a (Chl a) forms different structures. In 70/30, water/ACN ratio it forms a polymer (cylindrical reverse micelle) whose Qy band absorbs at ~750 nm. However, in 98/2 ratio, it shows two peaks at ~673 nm and ~713 nm due to hydrated monomer and aggregates (T-shaped oligomers which form micelles). These structures are quite different from Chl a in ACN only which absorbs at ~670 nm.

We studied ultrafast excited state dynamics of these architectures using pump-probe spectroscopy to unravel the structure-function relationship mediated via water molecules present within these architectures. All three architectures show a broad excited state absorption (ESA) band in the region of 490-650 nm. In ACN, the ESA band show no significant change in spectral traces with increasing probe delay. However, in the other two cases (different mixture of ACN/water), the ESA band show blue shift as well as spectral narrowing with the delay which clearly indicates presence of vibrational cooling which takes place due to faster thermal diffusivity in presence of water. Quite interestingly, the vibrational cooling is followed by stimulated emission with almost no (red) shift in spectra, suggestive of absence of polar solvation by water.

Further investigation using pump-probe anisotropy and two-dimensional electronic spectroscopy will also be discussed.

Institution: PhD student, Indian Institute of Science Education and Research Mohali

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Code: ULTPhoto_T28

Presenter: Marcos Dantus (USA)

Abstract Title: Ultrafast Reaction Dynamics and Control of Trihydrogen-cation Formation Triggered by Strong-field Laser Pulses

Co-Author(s): M. J. Michie, N. Ekanayake, M. Nairat, K. D. Carnes, D. Rolles, A. Rudenko, B. G. Levine, J. E. Jackson, I. Ben-Itzhak

Abstract: Strong field excitation of organic molecules triggers exotic chemical processes involving making and breaking of multiple chemical bonds that result in the formation of H_3^+, H_2O^+, and H_3O^+.The formation of H_3^+, following strong-field photodissociation of methanol, is preceded by the formation of a neutral H_2 molecule that roams the parent ion and extract a proton [Ekanayake, N. et al. Sci. Rep. 7, 4703 (2017)]. Site-specific details and femtosecond time-resolved dynamics of H_3^+ formation for a series of alcohols have been obtained through a combination of time-resolved mass spectrometry, photoion-photoion coincidence measurements, and ab initio calculations [Ekanayake, N. et al. Nat. Commun. 9, 5186 (2018)]. Of astrochemical importance is the fact that H_3^+ behaves as a Brønsted–Lowry acid, donating protons to carbon and oxygen atoms leading to the existence of organic molecules in the Interstellar Medium, the Central Molecular Zone of the Milky Way, and the ionospheres of our own planetary system’s gas giants. Our findings provide mechanistic and dynamic information about intriguing ultrafast chemical processes involving H_3^+ that may be relevant to the creation of water and organic molecules in our universe. Recent experiments indicate it is possible to enhance or suppress these strong-field triggered reactions via phase shaping, whilst maintaining the pulses’ spectrum, time-dependent intensity profile, and peak intensity constant [Michie, M.J. et al. J. Chem. Phys. 150, 044303 (2019)].

Institution: Michigan State University

Code: ULTPhoto_T29

Presenter: Michela Gazzetto (CHE)

Abstract Title: Surface Charge Mobility in Fluorescent Carbon Nanodots in Various Solvents by Means of Ultrafast Transient Absorption

Co-Author(s): A. Sciortino, M. Nazari, A. Das, E. Rohwer, T.Feurer, F. Messina, A. Cannizzo

Abstract: Carbon nanodots (CDs) are a novel family of optically-active carbonaceous nanomaterials, emerging at the beginning of 2000s and explored for many applications with the number of studies ranging now in the thousands per year. They are 1-10 nm nanoparticles endowed with a tunable and strong fluorescence in the visible, excellent solubility in aqueous environments and bio-compatibility, sensitivity to perturbations like the presence of metal cations and the capability of behaving as efficient photo-activated acceptors or donors of electrons and protons. Understanding their optical properties at a fundamental level is crucial to provide tailored designed samples.

As the fundamental properties are subject of strong debate in literature, we carried out an extensive ultrafast study femtosecond transient absorption (TA) spectroscopy on N-rich CDs in various solvents and pump-probe configurations. We could provide unanticipated insight on the photocycle of CDs, unravelling the relaxation steps upon photo-excitation with the characteristic timescales. Moreover ultrafast anisotropy studies in different solvents as water, ethanol, DMF and deep eutectic solvents (DES) allowed us to study the rotational diffusion of the transition dipole moment on fast timescales (10s ps), much faster than the rotational diffusion of the entire nanoparticles (10s ns). This finding reveals a diffusional energy transfer occurring through surface electronic states of the nanodots assisted by solvent fluctuations. The extensive study in DES, newly studied bio-compatible solvents related to ionic liquids, allowed important findings on the nature of the emission efficiency thanks to the possibility of varying the amount of water in solution.

Institution: Institute of Applied Physics, University of Bern, Sidlerstrasse 12, 3012 Bern, Switzerland

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Code: ULTPhoto_T30

Presenter: Xihan Chen (USA)

Abstract Title: Carrier Diffusion Length of >2.5 um in Sn-Pb Perovskites Enable Efficient Solar Cells

Co-Author(s): Jinhui Tong, Zhaoning Song, Dong Hoe Kim, Matthew C. Beard, Joseph J. Berry, Yanfa Yan, Kai Zhu

Abstract: Ultrafast carrier dynamics at interfaces plays a major role in governing solar energy conversion efficiency. For example, surface carrier dynamics in solar cells has a huge impact on its performance because it affects carrier lifetimes which can alter the attainable short-circuit current and open-circuit voltage.(1) Here, we developed a transient reflection spectroscopic (TR) techniques to probe the surface recombination velocity (SRV) and diffusion constant (D) for surface passivated low bandgap perovskite material. The SRV is found to decrease 10 times after surface treatment and has the value of 1.0 × 102 cm s−1. The diffusion length also shows a five time increase that can reach 2.5 um.(2) Our result suggests that the addition of GuaSCN could effectively increase the grain size and reduces defects to avoid surface recombination.

(1) Y. Yang, M. Yang, D. T. Moore, Y. Yan, E. M. Miller, K. Zhu, M. C. Beard, Top and bottom surfaces limit carrier lifetime in lead iodide perovskite films. Nat. Energy 2, 16207 (2017)
(2) J. Tong et. al., Carrier lifetimes of >1 μs in Sn-Pb perovskites enable efficient all-perovskite tandem solar cells. Science, published online, DOI: 10.1126/science.aav7911

Institution: National Renewable Energy Laboratory

Code: ULTPhoto_T31

Presenter: Dr. Julien Gorenflot (SAU)

Abstract Title: From Transient Spectroscopy on Films to Steady-state Solar Cell Device Performance

Co-Author(s): Dr. Safakath Karuthedath, Dr. Armantas Melianas, Prof. Zhipeng Kan, Prof Martijn Kemerink, Prof. Frederic Laquai

Abstract: Time-resolved spectroscopy is an unrivalled tool to study photophysical phenomena, involving both neutral and charged excited species, for instance, the processes involved in photocurrent generation and those limiting the device efficiency. However, it is not straightforward to extrapolate (transient) spectroscopy results acquired after pulsed laser excitation with high photon density to devices operating under steady-state one sun illumination conditions. In order to bridge that gap, we quantified the rates of the different photophysical processes, which we identified by transient absorption spectroscopy, and used them to simulate operating solar cell devices. The simulations indeed reproduce the experimentally-measured performances and thus explain the losses during photocurrent generation. Finally, our simulations enable us to gain information, which are experimentally not accessible, such as the density of neutral excited states, namely singlet and triplet excitons, in an operating organic solar cell. This paves the way to a better understanding of the impact of those states on the device performance.

Institution: King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC)

POSTERS

Code: ULTPhoto_P1

Presenter: Aamir Mushtaq (IND)

Abstract Title: An Insight into Strong Many-body Interactions in Ultrathin Anisotropic Tin (II) Monosulfide

Co-Author(s): Dr. Suman Kalyan Pal

Abstract: Layered two-dimensional (2D) transition metal chalcogenides have attracted incredible interest due to their intriguing electronic, electrical, and optical properties [1, 2]. Liquid phase exfoliation (LPE) technique has been employed for the synthesis of ultrathin tin sulfide (SnS) sheets. In our study ultrafast Transient absorption established many body process in this system, exciton-exciton annihilation was found to be significant in such anisotropic nanosheets of reduced dimensionality. Moreover, femtosecond Z-scan measurement infers that these 2D materials exhibit saturable absorption property because of optical transitions, which result in band filling from low to high energy band. The value of non-linear absorption coefficient was found greater and saturation intensity was found lower than that of other 2D materials. By taking the advantage of high nonlinear absorption coefficient and low saturation intensity ultrathin SnS nanosheets may prove to be a suitable candidate for various applications like saturable absorber, Q-switching.

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Code: ULTPhoto_P2

Presenter: Ming-Lun Syue (TWN)

Abstract Title: Photoisomerization of Retinal in Bacteriorhodopsin in Different Solubillization Conditions

Co-Author(s): Chung-Hao Cheng, I-Chia Chen

Abstract: Monomerized bacteriorhodopsin (mbR) was embedded in lipid nanodisc (nbR) using different sizes of covalently circularized membrane scaffold proteins and different lipid compositions. For comparison with varied oligomeric statuses of bR, native bR in purple membrane (PM), partially delipidated PM (dPM) and momeric bR solubilized in TX-100 (mbR) were also prepared. When bR is excited by light, the retinal of bR undergoes photoisomerization from all-trans, 15-anti to 13-cis, 15-anti via an intermediate state (I state), then initiates a photocycle reaction. The lifetime of the I state was detected using femtosecond transient absorption upon excitation at 575 nm and 550 nm, to confirm the excitation wavelength dependent photoisomerization kinetics. We found that the bR in trimeric forms, including PM and dPM, possess similar retinal photoisomerization kinetics (lifetime of I state τ_I=0.6~0.7 ps), which is different from monomeric bR, including mbR and nbR (τ_I=0.9~1.4 ps). Moreover, there is no distinguishable difference in photoisomerization when monomeric bR was embedded in different sizes of nanodiscs or different composition containing dioleoyl phosphatidylglycerol (DOPG) and dioleoyl phosphatidylcholine (DOPC). Besides, the retinal photoisomerization kinetics upon excitation at 575 nm and 550 nm seemed to behavior similarly. We thus suggested that the positions of the charged residues at the vicinity of retinal in the monomerized bR differ from those in the trimer form and thus altered the rate of photoisomerization. However, the size of nanodisc and lipid composition of nbR have less effect on protein structures and charge distribution around retinal, resulting in similar kinetics of photoisomerization.

Institution: Department of Chemistry, National Tsing Hua University

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Code: ULTPhoto_P3

Presenter: Changmin Lee (KOR)

Abstract Title: Photoinduced Symmetry-Breaking Charge Transfer Dynamics of 9,9'-Bianthracene

Co-Author(s): Cheol Ho Choi, Taiha Joo

Abstract: 9,9’-Bianthracene (BA) is a representative molecule showing symmetry-breaking charge transfer (SBCT), which is important in the early stage of photosynthesis [1]. BA, which consists of two anthracene rings, has an orthogonal torsional angle between two rings in the ground state. Upon photoexcitation, only one anthracene ring is excited, and the state is called a locally excited state (LE state). Additional charge transfer (CT) from one anthracene ring to another ring occurs only in polar solvents [2]. Using time-resolved fluorescence (TF) with high time resolution and excited-state quantum mechanics (QM)/molecular mechanics (MM) molecular dynamics (MD) simulation, dynamical details of BA are investigated.

Reaction rate obtained from the TF spectra of BA in ethanol and acetonitrile is almost the same as the rotational part of the solvent time correlation function [3]. Excited-state QM/MM MD simulation is performed with BA as the QM part and 378 acetonitrile molecules as the MM part in 65 Franck-Condon points. The torsional angle between two rings is found to be a reaction coordinate from the LE state to the CT state. Partial charge transfer occurs by the fluctuation of the solvent that gives an electric field about 1.0×108 V·m-1 followed by a cooperative motion of the solvent and the solute that strengthening the charge transfer, and to the full charge transfer is achieved.

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Code: ULTPhoto_P4

Presenter: Seongsoo Kang (KOR)

Abstract Title: Ultrafast Coherent Exciton Dynamics in Size-controlled Perylene Bisimide Aggregates

Co-Author(s): Christina Kaufmann

Abstract: Our time-resolved emission spectroscopic observation of perylene bisimide (PBI) H-aggregates showed that an initially delocalized Frenkel exciton is localized by ultrafast excimer formation. The exciton migration dynamics that was not observed in small aggregates comprising less than four PBI subunits was observed only in larger aggregates consisting of at least more than 10 PBI subunits. In this study, we focused on the transient re-orientations of electronic transition dipoles by interactions between the PBI subunits in PBI H-aggregates. The disparity of ultrafast coherent exciton dynamics according to the molecular aggregate sizes can be distinguished using polarization-dependent fs-transient absorption anisotropy (TAA) spectroscopic measurements with a time resolution of ~40 fs. The decay profiles of the anisotropy values are unaffected by vibrational relaxation and rotational diffusion processes; hence, the coherent exciton dynamics of the PBI H-aggregates prior to the excimer state formation can be revealed by our TAA measurements.

Institution: Yonsei University

Code: ULTPhoto_P5

Presenter: Jumi Park (KOR)

Abstract Title: Ultrafast Charge Transfer in Pyrenyl Derivatives through Adiabatic Potential Energy Surface

Co-Author(s): Jooyoung Sung

Abstract: Optically induced charge transfer (CT) is at the heart of many dynamic processes in chemistry and biology. Since the efficiency of CT is often decisive for the overall functions, it is crucial to understand the CT dynamics. In this study, we have revealed the mechanism of ultrafast CT processes in pyrenyl derivatives. Because the CT dynamics in these push-pull systems leads to initial CT emission in the same spectral range as the locally excited (LE) emission, it has been challenging to unravel the ultrafast CT processes. Based on fluorescence anisotropy decay processes, we suggest that pyrenyl derivatives exhibit the precursor-successor type CT dynamics. Furthermore, a comparative analysis allows us to suggest that photoexcitation of bridge moiety in pyrenyl derivatives leads to strong electronic coupling between the LE and CT state. Therefore, the enhanced CT mechanism through the adiabatic potential energy surface (PES) occurs.

Institution: ULTPhoto!Fxx

Code: ULTPhoto_P6

Presenter: Kathryn Ledbetter (USA)

Abstract Title: Time-Resolved X-ray Diffuse Scattering as a Probe of Site-Specific Solvation

Co-Author(s): K Kunnus, R Parrish, E Hohenstein, E Biasin, M Reinhard, TB van Driel, R Alonso-Mori, AA Cordones-Hahn, TJ Martinez, KJ Gaffney

Abstract: When the structure or charge distribution of a molecule in solution changes, the solvent cage rearranges, with consequences for the outcome and efficiency of chemical reactions. For systems with specific solvent-solute interactions, such as hydrogen bonding, continuum solvation models can fail, requiring a molecular approach to understanding solvation and a corresponding direct experimental probe. Time-resolved X-ray diffuse scattering (TR-XDS) offers such a probe, as it directly encodes information about all pair correlations between atoms in a solution. It is straightforward to obtain simulated scattering signals from molecular dynamics calculations and compare these to the data. Thus, XDS can be used as a tool to validate molecular simulations of solvation at various levels of theory.

Data taken at the LCLS on aqueous [Fe(2,2'-bipyridine)(CN)4]2- offer preliminary insight into specific solvent interactions. The molecule is excited to an MLCT state, which decays (87 fs) into a metal-centered triplet (3MC) state with a 13 ps lifetime[1]. The TR-XDS signal for the 3MC state, in conjunction with quantum chemical calculations of the solute structural changes, reveal a solvent cage contribution of comparable magnitude to the solute signal. This implies a sensitivity to changes in average N-(H)-O distances set by hydrogen bonding of the cyano ligands with surrounding water. Continued work will determine the level of theory necessary to model the data, and a successful model will offer insights into the nature of specific solute-solvent interactions.

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Institution: Department of Physics, Stanford University; PULSE Institute, Stanford University/SLAC Linear Accelerator Laboratory

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Code: ULTPhoto_P7

Presenter: Jungsoo Ahn (KOR)

Abstract Title: Investigation of the non-Condon Effect through Oscillatory Signals of Transient Absorption

Co-Author(s): Taiha Joo

Abstract: Probing nuclear wave packet evolution has made it practicable to observe molecular vibrations and reaction dynamics in real time. A propagation of the wave packet on the excited or ground states is reflected in a time-dependent spectroscopic signal. Transient absorption (TA) [1], time-resolved fluorescence (TF) [2], and transient grating [3] are the representative techniques in which the wave packet motions are revealed in their intensity modulations.

Notwithstanding the practicability, it is not easy to pinpoint the origin of observed intensity modulation. The Condon approximation has been generally applied, that is, the change of transition dipole moment upon vibrational motions is ignored. Therefore, intensity modulations in TA and TF are assumed to originate from the oscillation of the transition energy over time. Recently, however, the non-Condon effect have gained attention as its effects on quantum coherence has pointed out. For example, the non-Condon effect was claimed to intensify the dynamical electronic vibrational energy transfer, and to enhance the total system-and-bath quantum coherences [4].

On that account, it is useful to analyze the influence of the non-Condon effect on the intensity modulation. It would be possible by analyzing the initial phase difference of the oscillations recorded at the blue and red side wavelengths of a spectral band. If the non-Condon effect is indeed negligible, phases of the oscillations at the blue and red wavelengths would be 180° out of phase. Conversely, if an oscillation is originated solely from change of the transition dipole moment by a particular molecular vibration, phases of the oscillations at the blue and red wavelengths would be in phase. The analysis can be a key to elucidate which specific normal modes induce the change of transition dipole moment.

In this work, we present TA spectra of indocyanine green, (ICG; also known as IR-125). From the TA spectra, we can observe several intensity modulations. The influence of the non-Condon effect can be estimated using the initial phase difference analysis. The analysis and discussion about the non-Condon effect from vibrational modes will be presented.

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Institution: Pohang University of Science and Technology

Code: ULTPhoto_P8

Presenter: PyoungSik Shin (KOR)

Abstract Title: Ultrafast (20 fs) Time-resolved Fluorescence Spectroscopy

Co-Author(s): Taiha Joo

Abstract: Time-resolved fluorescence (TF) provides information on the photo-induced reaction dynamics occurring in the excited state exclusively. By monitoring the coherent vibrational state in the excited state induced by short optical pulses, the real-time molecular vibrations as well as the clear reaction rate can be observed [1]. To improve the bandwidth of a vibration spectrum via wave packet evolution in the excited state, time resolution of the TF apparatus should be improved. Considering the effect of dispersion and phase matching conditions, We developed a fluorescence up-conversion apparatus with time resolution better than 18 fs, which could give a vibration spectrum via wave packet up to 2000 cm-1 including C=O stretching [2].

We employed a Ti: sapphire laser generating < 7 fs pulses at 800 nm to fabricate the fluorescence up-conversion apparatus. To minimize the group velocity dispersion (GVD) and the third order dispersion (TOD), a chirped mirror pair and reflective optics were used instead of a prism pair and lenses. A crossing angle between the gate and the fluorescence signal at the noncollinear crystal, at which sum frequency generation (SFG) occurs, was optimized to 4 degrees. The FWHM of the cross-correlation between the scattered pump and the gate pulses was 18 fs by using a 50-μm-BBO crystal. We have studied the excited state intramolecular proton transfer dynamics of 10-hydroxybenzo[h]quinolone (HBQ) by the TF apparatus.

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Institution: POSTECH

Code: ULTPhoto_P9

Presenter: Taisei Kataoka (JPN)

Abstract Title: Photochromic Reaction of CdTe Quantum Dots-Diarylethene Derivative Hybrid System In Silent Wavelength

Co-Author(s): Yuta Usui, Daiki Shibayama, Tetsuro Katayama, Masakazu Morimoto, Masahiro Irie, Naoto Tamai

Abstract: Diarylethene derivatives (DAE) are well known compounds to show reversible photochromic reactions with UV and visible light. By attaching DAE on surface of semiconductor quantum dots (QDs), a new optical function will be expected. In the present study, we constructed a hybrid system of CdTe QDs with DAE and analyzed excitation wavelength dependence on the photochromic reaction yield.
We synthesized CdTe QDs (diameter ≈ 3.6 nm) with 600 nm luminescence maximum by a colloidal synthetic method [1]. It was found that the reaction yield from the open (DAEO) to closed (DAEC) isomers in the hybrid system (CdTe QDs-DAE) was much higher than that in DAE solution even though the excitation at 420 nm, in which the absorption coefficient of DAEO is negligibly small.
In addition, the ring-closure reaction proceeds in the hybrid system even in longer wavelength region at 460 nm, although no reaction was observed in DAE solution. These data indicated that the hybrid system has the process of promoting the ring-closure reaction in silent wavelength region without absorption of DAEO.
Time-resolved luminescence and femtosecond transient absorption spectroscopy were applied to reveal the mechanism of the process of promoting the ring-closure reaction in the hybrid system.

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Institution: Department of Chemistry, Kwasei Gakuin University

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Code: ULTPhoto_P10

Presenter: Yoko Tanabe (JPN)

Abstract Title: Elementary Carrier Relaxation and Transfer Processes of ZnSe QDs

Co-Author(s): Shota Kori, Yuta Usui, Tetsuro Katayama, Naoto Tamai

Abstract: Among the variety of Ⅱ-Ⅳ semiconductor quantum dots (QDs) such as CdSe and CdTe, ZnSe QDs have high potential applications to UV-blue-emitting materials, since ZnSe has the bulk band gap of 2.7 eV at room temperature and exciton Bohr radius of 5.7 nm and also less toxic, cadmium free chalcogenides [1]. However, very low luminescence quantum yields of ZnSe QDs have been reported and the elementary exciton processes have not been well explored yet. In the present study, we synthesized ZnSe QDs by using a colloidal synthesis with two different ways, a hot soap method and a flow injection, to improve luminescence quantum yields.
Elementary exciton relaxation and carrier transfer processes of ZnSe QDs were examined by picosecond luminescence spectroscopy and femtosecond transient absorption spectroscopy. Luminescence quantum yield (QY) and luminescence lifetime of ZnSe QDs by a flow injection are higher and shorter than ZnSe QDs by a hot soap method. However, exciton lifetime of ZnSe QDs by a flow injection is shorter than ZnSe QDs by a hot soap method. These results suggest that luminescence spectrum of ZnSe QDs is probably originated from defect sites.

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Institution: Department of chemistry, Kwansei Gakuin University

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Code: ULTPhoto_P11

Presenter: Kosuke Tsuji (JPN)

Abstract Title: Hot Electron Transfer Dynamics of CdSe/ZnS Quantum Dots-Methyl Viologen Systems

Co-Author(s): Yuta Usui, Tetsuro Katayama Naoto Tamai

Abstract: Recently, much attention has been paid for the efficient carrier extraction from colloidal semiconductor nanocrystals. Especially, hot carrier transfer from higher excited states in NCs is useful for photovoltaic applications to overcome the Shockley-Queisser limit in solar energy conversion [1]. Hot carrier transfer in heterostructured semiconductor quantum dots (QDs) has not been well analyzed and fundamental understanding of this process is very poor, even though the band- edge electron transfer from core to organic acceptor molecule has been reported in CdSe/ZnS core/shell QDs [2]. In the present study, we synthesized CdSe/ZnS core-shell QDs and characterized their optical properties [3, 4]. In addition, electron acceptor molecule, methyl viologen (MV2+), was adsorbed on CdSe/ZnS core-shell QDs. Picosecond luminescence and femtosecond transient absorption spectroscopies were used to analyze the elementary electron transfer processes from higher excited states and band-edge states in CdSe/ZnS core-shell QDs-MV2+ systems. Ultrafast hot electron transfer (~ 100 fs) was detected from core CdSe to MV2+ even in the existence of ZnS shell. The rate and yield of hot electron transfer will be analyzed as a function of shell thickness.
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Institution: Department of Chemistry, Kwansei Gakuin University

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Code: ULTPhoto_P12

Presenter: Masafumi Koga (JPN)

Abstract Title: Photoionization Dynamics of Aromatic Compounds in Solution Phase Induced by Femtosecond Multiphoton Excitation

Co-Author(s): Yusuke Yoneda, Hikaru Sotome, and Hiroshi Miyasaka

Abstract: Photoionization is one of the simplest primary processes in photochemical reactions. The ionization in solutions can take place from higher excited (Sn) state due to the polarization of the surrounding media when the excitation energy is lower than the gas-phase ionization potential [1]. In order to elucidate the dynamical effect of the solvent polarization on the photoionization dynamics, we have investigated ionization dynamics of organic compounds in polar and non-polar solvents by femtosecond transient absorption spectroscopic system under double-pulse excitation. In this experiment, the first pump pulse (pump1) excites the molecule to the lowest-excited (S1) state and second pump (pump2) induce Sn-S1 transition. By monitoring the time evolution of the transient absorbance change induced by pump2 irradiation, we can observe the photoionization dynamics occurring from Sn state. The obtained results about photoionization of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) in ethanol show that the Sn state absorption appears immediately after photoexcitation, which is followed by the rapid deactivation in 70 fs. On the other hand, the absorption of the radical cation appears in the time scale of ~5 ps. This gradual generation of the cation clearly indicates that the ionization does not proceed directly from Sn state but through the specific intermediate state.

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Institution: Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University, Japan

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Code: ULTPhoto_P13

Presenter: Stefan Haacke (FRA)

Abstract Title: Retinal-protein Interactions Tune the Excited State Electronic Structure in Retinal Proteins: Example Anabaena Sensory Rhodopsin

Co-Author(s): D. Agathangelou, M. del Carmen Marin Pérez, Y. Orozco-Gonzalez, J. Brazard, H. Kandori, K-H. Jung, J. Léonard, M.Olivucci

Abstract: nabaena sensory rhodopsin (ASR) is a microbial retinal protein for which the protonated Schiff base of retinal (PSBR) adopts the the all-trans,15-anti (AT) and 13-cis, 15-syn (13C) conformations in a ratio depending on illumination conditions. AT and 13C undergo two distinct photo-cycles [1]. The interest of studying the primary steps of retinal proteins' photo-cycle via femtosecond spectroscopy originates from a long-standing question, on how the protein environment tunes and optimizes the photoisomerization reaction speed and yield. In this context, ASR is a particularly suitable model system, since it allows to study the photoreaction of both conformers in the same protein environment at the same time. In particular, the excited state lifetime (ESL) is representative of the photoisomerization speed. In the wild-type protein (WT-ASR), it is only 110fs for 13C, and ~7 times longer for AT (750fs) [2,3]. We report on point mutated proteins showing in single mutants an unexpected reduction of the AT isomer ESL with respect to WT-ASR, with a trend indicating a correlation between ESL and absorption maximum wavelength [4]. Interestingly, the 13C isomer ESL shows the opposite effect, i.e. the excited state decay is slowed down upon mutation. In a special double mutant, the AT/13C lifetime increases up to 6 ps [5]. Quantum chemistry calculations show subtle effects of protein-PSBR interactions on the excited state electronic structure, in particular non-adiabatic S1/S2 mixing, which may introduce shallow excited state barriers, slowing down the photo-reaction [5].

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Institution: University of Strasbourg & CNRS, IPCMS, F-67034 Strasbourg Cedex

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Code: ULTPhoto_P14

Presenter: Ayana Fujitaka (KOR)

Abstract Title: Exciton Dynamics of Small Sized InP Quantum Dots and Its Core-shell Structure

Co-Author(s): Yuta Usui, Tetsuro Katayama, Naoto Tamai

Abstract: InP quantum dots (QDs) is a typical Cd-free QDs and bulk band gap (Eg) has similar with CdSe or CdTe. In recent years, a new synthetic method of high quality InP QDs has been developed1), in which various InX3 (X=Cl, Br, I) precursors were used to control QDs size. In addition, the attachment of ZnS or ZnSe shell on InP QDs is essential to enhance their luminescence quantum yield. However, very little is known on their exciton dynamics of bare InP QDs and core-shell InP QDs. In the present study, we synthesized InP QDs with a diameter smaller than 2.0 nm. Their exciton dynamics were examined by picosecond luminescence spectroscopy and femtosecond transient absorption spectroscopy. It was found that a few ps Auger recombination lifetime was observed for small sized InP QDs prepared from InI3. Ultrafast lifetime of Auger recombination is originated from strong Coulomb interaction of electron and hole in small confined region. In addition, the hot electron trapping from higher excited state to surface trap sites was observed with a lifetime of 140 fs. Exciton dynamics of core-shell InP QDs will be also analyzed by femtosecond state-selective transient absorption spectroscopy and the effect of shell on exciton dynamics will be discussed.

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Institution: Kwansei Gakuin University

Code: ULTPhoto_P15

Presenter: Olivia A. Krohn (USA)

Abstract Title: Time-Resolved Photochemistry of Stiffened Stilbenes

Co-Author(s): Martin Quick, Ilya N. Ioffe, Olga N. Mazaleva, Dieter Lenoir, Heiner Detert, and Sergey A. Kovalenko

Abstract: Broadband transient absorption spectroscopy is used to study the photoisomerization of stiffened stilbene derivatives in solution, an E/Z mixture of bis(benzocyclobutylidene) (t4, c4) and (E)-1-(2,2-dimethyltetralinylidene)-2-2-dimethyltetraline (t6). Upon excitation to S1, all evolve to perpendicular molecular conformation P, followed by decay to S0, but the exact kinetic behavior crucially depends on the type of the stiffening ring. In 4, the S1→ P torsion is characterized by the two distinct time constants of 172 and 77 ps in n-hexane, or 116 and 44 ps in acetonitrile. We attribute them to t4 and c4, respectively, while P itself cannot be discerned due to its rapid decay to S0. Faster isomerization in polar solvents confirms the zwitterionic character of the P-state. In t6, the transition to P is effectively barrierless and is completed within 0.3 ps, the P-state being directly traceable through its transient ESA features about 360 nm. In n-hexane P is remarkably long-lived, τP=1840 ps, while in acetonitrile its lifetime drops down to 35 ps. The t6 trans-to-cis photoisomerization yield is measured to be 20%. We discuss the effects of stiffening and substitution on the formation and lifetime of the intermediate states through which the stilbene molecules evolve on the S1 energy surface.

Institution: University of Colorado, Boulder

Code: ULTPhoto_P16

Presenter: Ifeanyi K. Madu (USA)

Abstract Title: Ultrafast and Nonlinear Spectroscopy, of New Naphtho[1,2-b:5,6-b']difuran Donor Organic Photovoltaic (OPV) Polymers

Co-Author(s): Muller, E. W.; Kim, H.; Shaw, J.; Burney-Allen, A. A.; Zimmerman, P.; Jefferies-El, M.; Goodson III, T

Abstract: Conjugated polymers are promising alternatives to inorganic semiconductors in a wide range of electronic applications such as organic photovoltaics (OPVs), organic thin film transistors, and sensors. Understanding the optical properties of these materials shed light to the electron-photon interactions (i.e. structure-function relationships) that occur in the molecular level within these materials. Photophysical properties of four novel conjugated donor OPV polymers were investigated to understand the influence of heteroatoms in the polymer backbone, and the sidechains were varied as well to study the effect of polymer solubility on these properties. Steady state absorption studies showed that the polymer with furan backbone displayed a favorable tendency of capturing more solar photons when used in a photovoltaic device. Excitonic lifetime was monitored using ultrafast dynamics, and the results obtained show that the kind of heteroatom used in the backbone affects the decay dynamics of the polymer; the side chain also plays a subtle role in determining the fluorescence decay time. Theoretical calculations confirm the two-photon absorption cross-section (TPA-δ) results obtained, illustrating the planarity of the molecules in relation to its torsional angles. The natural transition orbitals were also computed, describing the electron and hole transition orbitals for each of the molecule. A pump-probe technique was employed to probe the non-emissive and charge transfer states of the polymers.

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Madu, I. K.; Muller, E. W.; Kim, H.; Shaw, J.; Burney-Allen, A. A.; Zimmerman, P.; Jefferies-El, M.; Goodson III, T. Heteroatom and side chain effects on the optical and photo-physical properties: Ultrafast and non-linear spectroscopy of new Naphtho[1,2-b:5,6-b'] difuran donor polymers. J. Phys. Chem. C, 2018, 122(30), 17049 – 17066.

Institution: University of Michigan, Ann Arbor

Code: ULTPhoto_P17

Presenter: Madu K. Ifeanyi (USA)

Abstract Title: Ultrafast Excited State Dynamics of Partially and Fully Functionalized Silsesquioxanes

Co-Author(s): Jin Zhang, Santy Sulaiman, Richard. M. Laine, Theodore Goodson III

Abstract: A series of dimethylaminostilbene substituted silsesquioxanes (SQs) – Me2NStilbeneSi(OSiMe3)3 {Corner}, [Me2NStilbeneSi(O)(OSiMe3)]4 {Half} and [Me2NStilbeneSiO1.5]8 {Cube}, which contain partially and fully functionalized cages were investigated by ultrafast fluorescence upconversion and femtosecond transient absorption spectroscopy. These nonlinear techniques were used to study the mechanism of excitation energy transport and excited state dynamics of these functionalized SQ structures. A strong fluorescence lifetime dependence was observed in all three systems. Depolarization of the fluorescence in the Half and Cube systems indicates excitation energy delocalization between the chromophores due to strong electronic coupling. The ultrafast rise time obtained from the upconversion experiment clearly depicts the fast transition taking place in the system after photoexcitation. Transient absorption dynamics and two photon absorption (TPA) measurements reveal the presence of ultrafast charge delocalization in the Half and Cube systems. Blue shifts in the excited state absorption (ESA) observed in all three SQ systems correlate with the solvation process and reveal a solvent-stabilized state. The amount of ESA blue shift indicates an increase in the charge-transfer character of the excited state in the case of the Half and Cube systems. This explains their enhanced two-photon cross sections in comparison to that of the Corner SQ system.

Reference:
Zhang, J.; Madu, I. K.; Sulaiman, S.; Goodson III, T. Ultrafast excited state dynamics of partially and fully-functionalized silsesquioxanes. J. Phys. Chem. C, 2019, 123(8), 5048 – 5060.

Institution: University of Michigan

Code: ULTPhoto_P18

Presenter: Andrew J. Chomas (USA)

Abstract Title: The 1(TT) State in a Covalently Linked Double Benzene: Relation of Intramolecular Photocycloaddition to Singlet Fission

Co-Author(s): Jörn Tonne, Eberhard Riedle, Zdenek Havlas, Josef Michl

Abstract: The [3.3]-o-cyclophane 4,5;9,10-Dibenzotetracyclo[6.6.1.1^3,6.0^2,7]dodeca-4,9-diene (1) contains two covalently linked benzene moieties. After excitation to S1 a photochemically reversible intramolecular [2 + 2] photocycloaddition to Octacyclo[12.5.1.0^2,7.0^2,13.0^7,18.0^8,13.0^8,16.0^17,20]icosa-3,5,9,11-tetraene (2) occurs on the order of one hundred picoseconds in competition with excimer-like fluorescence; it is suppressed at low temperatures. Upon initial excitation to a higher singlet excited state, the fluorescence quantum yield decreases and the cycloaddition yield increases, indicating an additional pathway to the S1/S0 conical intersection that is associated with the crossing of the ground and doubly excited 1(TT) configuration and accounts for the formation of 2. Femtosecond transient absorption spectroscopy in the UV shows that upon the higher energy excitation a fraction of 2 forms on a sub-picosecond time scale, competing with internal conversion to S1. CASPT2 calculations suggest that the photocycloaddition from S1 is slow since an activation barrier is present on the way from the excimer minimum to the S1/S0 conical intersection, whereas the pathway from the higher excited singlet resembles the singlet fission process, with the 1(TT) doubly excited state leading directly to the conical intersection. The results tie the singlet fission process to the Woodward-Hoffmann-Oosterhoff description of photochemical pericyclic reactions and suggest potential pathways for some of the ultrafast decay to S0 occasionally observed in singlet fission studies.

Institution: University of Colorado Boulder

Code: ULTPhoto_P19

Presenter: Stephen Roille (CHE)

Abstract Title: 2D Spectroscopy on Molecular J-aggregates using Shaped Pulses

Co-Author(s): Andrea Cannizzo, Thomas Feurer

Abstract: The presence of long-lived oscillations is regularly observed in biological light harvesters (Fenna−Mathews−Olson complexes) [doi: 10.1038/nature05678] and is also found in artificial systems [doi:10.1038/ncomms8755]. While the role played by the electronic coherence in conveying energy is still debatable, the lifetime of these collective motions is unexpectedly long and seem to be supported through vibronic couplings.

Self-assembled aggregates have a long-range molecular order that promotes excitonic delocalization. In particular, J-aggregates (S2284) form long cylindrical tubes and present a simple 3-fold excitonic structure with orthogonal transition dipole moments that can align macroscopically in a flow-jet. This particular system is an ideal test case to identify microscopic mechanisms behind long-lasting coherences and exciton dynamics.

Investigation of coherent energy transfers and couplings is possible via two-dimensional spectroscopy but requires interferometric phase stability. We reported the viability of this approach using a spatial light modulator to independently control pulse delays and perform phase cycling to remove noise scattering in the four-wave mixing interaction [doi: 10.1063/1.4921793]. The spatial separation of the interacting fields allows independent control of the polarization to selectively excite the dipole moments.

To further investigate the nonlinear optical response of the aggregates the spatial light modulator is used to shape amplitude and phase of each pulse. This allows decongesting even further the two-dimensional spectra through selective spectral excitation. In addition, a novel variation of time-domain ptychography is presented as a robust pulse reconstruction technique to measure and correct the phase at the sample position [doi:10.1103/PhysRevA.91.021803].

Institution: Institute of Applied Physics, University of Bern, Switzerland

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Code: ULTPhoto_P20

Presenter: Martha. A. Hermosilla-Palacios (USA)

Abstract Title: Using 2D Spectroscopy to Understand Excited State Dynamics

Co-Author(s): Sofia Eugenia Dominguez, Luis Baraldo-Victorica and Valeria D. Kleiman

Abstract: We will present studies of polypyridine ruthenium complexes. These light-harvesting materials present complex excited state dynamics that are difficult to understand using one-dimensional time-resolved spectroscopies. We tackle this challenge using two-dimensional spectroscopy in the visible regime to identify multiple excited states and their couplings.

Institution: University of Florida

Code: ULTPhoto_P21

Presenter: Laura Estergreen (USA)

Abstract Title: Anisotropic Study of Coupled Chromophores towards the Application of Symmetry Breaking Charge Transfer

Co-Author(s): Jessica H. Golden, Mark Thompson and Stephen Bradforth

Abstract:

Symmetry breaking charge transfer (SBCT) is the process in which a pair of identical, orthogonal chromophores are coupled, either by a bridging carbon-carbon bond or through a d0 or d10 metal, such that post excitation the exciton (electron-hole pair) can dissociate between the two chromophores. The end-product is a positive and negative chromophore which are orthogonal to one another, reducing the probability of recombination of the electron and hole. By inhibiting recombination of charges, this process could beneficial for photoelectrochemistry and photovoltaic applications. Herein we compare the time-resolved anisotropy of two compounds; a meso bridged borondifluoro dipyridylmethene (bis-DIPYR) dimer and a dipyrrinato dimer system bridged by a Zn2+ (zDIP2). The Zinc in the later is a d10 metal whose higher lying orbitals do not participate in the movement of the electron or hole as populating them is very energetically unfavorable. However, in the DIPYR dimer charge transfer can occur through the carbon-carbon bond where molecular torsions and vibrations can assist in or couple to charge separation. zDIP2 has been shown to have a typical solvent dependence, where in nonpolar solvents SBCT does not occur, but in weakly polar to very polar solvents SBCT occurs from picoseconds to hundreds of femtoseconds, respectively. Bis-DIPYR, however, has been shown to have a slight solvent dependence where SBCT still occurs in cyclohexane but occurs more rapidly in more polar solvents like tetrahydrofuran and acetonitrile. These differences imply a difference in mechanism of SBCT and can be investigated through ultrafast pump-probe anisotropy.

Institution: University of Southern California

The 29th International Conference on Photochemistry
Boulder, Colorado
July 21 – 26, 2019

ATMOSPHERIC AND ENVIRONMENTAL PHOTOCHEMISTRY (ATMEnv)
ABSTRACTS

INVITED TALKS

Code: ATMEnv_I1

Presenter: Kristopher McNeill (CHE)

Abstract Title: Energy and Electron Transfer Properties of Triplet State Natural Organic Matter

Co-Author(s): Kyle Moor, Markus Schmitt, Paul Erickson

Abstract: Natural organic matter (NOM) is a complex mixture of naturally occurring organic compounds that come from the breakdown of terrestrial and aquatic plants, and is ubiquitous in natural waters. In many, if not most, surface water systems, NOM is the dominant photosensitizer, responsible for both the direct oxidation of target molecules (e.g., pollutants) and also for the production of downstream oxidants, such as singlet oxygen. Studying triplet state NOM is made challenging by the fact that it is a complex mixture and conventional methods to study triplet states (e.g., transient absorbance) do not work well. In this presentation, an overview of steady-state and laser spectroscopy-based time-resolved techniques used to study triplet NOM will be presented. This will include a synopsis of what we have learned so far and where the knowledge gaps that must be addressed in the future lay.

Institution: ETH Zurich

Code: ATMEnv_I2

Presenter: Vicki H. Grassian (USA)

Abstract Title: Multiphase Photochemistry Relevant to Marine Environments

Co-Author(s): Jonathan Trueblood, Man Luo, Michael Alves, Michael Sullivan, Stephanie Mora-Garcia

Abstract: This talk will focus on some recent advances in measurements of the multiphase chemistry and photochemistry relevant to marine environments and sea spray aerosol. Photochemistry in the marine boundary layer gives rise to: new particle formation, aerosol and molecular transformations and production of key atmospheric gases in the troposphere including nitrous acid. The overall goal is to delineate the importance of photochemistry in the marine boundary layer and its role in atmospheric chemistry by providing a molecular description of light absorbing components within the sea surface microlayer and sea spray aerosol and a molecular understanding of the photo-processes involved. Thus this talk will focus on studies that on new studies of light absorbing components within the sea surface microlayer and in sea spray aerosol; understand model systems from theoretical and experimental perspectives from simple to more complex chromophores - role of ions, pH, speciation and surface versus bulk energetics.

Institution: University of California San Diego

Code: ATMEnv_I3

Presenter: Sergey A. Nizkorodov (USA)

Abstract Title: Condensed-phase Photochemistry in Organic Aerosol Particles

Co-Author(s): Multiple collaborators will be acknowledged during the presentation

Abstract: While the organic photochemistry is a mature field, the photochemical behavior of organic molecules in atmospheric aerosol particles remains poorly understood. The particles contain highly complex mixtures of organics in a highly-viscous or even glassy state, which is a very different environment compared to the much simpler solutions typically studied in organic photochemical experiments. In addition, only relatively low energy radiation with wavelengths above 300 nm is available for photochemistry in the lower atmosphere, whereas most organic photochemistry experiments rely on the standard 254 nm Hg-lamp irradiation. This presentation will describe our recent experiments on condensed-phase photochemistry of organic compounds in primary (such as biomass burning) and secondary organic aerosols. The exposure of organic aerosols to solar radiation produces a number of important effects: the chemical composition of aerosols changes; the particles tend to lose material due to the preferential photodegradation of larger, less volatile compounds leading to smaller, more volatile products; the light absorption properties of the organic material changes. These effects have important consequences for understanding the effect of aerosol particles on climate and health. These projects involve multiple collaborators who will be acknowledged during the presentation.

Institution: Department of Chemistry, University of California, Irvine

Code: ATMEnv_I4

Presenter: Joseph S. Francisco (USA)

Abstract Title: Atmospheric Spectroscopy and Photochemistry at the Air-Water Interface

Co-Author(s): Jie Zhong

Abstract: The air–water interface is ubiquitous in nature, as manifested in the form of the surfaces of oceans, lakes, and atmospheric aerosols. The aerosol interface, in particular, can play a crucial role in atmospheric chemistry. The adsorption of atmospheric species onto and into aerosols modifies their concentrations and chemistries. Moreover, the aerosol phase allows otherwise unlikely solution-phase chemistry to occur in the atmosphere. The effect of the air–water interface on these processes is not entirely known. This talk will review recent theoretical investigations of the interactions of atmosphere species with the air–water interface, including reactant adsorption, photochemistry, and the spectroscopy of reactants at the water surface, with an emphasis on understanding differences between interfacial chemistries and the chemistries in both bulk solution and the gas phase.

Institution: University of Pennsylvania

CONTRIBUTED TALKS

Code: ATMEnv_T1

Presenter: Marat R. Talipov (USA)

Co-Author(s): Punhasa Senanayake, Raulia Syrlybaeva

Abstract Title: Prediction of the Structure and Reactivity of Long-Bonded Molecules

Abstract: Long-bonded molecules form a subclass of reactive intermediates in which some of the chemical bonds arise from the interaction of the opposite-spin electrons localized on non-adjacent atoms. One example of such long-bonded molecules is isonitrosyl hydroxide, HO—ON. Using ab initio electronic structure methods, we have investigated the electronic structure, thermodynamic stability, and chemical reactivity of HO—ON and its analogues. The computational analysis demonstrates that the formation of such long-bonded molecules significantly impacts the electronic structure and chemical reactivity of the involved radical fragments. On the example of the reaction of molecular bromine and nitric oxide, we show that awareness of the long-bonding interactions can be used for the prediction of hitherto unknown low-energy reaction pathways. To summarize, this study contributes to the development of a better understanding of the properties and reactivity of reactive intermediates.

Institution: New Mexico State University

Code: ATMEnv_T2

Presenter: Baoshan Wang (CHN)

Co-Author(s): Xiaojuan YU, Hua HOU

Abstract Title: Theoretical Study on the Photodissociation of Heptafluoroisobutyronitrile: Intersystem Crossing and Nonadiabatic Mechanisms

Abstract: Heptafluoroisobutyronitrile (C4) has been developed as a very promising environmentally sustainable alternative to SF6 which is the most important dielectric gas with massive applications in high-voltage electrical industry but suffers from the strongest greenhouse effect. Prior to its large-scale industrial use, an assessment of atmospheric chemistry and environmental impact of C4 is needed. The unimolecular decomposition of C4 and reaction with hydroxyl radical were studied by the authors[1,2]. However, the photodissociation of C4, an apparently important degradation mechanism in atmosphere, has never been studied experimentally or theoretically. Herein, the electronically excited states of C4 are investigated using various ab initio methods including time-dependent density functional theory, multiconfiguration self-consistent-field, multireference second-order Rayleigh-Schrodinger perturbation theory and configuration interaction. The UV absorption spectrum is produced using the nuclear-ensemble approach. Decomposition of C4 on a total of 11 excited potential energy surfaces (5 singlets and 6 triplets) has been clarified for the first time. The minima on seams of crossing including conical intersection together with the spin-orbital coupling between various states are obtained as well. It was found that C4 has a broad UV adsorption band in the range 120 - 320 nm. Photoexcitation from S0 through □□□* or n□□* produces the excited species, which can either dissociate straightforwardly or be trickled down nonadiabatically via the intersystem crossing. The reaction paths on the excited surfaces are significantly different from the ground-state reactions. In comparison with the analogous perfluoroketone (e.g., C5)[3], new insights are gained into the photochemistry of perfluoronitriles.

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2. X. Yu, H. Hou, B. Wang. Mechanistic and Kinetic Investigations on the Thermal Unimolecular Reaction of Heptafluoroisobutyronitrile. J. Phys. Chem. A, 2018, 122, 7704-7715.
3. X. Yu, H. Hou, B. Wang. Atmospheric Chemistry of Perfluoro-3-methyl-2-butanone [CF3C(O)CF(CF3)2]: Photodissociation and Reaction with OH Radicals. J. Phys. Chem. A, 2018, 122, 8840-8848.

Institution: College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, 430072, P. R. CHINA

Code: ATMEnv_T3

Presenter: Zhe Peng (USA)

Co-Author(s): Jose-Luis Jimenez

Abstract Title: Photochemistry in Oxidation Flow Reactors for Atmospheric Chemistry Research

Abstract: Environmental chambers have been playing a vital role in atmospheric chemistry research over seven decades. In last decade, oxidation flow reactors (OFRs) have emerged as a promising alternative to chambers to study complex multigenerational chemistry (and different from the flow tubes typically used to study elementary reactions). OFR can generate higher-than-ambient concentrations of oxidants via H2O, O2 and O3 photolysis by low-pressure Hg lamp emissions and reach hours to days of photochemical aging in just minutes of real time. The use of OFRs for volatile organic compound (VOC) oxidation and secondary organic aerosol (SOA) formation has grown explosively recently. However, the lack of detailed understanding of OFR photochemistry left room for speculation that OFR chemistry may be irrelevant to the troposphere, since initial oxidant generation is similar to stratosphere. We have conducted a series of studies to address important open questions on OFR photochemistry and to guide experimental design and interpretation. We present a comprehensive picture connecting the chemistries of HOx, NOy and RO2 in OFRs. OFR conditions are often similar to those in the troposphere as OH dominates against undesired non-OH effects. The key reason why some conditions lead to tropospherically irrelevant/undesired processing of VOCs is that under some conditions, OH is drastically reduced while non-tropospheric/undesired VOC reactants are not. We have identified the physical conditions resulting in the tropospheric irrelevance of OFR photochemistry. The most frequent problems are running experiments with too high precursors, too high UV and/or too low humidity. We also discuss how to achieve the tropospheric relevance needed for different purposes (ranging from organic aerosol heterogeneous oxidation to chemical speciation of SOA) in OFR experimental planning.

Institution: University of Colorado Boulder

Code: ATMEnv_T4

Presenter: Stephanie Helen Jones (CAN)

Co-Author(s): D. James Donaldson

Abstract Title: Investigating the Photoenhanced Uptake of NOx on Indoor Painted Surfaces under Different Illumination Conditions

Abstract:

The high surface-to-volume ratio (1) present in the indoor environment suggests that heterogeneous chemistry could play an important role indoors. To further understand the mechanisms of chemical processes occurring indoors it is necessary to study reactions that may occur on indoor surfaces. Typical photochemical processes are not thought to be efficient indoors owing to the lack of significant UV radiation < 320 nm. However, the presence of photosensitizing compounds in common indoor paints and organic coatings deposited on surfaces suggests that heterogeneous photosensitized chemistry could indeed be important indoors.

It has recently been shown that renoxification can occur from proxy indoor surfaces illuminated with indoor light sources (2). It is also known that substrates analogous to those expected indoors i.e. surfaces coated with organic material, may act as heterogeneous chemical photosensitizers that are able to reduce gas phase NO2 to the OH precursor HONO (3). NOx is present in the indoor environment from cooking and cleaning emissions as well as from infiltration (4). Thus we have investigated the photoenhanced uptake and heterogeneous reactions of gaseous NO and NO2 on illuminated substrates painted with commercial indoor paints. The effects of relative humidity and the presence of different paint pigments will be discussed, as well as the potential occurrence of heterogeneous reactions which could result in the formation of gaseous HONO and other NOx species.

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2. H. Schwartz-Narbonne et al., Environ. Sci. Technol., 2019
3. C. George et al., Chem. Rev., 2015
4. N. Carslaw, Atmos. Environ., 2007

Institution: University of Toronto

Code: ATMEnv_T5

Presenter: Frank Leresche (USA)

Co-Author(s): Tyler Kurtz, Jeremy Torres-Ruiz, Garrett McKay, Silvio Canonica, Urs von Gunten and Fernando L. Rosario-Ortiz

Abstract Title: Effects of Ozone on the Optical and Photochemical Properties of Dissolved Organic Matter

Abstract:

Ozone is a cost-effective and efficient disinfectant, often used in water potabilization or as a last polishing step in wastewater treatment. In addition to disinfection, ozone reacts with the water matrix and in particular with the dissolved organic matter (DOM). Investigations on the effects of ozonation on the optical properties of model DOM isolates will be presented in conjunction with ozone-induced changes of DOM's potential to generate singlet oxygen (1O2) under simulated solar irradiation.

Our results indicate that ozonation produces a large decrease (≤ factor 50) in light absorption but also an increase (≤ factor 2) in fluorescence quantum yield (Φf) and a very important increase in Φ1O2 (≤ factor 15) these decrease and increases being more important in the absence of a •OH quencher.

Following these investigations on the effects of ozone on the DOM, we will present some considerations into the photophysic that lead to the observed effects of ozonation on DOM optical properties and on the formation of reactive intermediates photoproduction from DOM irradiation.

This study is an important step forward in explaining the effects of ozonation on the photophysical and photochemical properties of DOM and to a better understanding to the photophysics that govern to the production of reactive intermediates from DOM irradiation.

Institution: University of Colorado Boulder

Code: ATMEnv_T6

Presenter: Cornelius Zetzsch (DEU)

Co-Author(s): Lei Han and Cornelius Zetzsch

Abstract Title: Heterogeneous Reaction of OH Radicals with a Pesticide Adsorbed on Silica Particles Dispersed in an Aerosol Chamber

Abstract:

Terbuthylazine (TBA) has been regarded as a reference compound for the reaction of semi-volatile organic compounds with OH radicals. However, the reaction rate constants from different studies vary by more than an order of magnitude.

We investigated the heterogeneous reaction of OH radicals with TBA by exposing a coating on self-synthesized silica particles (Stöber-SiO2 with a diameter of 160 nm) and on two types of commercial fused silica (the hydrophilic Aerosil 200 and the hydrophobized Aerosil R812) as aerosol in a 3.2 m3 glass chamber at room temperature. The second-order rate constant for OH + TBA@Stöber-SiO2 was determined to be (2.4 ± 0.3) × 10-12 cm3 molecule -1 s-1, whereas our reinvestigation of OH + TBA@Aerosil-200 confirmed the much higher value of of Palm et al. (1997) and led to a combined value of (8.9 ± 0.7) × 10-12 cm3 molecule-1 s-1. Our chamber runs on OH + TBA@Aerosil-R812 delivered a value which is more than ten times higher than the (1.5 ± 0.8) × 10-13 cm3 molecule-1 s-1 reported by Pflieger et al. (2014) for the reaction OH + TBA@Aerosil-R812. The different experimental setups (and surface properties of the silica particles, where a methylated surface like Aerosil R812 may shield adsorbed TBA against OH attack) are discussed. Shielding can affect both the lifetimes of pesticides in experiments and their persistence in the atmosphere.

Palm, W.-U.; Elend, M.; Krüger, H.-U.; Zetzsch, C., OH Radical Reactivity of Airborne Terbuthylazine Adsorbed on Inert Aerosol, Environ. Sci. Technol. 1997, 31, 3389–3396.

Pflieger, M.; Monod, A.; Wortham, H., Heterogeneous Oxidation of Terbuthylazine by "Dark" OH Radicals under Simulated Atmospheric Conditions in a Flow Tube, Environ. Sci. Technol. 2013, 47, 6239–6246.

Institution: University of Bayreuth and Multiphase Chemistry Department, Max Planck Institute for Chemistry, 55128 Mainz, Germany

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Code: ATMEnv_T7

Presenter: Tamara Felber (DEU)

Co-Author(s): Thomas Schaefer, and Hartmut Herrmann

Abstract Title: Photochemical Properties of Photosensitizers in the Tropospheric Aqueous Phase

Abstract: The presence of light absorbing compounds in ambient aerosol particles (Teich et al., Environ. Sci. Technol., 2016) establishes a new pathway to secondary organic aerosol formation due to their potential to act as photosensitizers (Monge et al., PNAS, 2012; Aregahegn et al., Faraday Discuss., 2013). Photosensitized processes are known from other scientific fields like the surface water chemistry, where quenching reactions by dissolved organic matter are investigated (Canonica et al., Environ. Sci. Technol., 1995; Canonica et al., J. Phys. Chem., 2000). However, photochemical and kinetic data as well as the mechanisms for these photosensitized reactions in the particle/ aqueous phase are scarcely available.

In the present study, different photosensitizers such as imidazole-2-carboxaldehyde (2-IC), and 3'-methoxyacetophenone (3’-MAP) were investigated regarding their photochemical behavior and properties. Therefore, trapping reaction experiments were performed using a laser flash excitation-laser long path absorption setup to determine the quantum yields of the excited triplet states of the photosensitizers (ϕ(2-IC) = 0.85, ϕ(3’-MAP) = 0.78 at pH = 5 and T = 298 K). In addition, spectroscopic studies were conducted to observe the formation of the excited triplet state of the photosensitizers at a specific time after the laser pulse (tdelay = 200 ns – 500 µs) resulting in time-resolved absorbance spectra (λ = 200 – 800 nm). The obtained data will be included for further studies to evaluate the importance of particle-/ aqueous-phase chemistry of photosensitizers for atmospheric processes as well as the impact of photosensitized reactions on atmospheric particles possibly contributing to SOA formation.

Institution: Leibniz Institute of Tropospheric Research (TROPOS), Atmospheric Chemistry Department (ACD)

Code: ATMEnv_T8

Presenter: Arianna H. Kazez (USA)

Co-Author(s): Kristie A. Boering

Abstract Title: Understanding the Isotope Anomaly in Ozone: Bath Gas and Pressure Dependence

Abstract: Contrary to predictions of statistical reaction rate theories, ozone in atmospheric samples and laboratory preparations is found to be highly enriched in rare isotopes 17O and 18O, arising from the O+O2->O3*+M->O3+M# recombination reaction. The unique isotopic composition of ozone can be quantified as a deviation from expected fractionation patterns, i.e. in ozone Δ17O=δ18O–0.52*δ17O≠0, whereas all oxygen-containing compounds are predicted to have Δ17O=0. Because ozone exchanges isotopes with many oxygen-containing molecules in the atmosphere, carbon dioxide, nitrates, sulfates, and O2 can obtain some of their isotopic composition from ozone and thus may acquire nonzero Δ17O. The interpretation of Δ17O (or “isotope anomaly”) in these species is contingent on a better understanding of the chemical physics that underlies the anomaly in ozone, which has remained largely mysterious.

Herein we present the pressure and bath gas (M) dependence of the 17O and 18O isotopic compositions of ozone formed in the laboratory by photolysis of O2. Altering the bath gas in which ozone is formed changes: the collision frequency of M with O3* at a given pressure, the average energy transferred from O3* to M per collision (<ΔE>), and potentially the relative contribution of the radical complex mechanism to ozone’s formation. Results indicate that the driving factor in determining the low pressure limit of the isotopic composition of ozone is <ΔE>. This emphasizes the importance of the energy transfer mechanism in determining the isotope anomaly in ozone, and clarifies that no other mechanism significantly affects the low-pressure isotope anomaly in ozone.

Institution: University of California, Berkeley, Department of Chemistry

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Code: ATMEnv_T9

Presenter: Quynh L. Nguyen (USA)

Abstract Title: Highly Excited States of Cumulenone Chlorides in the Vacuum-Ultraviolet Region

Co-Author(s):	William K. Peters, Ryan C. Fortenberry	**Abstract:**	Observations of chloromethane in interstellar environments suggest that other organohalogens—known to be critically important in Earth's atmosphere—may also be of significance beyond our own terrestrial veil. This raises the question of how such molecules behave under extreme conditions, such as exposure to vacuum ultraviolet (VUV) radiation present in circumstellar and photodissociation regions. VUV photons promote molecules to highly excited states, which fragment in non-statistical patterns controlled by the initial femtosecond dynamics. Developing a detailed understanding of VUV-driven photochemistry is a challenging task, especially in complex organic molecules with more than one functional groups. Here, we conduct a quantum chemical analysis of the chlorine-substituted cumulenone series molecules and report the electronic states and ionization potentials in the VUV range (6 - 11 eV). We explore the valence and Rydberg properties of lone-pair terminated, pi-conjugated systems for their potential resonance with lone pairs from elsewhere in the system. The carbon chain elongation within the family ClHCnO, n=1-4, influences the electronic excitations, associated wavefunctions, and ionization potentials of the molecules. The predicted geometries and ionization potentials are in excellent agreement with the available experimental photoelectron spectra for formyl chloride and chloroketene, n=1-2. The cumulenone species and the corresponding chlorinated derivatives exhibit similar behaviors, especially for the n=3 corresponding pair where the allene backbone in propadienone chloride is severely bent in-the-plane as in previous predictions for propadienone. Most notably for the excited states is that the Rydberg character becomes more dominant as the energy increases, which is exhibited for the entire series.
Institution:	Department of Chemistry, University of Colorado, Boulder, Colorado, 80309, USA		

POSTERS

Code:	ATMEnv_P1		
Presenter:	Selvendiran Periyasamy (CHN)	**Abstract Title:**	Surface Modification of Magnetite/Zincoxide Hybrid Nanocomposite System
Co-Author(s):	Dezhao Liu	**Abstract:**	The present work demonstrates the preparation of magnetite (Fe3O4)/Zinc oxide (ZnO) hybrid nanocomposites by a simple co-precipitation assisted reflux condensation method. The X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM), Trans-mission electron microscopy (TEM), Energy-dispersive X-ray spectroscopy (EDS), Thermo gravimetric analysis (TGA) and UV-Vis DRS were applied for the characterization of structural, morphological, compositional, thermal and optical properties of the resultant samples. FESEM images reveals the hybrid structure with ZnO as matrix and Fe3O4 as filler. The nanostructures can be magnetically retrieved using a commercial magnet and can be reused in the visible light catalytic degradation. Therefore, the obtained hybrid nanocomposites exhibit great potential in environmental remediation.
Institution:	College of Biosystems Engineering and Food Science, Zhejiang University, Hangzhou 310058, China		

Code:	ATMEnv_P2		
Presenter:	Chenyi Yuan (USA)	**Abstract Title:**	Prediction of Direct Phototransformation Products for Aquatic Organic Contaminants: A Reaction Library Approach
Co-Author(s):	Caroline Tebes-Stevens, Eric J. Weber	**Abstract:**	Cheminformatics-based applications to predict transformation pathways of environmental contaminants are of interest to quickly prioritize contaminants and identify toxic products. We present the development of the first publicly available direct phototransformation pathway predictive tool using a rule-based reaction library. Systematically compiled journal publications and regulatory reports about diverse contaminants (such as pesticides, pharmaceuticals, and energetic compounds) were used to encode 144 reaction schemes into the reaction library through ChemAxon's Reactor application. The execution of this reaction library was internally evaluated against the more than 500 compounds in the compiled journal publications with an overall sensitivity and selectivity of about 0.5 and up to 0.4, respectively. The tool will be available through the execution of the Chemical Transformation Simulator, a web-based tool developed by the Environmental Protection Agency. Challenges remain such as capturing the dramatic reactivity differences among compounds of similar structure and prioritizing predicted products to reduce the likelihood of combinatorial explosion.
Institution:	ORISE hosted by EPA		

Code:	ATMEnv_P3		
Presenter:	Seunghwan Seo (KOR)	**Abstract Title:**	Investigation of Weekend Ozone Effects in Seoul

Co-Author(s): Si-Wan Kim

Abstract: Ozone (O3) in the urban atmosphere can accumulate from photochemistry involving nitrogen oxides (NOx), carbon monoxide (CO), and volatile organic compounds (VOC) that primarily originate from fossil fuel combustions and the use of solvents. Excessive ozone near the surface has detrimental impacts on public health as well as the ecosystem. In cities, mobile sources emit significant portion of ozone precursors. Since on-road mobile source activities vary depending on the day of week, the concentrations of NOx, CO, VOC, and O3 in the urban area show corresponding temporal changes. For example, in Los Angeles, reduced NOx emissions during weekends lead to increased O3 concentrations via enhanced photochemistry. The “weekend ozone effects”, the observation of higher O3 concentrations during the weekend than during the weekday, is frequently observed in cities. However, this temporal variability was not extensively explored for megacities in Asia that are currently considered global pollution hot spots. In this study, we investigate the day-of-week cycles of ozone and its precursor concentrations in Seoul, South Korea using satellite and in-situ observations. We also compare the weekly cycle patterns in Seoul with other megacities to characterize current chemical regimes in Seoul and establish better pollution control policies in this area.

Institution: Department of Atmospheric Sciences, Yonsei University, Seoul, South Korea

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Code: ATMEnv_P4

Presenter: Kyoung-Min Kim (KOR)

Abstract Title: The WRF-Chem Model Simulations of Photochemical Pollution Events during the KORUS-AQ Campaign

Co-Author(s): Si-Wan Kim, Seunghwan Seo, Yujoo Jeong, and Jeongyeon Kim

Abstract: Asia has experienced unprecedentedly rapid economic growth in the past decades, which resulted in severe local and global air quality problems. The air quality in this region is not only affected by anthropogenic sources but also by natural sources such as dust and plants. Currently understanding of the complicated interplay between the emissions and chemistry in this area is limited. An International Cooperative Air Quality Field Study in Korea (KORUS-AQ) in 2016 provides a unique opportunity to explore the emissions and photochemistry in the continental Asia and South Korea. In this study, we use Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) to simulate multiple photochemical pollution cases during the KORUS-AQ campaign. By comparing the model results with the airborne and ground-based observational data collected during the campaign, the current understanding of the emissions and chemistry relevant to tropospheric ozone and aerosols in this region is assessed. Our modeling approach also clarifies the contribution of local and regional sources to the air quality in the Korean Peninsula.

Acknowledgement
This work was supported by the NIER as a “Public Technology Program based on Environmental Policy” and “Development of Climate and Atmospheric Environmental Applications” project, funded by ETRI which is a subproject of NMSC-2019-01 funded by KMA. And we would like to thank NIER and NASA for the KORUS-AQ data.

Institution: Department of Atmospheric Sciences, Yonsei University, Seoul, Republic of Korea

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Code: ATMEnv_P5

Presenter: Kylie D. Couch (USA)

Abstract Title: Investigation of the Production of Hydroxylating Species from DOM Photolysis

Co-Author(s): Frank Leresche, Garrett McKay, and Fernando L. Rosario-Ortiz

Abstract: The photochemical production of hydroxylating species (e.g., hydroxyl radical-OH) from dissolved organic matter (DOM) has been well documented. Quantum yields for the production of these species have been quantified in previous studies and are in the order of 10-5 – 10-4 depending on the source of the organic matter. These quantum yields are, in part, independent of photo-Fenton chemistry, and represent hydrogen-peroxide independent production of these species. It has been shown that lower energy hydroxylating species, in addition to free hydroxyl radical, are present upon the photolysis of DOM. In this study, the ability of DOM isolates and DOM model sensitizers to photohydroxylate •OH probe compounds was examined, with the overall goal of identifying species responsible for low-energy photohydroxylation reactions. The main classes of sensitizers tested were aromatic ketones, quinones, and hydroxybenzoic acids. Preliminary results indicate that all classes of sensitizers have the capacity to hydroxylate •OH probe compounds when photolyzed, with quinones having the highest quantum yields.

Institution: University of Colorado Boulder

Code: ATMEnv_P6

Presenter: Christopher Cantrell (USA)

Abstract Title: Measurements and Modeling of HOx during the 2017 Study at the Indiana University Research and Teaching Preserve

Co-Author(s): Lee Mauldin, Phil Stevens, Ezra Wood, Dan Anderson, Jonathan Raff,Colleen Rosales, Emily Reidy, Michelle Lew, Brandon Bottorff

Institution: University of Colorado and Laboratoire Interuniversitaire des Systemes Atmospheriques

Abstract: HOx radicals are critically important to tropospheric chemical cycles that oxidize emitted species and lead to production of ozone, growth of aerosols, and presence of oxidized organic compounds. Measurements of OH, HO2, and RO2, along with accurate and comprehensive observations of species and processes that control their concentrations, provide important tests of current understanding of detailed chemistry.

Described here are the results of ambient measurements during the summer of 2017 using the University of Colorado instruments that included two quadrupole CIMS (chemical ionization mass spectrometers) for peroxy radicals and OH, and a nitrate-CIMS time-of-flight instrument (NO3-ToF-CIMS) that observed highly oxidized organic compounds and peroxy radicals. Measurements were also made with the Indiana University Laser Induced Fluorescence FAGE instrument for OH and HO2, and the Drexel University Ethane Chemical Amplifier (ECHAMP). The ambient measurements will be compared with results from a constrained steady-state box model.

Code: ATMEnv_P7

Presenter: Ajaya K. Sankara Warrier (USA)

Co-Author(s): Rachel Hartley

Institution: Assistant Teaching Professor, Penn State University, Fayette The Eberly Campus

Abstract Title: A Combinatorial Approach to Develop Mixed Metal Oxide Photocatalysts Consisting of TiO2 and Other Metal Oxides

Abstract: Photocatalytic capacity of Titanium dioxide (TiO2) stems from its optimum optical and semiconductor properties. The annexation of other metal oxides is supposed to change the optical and electrical properties of TiO2 photocatalyst. A comparative study on the photocatalytic efficiency of a ternary mixture of metal oxides has been carried out. The selected metal oxides consist of TiO2 and any two of the oxides of Iron, Zinc and Cobalt in the ratio 1:1:1, 1:2:1, 1:2:2, 2:2:1, and 2:1:1. These were prepared from transition metal salts of Iron, Cobalt and Zinc and Titanium isopropoxide. In our current experiment, we have synthesized multiple catalysts using a 24 well tray as a template, in small amounts. We have compared their efficiency in photocatalytic decomposition using a model organic compound such as methylene blue. Our preliminary studies indicate that a metal oxide mixture containing 1:2:2 of TiO2, ZnO and Fe2O3 has best catalytic efficiency among selected mixtures. Based on this comparison, the superior catalysts will be studied in detail.