



Wazapalooza 2019

**A Celebration of
Michael Wasielewski's
Contributions to Science**

**Northwestern University
September 20-21, 2019**

- 1:00 – 1:25: Emily Weiss (Northwestern University)**
"Selective Triplet-Initiated Intermolecular [2+2] Cycloadditions Photocatalyzed by Quantum Dots"
- 1:25 – 1:50: Bern Kohler (Ohio State University)**
"Seeing the Colors in Black: Probing Distinct Chromophores in Eumelanin and their Carbon Dot-like Dynamics"
- 1:50 – 2:15: Atsushi Osuka (Kyoto University)**
"Stable Porphyrin Radicals"
- 2:15 – 2:40: Michael Therien (Duke University)**
"U-Turn Electron Transfers in Chemistry and Biology"
- 2:40-3:05: Malcolm Forbes (Bowling Green State University)**
"Molecules, Photons, and Spins"
- 3:05– 3:30: Coffee break**
- 3:30 – 3:55: David Beratan (Duke University)**
"Electron Bifurcation without Maxwell Demons"
- 3:55- 4:20: Frank Würthner (Universität Würzburg)**
"Supramolecular Materials Based on Perylene Dyes"
- 4:20– 4:45: Hiroko Yamada (Nara Institute of Science and Technology)**
"Engineering Thin Films of a Tetrabenzoporphyrin toward Efficient Charge-Carrier Transport"
- 4:45 – 5:15: Group Photo**
(Assemble in front of Tech Building, Northwestern)
- 5:15– 7:00: Poster Session in ISEN Atrium**
(J-wing, Tech Building, Northwestern)

Thank you to our speakers!

Please stay tuned for Professor Wasielewski's Festschrift in Chemical Science, coming in 2020!

- 9:00 – 9:25** **Josh Vura-Weis (University of Illinois-Urbana Champaign)**
“What did the metals know, and when did they know it ?”
- 9:25 – 9:50** **Dirk Guldi (Friedrich-Alexander-Universität Erlangen-Nürnberg)**
“Towards breaking the barrier to 100% charge transfer”
- 9:50 – 10:15** **Gary Brudvig (Yale University)**
“Molecular Catalysts for Water Oxidation”
- 10:15 – 10:40** **Coffee break**
- 10:40 – 11:05** **Ana & Thomas Moore (Arizona State University)**
“Multiple Proton Transfers Coupled to a Single Electron Transfer in Artificial Photosynthesis”
- 11:05 – 11:30** **Boris Rybtchinski (Weizmann Institute)**
“Noncovalent Aqua Materials”
- 11:30 – 11:55** **Felix “Phil” Castellano (North Carolina State University)**
“Triplet Migration Across Quantum Dot-Molecular Interfaces”
- 12:00 – 1:00** **Break**
- 1:00 – 1:25** **Raanan Carmieli (Weizmann Institute)**
“EPR and ENDOR Characterization of Cu-Chelex, a Comparison Study with Cu(Gly)₂ and Cu(IDA)₂”
- 1:25 – 1:50** **Qixi Mi (Shanghai Tech University)**
“Charge Separation and Energy Transfer in Photoexcited Tin-Based Perovskite Materials”
- 1:50 – 2:15** **Yasuhiro Kobori (Kobe University)**
“Transport of Spin-Correlated Multiexciton via Singlet Fission”
- 2:15 – 2:40** **Coffee break**
- 2:40 – 3:05** **Gary Wiederrecht (Argonne National Lab)**
“Ultrafast Nanophotonics and Quantum Optics Research at the Center for Nanoscale Materials”
- 3:05- 3:30** **Claudia Turro (Ohio State University)**
“Excited States of Transition Metal Complexes: What Can We Do with Them?”
- 3:30- 3:55** **Alexey Gusev (Ultrafast Systems)**
“Ultra-broadband transient absorption”
- 3:55 – 4:20** **Stenbjörn Styring (Ångström Laboratory)**
“Far Red photochemistry in Photosystem II”
- 4:20 – 4:45** **Jim McCusker (Michigan State University)**
“Using Spin to Control Excited-State Reactivity”
- 4:45** **Closing Events**

Speakers and Abstracts- Friday



Emily Weiss

Professor of Chemistry, Northwestern University

e-weiss@northwestern.edu

"Selective Triplet-Initiated Intermolecular [2+2] Cycloadditions Photocatalyzed by Quantum Dots"

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 of the long lifetime of a triplet and because they avoid the use of UV light. Synthetic applications of [2 + 2] photocycloadditions demand high selectivity, not only for specific coupling products, but also for particular stereo- and regioisomers of those products, which still remains a challenge in the field. Here, we discuss the use of colloidal CdSe quantum dots (QDs) as visible light absorbers, triplet exciton donors, and scaffolds to drive homo- (photodimerization) and hetero- (cross coupling) 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 diastomeric 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.



Atsuhiko Osuka

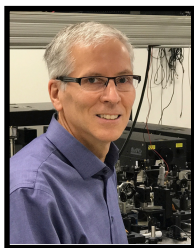
Professor, Department of Chemistry, Graduate School of Science, Kyoto University

osuka@kuchem.kyoto-u.ac.jp

⁸
"Stable Porphyrin Radicals"

Abstract: In recent years, we have revealed that various porphyrinoids such as subporphyrin, meso-aryl-substituted porphyrin, and hexaphyrin can stabilize meso-oxy radicals, meso-aminyl radicals, and meso-carbon radicals to the extent that radicals can be handled like usual closed-shell molecules under ambient conditions.^{1,2)} The high stabilities of these radicals have been ascribed mainly to the effective spin delocalization over the large and flexible conjugation systems of porphyrinoids. These radicals show characteristic structural, magnetic, optical, and electrochemical features. Typically, these radicals show significantly red-shifted absorption bands in the near-IR region and undergo one-electron oxidation and reduction in a reversible manner within narrow potential windows.

We also explored an aminyl triradical that possesses the quartet ground state with a doublet-quartet energy gap of +3.1 kJ/mol. Despite the high-spin nature, this triradical is remarkably stable, allowing for its separation and recrystallization under ambient conditions. Moreover, this triradical can be stored as solids more than one year without serious deterioration. We also synthesized a porphyrin-stabilized trimethylenemethane (TMM) diradical that has the triplet ground state with a positively large EST. Despite the apparent TMM structure, the diradical is reasonably under ambient conditions and storable over months in the solid state.



Bern Kohler

*Professor, Department of Chemistry &
Biochemistry, The Ohio State University*

kohler.40@osu.edu

*"Seeing the Colors in Black: Probing Distinct
Chromophores in Eumelanin and their
Carbon Dot-like Dynamics"*

Abstract: The black pigment eumelanin colors human skin and is found in organisms throughout the tree of life. In addition to its natural sunscreens properties, eumelanin is attractive for photocatalysis and light harvesting due to its extremely broad absorption spectrum and the ability to manipulate its redox state with light. Eumelanin is thought to consist of a heterogeneous collection of chromophores that absorb from the UV to the near infrared, but the nature of these chromophores and their excited state decay pathways are highly uncertain because the microscopic structure of eumelanin is unknown despite decades of study. Using tunable femtosecond laser pulses to selectively excite subensembles of chromophores, broadband transient absorption experiments on a synthetic eumelanin polymer reveal transient spectral holes 0.6 eV wide that track the excitation wavelength. Hole burning proves that absorption by eumelanin is due to chemically heterogeneous chromophores, and the observed bleach recovery dynamics provide insights into interchromophore couplings. The results rule out energy migration and point instead to the ultrafast formation of charge transfer excitons. Raman spectra and TEM images disclose deep parallels between eumelanin and disordered carbon nanomaterials such as graphene oxide, graphitic carbon nitrides, and carbon dots. It is proposed that common noncovalent motifs and interactions among the chemically diverse chromophores found in this superfamily of carbonaceous materials give rise to their distinctive and nearly universal response to photoexcitation.



Michael Therien

William R. Kenan Jr. Professor of Chemistry, Duke University

michael.therien@duke.edu

"U-Turn Electron Transfers in Chemistry and Biology"

Abstract: Efficient photosynthetic energy conversion requires quantitative, light-driven formation of high-energy, charge-separated states. However, energies of high-lying excited states are rarely extracted, in part because the congested density of states in the excited-state manifold leads to rapid deactivation. Conventional photosystem designs promote electron transfer (ET) by polarizing excited donor electron density toward the acceptor ("one-way" ET), a form of positive design. Curiously, negative design strategies that explicitly avoid unwanted side reactions have been under-explored. This talk describes how the electronic polarization of a molecular chromophore can be used as both a positive and negative design element in a light-driven reaction. Intriguingly, appropriate engineering of polarized excited states can steer a "U-turn" electron transfer—where the excited electron density of the donor is initially pushed away from the acceptor—to outcompete a conventional one-way ET scheme. Direct comparison of one-way vs. U-turn ET strategies is achieved in a linked donor-acceptor (DA) assembly in which selective optical excitation produces donor excited states polarized either toward or away from the acceptor. Ultrafast spectroscopy of DA pinpoints the importance of realizing donor singlet and triplet excited states that have opposite electronic polarizations to shut down intersystem crossing. These results demonstrate that oppositely polarized electronically excited states can be employed to steer photo-excited states toward useful, high-energy products by routing these excited states away from states that are photosynthetic dead-ends.



David Beratan

*R.J. Reynolds Professor of Chemistry,
Duke University*

david.beratan@duke.edu

*"Electron Bifurcation without
Maxwell Demons"*

Abstract: I will discuss mechanistic riddles surrounding electron bifurcation reactions in biology. In these reactions, two-electrons are released in two different directions, from a single donor, at potentials that differ by hundreds of millivolts. The reactions are typically carried out at high thermodynamic efficiency, without “short circuits” or violating the second law of thermodynamics. I will explore some of the strategies that biomolecules seem to have discovered in order to bifurcate electrons, and will explore design challenges faced in designing synthetic mimics of the electron bifurcating and confurcating machinery of life.



Malcolm Forbes

*Director, Professor of Chemistry, Center
for Photochemical Sciences, Bowling
Green State University*

forbesm@bgsu.edu

"Molecules, Photons, and Spins"

Abstract: This talk will provide an overview of Chemically Induced Electron Spin Polarization (CIDEP) for non-experts, with examples from several laboratories in addition to my own. We study the structure, reaction kinetics, and dynamics of free radicals and radical ions using steady-state and time-resolved electron paramagnetic resonance (EPR) spectroscopy. The time resolved experiment can be thought of as nanosecond laser flash photolysis with EPR detection. We create photoexcited states that release neutral radical pairs by bond homolysis, or radical ion pairs via electron transfer reactions. The excited state precursor can be in either the singlet (S) or triplet (T) spin state, and the resulting radicals retain this spin information, even long after they have diffused apart. Radical pair S and T states can evolve and mix over time, due to local magnetic field differences at each radical site (g-factor differences or electron nuclear hyperfine interactions). This often leads to non-Boltzmann spin state populations in the radicals, giving rise to strongly spin polarized (CIDEP)spectra. The polarization pattern (absorption, emission, or both) provides immediate and conclusive mechanistic information about the initial photochemical reaction. There is a delicate interplay between this S-T mixing and inter-radical diffusion ("encounters"), therefore confinement of the radicals, for example in micelles or nanocrystals, produces very interesting dynamic effects on the spectra. With our well-established nano-reactor model, we obtain highly detailed structural, kinetic, and dynamic information about the radicals themselves and their micro environment. It is fair to say that the "entangled" S and T states of a radical pair in solution, known in Spin Chemistry for 50 years, were some of the first examples of what physicists call "qubits" in the field of quantum information systems (QIS). Indeed, the photochemical preparation of radical pairs is one of the most reliable methods for constructing real-life qubits with sufficient lifetimes and spin relaxation times for applications such as quantum computing, quantum sensing, and quantum communications.



Frank Würthner

*Professor of Chemistry – Universität
Würzburg, Center for Nanosystems
Chemistry*

wuerthner@uni-wuerzburg.de

"Supramolecular Materials Based on Perylene Dyes"

Abstract: During the last years, we have intensively investigated the organization of perylenedyes by non-covalent forces into desirable nanoscale architectures as well as liquid-crystalline and crystalline solid state materials which nurtured successful research in organic electronics and photovoltaics. In this lecture, I will highlight three recent achievements: The realization of the first perylene bisimide (PBI) solid state emitters with a fluorescence quantum yield close to unity, hydrogen-bonded PBI J-aggregate solid state and LC materials, and the development of photoconductive interlayers for high performance organic solar cells based on hybrid materials composed of novel tetrahydroxy-PBIs and zinc oxide.



Hiroko Yamada

Professor, Graduate School of Science and Technology, Nara Institute of Science and Technology, Ikoma, Japan

hyamada@ms.nait.jp

*"Engineering Thin Films of a
Tetrabenzoporphyrin toward Efficient Charge-
Carrier Transport"*

Abstract: Tetrabenzoporphyrin (BP) is a p-type organic semiconductor characterized by the large, rigid -framework, excellent stability, and good photoabsorption capability. These characteristics make BP and its derivatives prominent active-layer components in organic electronic and optoelectronic devices. However, the control of the solid-state arrangement of BP frameworks, especially in solution-processed thin films, has not been intensively explored, and charge-carrier mobilities observed in BP-based materials have stayed relatively low as compared to those in the best organic molecular semiconductors. This work concentrates on engineering the solid-state packing of BP derivatives toward achieving efficient charge-carrier transport in its solution-processed thin films.

Speakers and Abstracts- Saturday



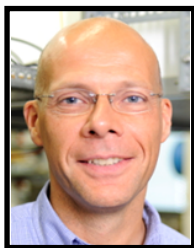
Josh Vura-Weis

Assistant Professor of Chemistry – University of Illinois at Urbana-Champaign

vuraweis@illinois.edu

"What did the metals know, and when did they know it? Femtosecond M-edge XANES reveals short-lived states in transition metal complexes"

Abstract: X-ray absorption near edge spectroscopy (XANES or NEXAFS) is a powerful technique for electronic structure determination. However, widespread use of XANES is limited by the need for synchrotron light sources with tunable x-ray energy. Recent developments in extreme ultraviolet (XUV) light sources using the laser-based technique of high-harmonic generation have enabled core-level spectroscopy to be performed on femtosecond to attosecond timescales. We have extended the scope of tabletop XUV spectroscopy and demonstrated that M_{2,3}-edge XANES, corresponding to 3p - 3d transitions, can reliably measure the electronic structure of first-row transition metal coordination complexes with femtosecond time resolution. We use this ability to track the excited-state relaxation pathways of photocatalysts and spin crossover complexes. The spin selectivity of M-edge XANES is an especially good diagnostic of intermediate states in Fe(II)N₆ dynamics. This work establishes extreme ultraviolet spectroscopy as a useful tool for mainstream research in inorganic, organometallic, and materials chemistry.



Dirk M. Guldi

*Professor, Department of Chemistry and Pharmacy
& Interdisciplinary Center of Molecular Materials,
Friedrich-Alexander-Universität Erlangen-Nürnberg*

dirk.guldi@fau.de

"Towards breaking the barrier to 100% charge transfer"

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 (S_1) that is positioned next to a second molecule in its ground state (S_0) is down-converted into two triplet excited states (T_1) each residing on one of the two adjacent molecules. The two triplet states initially form a correlated pair state $1(T_1T_1)$, which then evolves into two separated triplet states ($T_1 + T_1$). As such, the energetic requirement for SF is $E(S_1) \geq 2 E(T_1)$. 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.



Gary Brudvig
Professor, Yale University

gary.brudvig@yale.edu

*"Molecular Catalysts for Water
Oxidation"*

Abstract: Devising cost effective methods for efficiently capturing and storing solar energy is among the grand challenges of science. We are using insights from studies of natural photosynthetic systems to develop bioinspired catalysts for photo- and electrochemical water oxidation necessary for solar fuel production. Molecular catalysts are known for their high activity and tunability, but their solubility and limited stability often restrict their use in practical applications. 2-pyridyl-2-propanoate (py-alk) has been found to perform extremely well as a ligand for water oxidation catalysts owing to its oxidation resistance and exceptional donor strength that enables high oxidation states to be accessed. Our progress on the development and characterization of molecular iridium, manganese, copper and nickel water-oxidation catalysts will be discussed.



**Ana L. Moore &
Thomas M. Moore**

*Professors of Chemistry, Center
for Bioenergy and Photosynthesis,
School of Molecular Sciences,
Arizona State University*

Contact info

***"Multiple Proton Transfers Coupled to a Single Electron
Transfer in Artificial Photosynthesis"***

Abstract: In photosystem II, tyrosine Z (Yz) functions as a redox relay between the photo-oxidized primary donor ($P680^{*+}$) and the oxygen-evolving complex, where water oxidation takes place. In an iconic proton-coupled electron transfer (PCET) process, the oxidation of Yz by $P680^{*+}$ occurs with the transfer of the proton to a hydrogen-bonded histidine (His190). Benzimidazole phenol (BIP) and several of its derivatives have been synthesized to mimic the behavior of the Yz-His190 pair. The phenol is a model of Yz, and the benzimidazole is a model of His190.1 With a simple BIP, proton transfer from the phenol to the imidazole takes place upon oxidation of the phenol; this is known as a one-electron one-proton transfer (E1PT) PCET process. A one-electron two-proton PCET process, known as an E2PT process, has been shown to take place in amino-substituted BIPs upon electrochemical oxidation of the phenol. In this case, a decrease in the redox potential of the phenoxyl radical/phenol couple by ~300 mV is observed.2 Theoretical calculations predicted that substituents with lower pKa's, such as substituted imines attached to BIP, would still undergo an E2PT process while maintaining considerably higher potential for the phenoxyl radical/phenol couple. Thus, as alternative models of the Yz-His190 pair, BIP with imine substituents were synthesized and results indicate that the phenol oxidation in these derivatives occurs at ~300 mV higher potential than in the amino-BIPs. Protonation of the benzimidazole, indicating an E1PT process and protonation of the imine, indicating an E2PT process can be unambiguously detected by infrared spectroelectrochemistry (IRSEC). IRSEC results demonstrate that an E2PT process takes place with sufficiently strong electron-donating groups at the para-position of the N-phenylimine group (e.g., -OCH₃ substitution). But when the imine basicity is reduced (e.g., with -CN substitution), an E1PT product is dominant.3 In new constructs, proton translocation up to 16 Å along extended H-bond networks has been observed to occur by E3PT and E4PT mechanisms.4 The aims of this study include determining how many proton transfers can be associated with a PCET process and how to manage the thermodynamic consequences. In the long view, we would like to engineer molecular proton wires where proton transport across lipid bilayers would generate proton-motive force in conjunction with PCET redox processes.



Boris Rybtchinski

Professor, Weizmann Institute of Science

aboris.rybtchinski@weizmann.ac.il

"Noncovalent Aqua Materials"

Abstract: Materials based on small molecules that are held together by noncovalent interactions can offer an alternative to conventional polymer materials for applications that require adaptive and stimuli-responsive features. However, it is challenging to engineer macroscopic noncovalent materials that are sufficiently robust for practical applications. We will describe our work on “aqua materials” based on well-defined organic molecules. These materials are uniquely assembled in aqueous media, where they harness the strength of the hydrophobic and π - π interactions to achieve robustness. Despite their high stability, these supramolecular systems can dynamically respond to external stimuli. We discuss design principles, fundamental properties and applications of two classes of aqua materials: (1) supramolecular gels and (2) nanocrystalline arrays. The functional materials based on them include recyclable filtration membranes for preparative nanoparticle separation, water purification and catalysis, as well as nanocrystalline films for switchable surface coatings and optoelectronic devices.



Felix Castellano

Professor, North Carolina State University

fncastel@ncsu.edu

"Triplet Migration Across Quantum Dot-Molecular Interfaces"

Abstract: The generation and transfer of triplet excitons across semiconductor nanomaterial-molecular interfaces will play an important role in emerging photonic and optoelectronic technologies and understanding the rules that govern such phenomena is essential. The ability to cooperatively merge the photophysical properties of semiconductor quantum dots, with those of well-understood molecular chromophores is therefore paramount. CdSe semiconductor nanocrystals, selectively excited by green light, engage in interfacial Dexter-like triplet-triplet energy transfer with surface-anchored polyaromatic carboxylic acid acceptors, thereby extending its excited state lifetime by 5 orders-of-magnitude. Net triplet energy transfer also occurs from surface anchored molecular acceptors to freely diffusing molecular solutes, further extending the triplet exciton lifetime while sensitizing singlet oxygen in aerated solution. The successful translation of triplet excitons from semiconductor nanoparticles to bulk solution implies a general paradigm that such materials are effective surrogates for molecular triplets.

Inspired by the notion that semiconductor nanocrystals present molecular-like photophysical and photochemical properties, 1-pyrenecarboxylic acid (PCA)-functionalized CdSe quantum dots are shown to undergo thermally activated delayed photoluminescence. This phenomenon results from a near quantitative triplet-triplet energy transfer from the nanocrystals to PCA, producing a molecular triplet-state reservoir' that thermally repopulates the photoluminescent state of CdSe through endothermic reverse triplet-triplet energy transfer. The resultant photoluminescence properties are systematically and predictably tuned through variation of the quantum dot-molecule energy gap, temperature, and the triplet-excited-state lifetime of the molecular adsorbate. The concepts developed here appear to be generally applicable to semiconductor nanocrystals interfaced with molecular chromophores enabling potential applications of their combined excited states.



Raanan Carmieli

*Staff scientist, Department of Chemical Research
Support, Weizmann Institute of Science*

raanan.carmieli@weizmann.ac.il

"EPR and ENDOR Characterization of Cu-Chelex, a Comparison Study with Cu(Gly)₂ and Cu(IDA)₂"

Abstract: Chelex chelating resin is classed among the weak acid cation exchange resins by virtue of its carboxylic acid groups, but it differs from ordinary exchangers in its high selectivity for metal ions and its much greater bond strength. Chelex chelating resin operates in basic, neutral, and weakly acidic solutions at pH=4 or higher. Another feature of the Chelex 100 resin is that its volume changes when its ionic form is altered. Because of their importance in analytical techniques, iminodiacetate (IDA) chelating resins have been widely studied. Absorption kinetics, pH absorption, and selectivity order toward metal ions have been defined. Actual selectivity values for any particular system depend on pH, ionic strength, and the presence of other complex-forming species. Several studies of coordination of the IDA ligand in solution and in the crystal state have been carried out recently, but no structural information is available for an IDA group included in a polymeric matrix (chelating resins). Several IDA group coordination modes could be hypothesized. IDA could use all three of its donor atoms, as free ligands do, or it could use only one or two atoms. It may be assumed that different species/complexes can be obtained. Structural information, as in many other areas of materials science, is essential to gain an understanding of the samples physical behavior. The major difficulties in determining the coordination structure of a metal ion with a chelating resin lie in its highly complex amorphous structure. Here we use EPR and ENDOR spectroscopy to derive the structure of the metal ion-binding site of the different complexes.



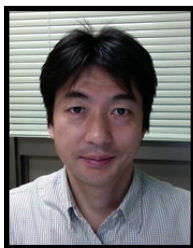
Qixi Mi

Assistant Professor, Shanghai Tech University

miqx@@shanghaitech.edu.cn

*"Charge Separation and Energy Transfer in
Photoexcited Tin-Based Perovskite
Materials"*

Abstract: In an effort to explore lead-free perovskite semiconductors, we recently reported all-inorganic CsSnBr_3 to have excellent semiconducting properties and thermal stability. Experiments and calculations indicate that the compact crystal structure of CsSnBr_3 reduces its band gap energy and charge-carrier reduced effective mass, while enhances its optical dielectric constant all by $\sim 19\%$. These merits accumulate to render an exciton binding energy of 19.6 meV for CsSnBr_3 , making it a black, free-carrier semiconductor, i.e., spontaneous charge separation takes place after photoexcitation of CsSnBr_3 at room temperature. In another example, [2] we studied the broad red photoluminescence (PL) from a yellow perovskite $\text{CsSn}_{0.9}\text{Mn}_{0.1}\text{Cl}_3$ peaking at 645 nm. To identify the luminescent center in $\text{CsSn}_{0.9}\text{Mn}_{0.1}\text{Cl}_3$, we built model compounds with discrete Mn^{2+} monomer, dimer, or trimer structures. Steady-state PL and electron paramagnetic resonance (EPR) spectra of $\text{CsSn}_{0.9}\text{Mn}_{0.1}\text{Cl}_3$ best match those of a Mn^{2+} trimer unit, whereas transient PL reveal an intermediate excited state on a single Mn^{2+} center. Therefore, we propose that energy transfer in $\text{CsSn}_{0.9}\text{Mn}_{0.1}\text{Cl}_3$ occurs from an interband excitation to an excited state at a single Mn^{2+} , before radiative emission from a Mn^{2+} trimer unit.



Yasuhiro Kobori

Professor, Molecular Photoscience Research Center and the Department of Chemistry, Graduate School of Science, Kobe University

ykobori@kitty.kobe-u.ac.jp

"Transport of Spin-Correlated Multiexciton via Singlet Fission"

Abstract: Applications of the singlet fission(SF) are expected to exceed the Shockley–Queisser theoretical limit of the solar cell efficiency. Quintet state generations in triplet–triplet pair have been reported and are thought to be essential for preventing the unwanted loss of the SF-born multiexciton through the singlet channels, although little is known on the primary multiexciton spin dynamics following the SF. Furthermore, transports of spin-entangled multiexcitons have recently been suggested by an ultrafast transient absorption spectroscopy. Although this phenomena may be highly significant for several applications including quantum information science, no direct evidences for the transportation of the spin-entanglements have been examined in correlated triplet–triplet pair states with the singlet and quintet characters. In this study, time-resolved electron paramagnetic resonance (TREPR) method has been applied to observe the transportations of the correlated triplet–triplet pair states by probing the electron spin polarization (ESP) generated in thin films of 6,13-bis(triisopropylsilylethynyl)pentacene. We have clearly obtained that the ESP detected in the resonance field positions of the individual triplet excitons are dependent of the film morphology and of the detection delay time after the laser flash. These observations were clearly explained by correlations of the singlet-triplet-quintet characters in the triple-triplet pair states as the electron spin polarization transfer from strongly exchange-coupled singlet and quintet characters to weakly-coupled spin sublevels formed by the singlet-triplet-quintet correlations in the presence of the external magnetic field. Accordingly, we have modeled the sublevel populations and EPR transitions in the excited multiexciton considering the modulation of the spin-spin exchange coupling and the subsequent decoherence processes to understand the dynamics of the multiexcitons.



Gary Wiederrecht

*Senior Scientist/Group Leader,
Nanophotonics and Biofunctional Structures,
Argonne National Lab*

wiederrecht@anl.gov

*"Ultrafast Nanophotonics and Quantum Optics
Research at the Center for Nanoscale Materials"*

Abstract: Light-matter coupling in varied nanostructures has produced phenomena of interest for nanophotonics applications, including the realization of single photon emitters for quantum optics, energy propagation and conversion in biomimetic materials, and the generation of energetic carriers in plasmonic metamaterials for enhanced light harvesting or ultrafast nonlinear optics. A detailed understanding of the ultrafast processes produced in these nanostructures following photoexcitation is important for realizing and improving the efficiency of a desired nanophotonic application. In this talk I will first describe recent efforts to produce high quality single photon emitters using colloidal CdSe/CdS semiconductor core/shell nanoplatelets. Interestingly, these structures have a size dependent biexciton production with a quantum yield that can approach unity under ideal conditions. The emission of correlated photons is of interest for the possibility of producing entangled photon pairs from a single nanostructure for quantum information science applications. We explore the necessary parameters to produce efficient biexciton production, and also how to improve polarized, directional emission from the nanostructures. These properties are ultimately important for coupling the emission to photonic networks. In the second part of the talk, I describe our recent work studying exciton transport in self-assembled peptide amphiphiles functionalized with a light activated zinc porphyrin chromophore. The dependence of energy transport on chromophore concentration and the impact of excimers that function as energy traps are discussed. Finally, our work in generating a larger number of hot electrons following ultrafast photoexcitation of nanostructured gap-plasmon metamaterials is described. In this work, efforts to alter the size, shape, composition, and gap-plasmon spacing to improve hot carrier production is introduced. As a result of greater hot carrier production and improved signal to noise, we are further able to spectroscopically characterize the decay pathways for energetic plasmonic electrons. This work was performed, in part, at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, and supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.



Claudia Turro

Professor, The Ohio State University

turro.1@osu.edu

*"Excited States of Transition Metal
Complexes: What Can We Do with Them?"*

Abstract: TBD



Alexey Gusev
CEO, Ultrafast System

"Ultra-broadband transient absorption"



Stenbjörn Styring
*Professor emeritus at Department of Chemistry -
Ångström Laboratory, Molecular Biomimetics;
Photosynthesis group*

Stenbjorn.Styring@kemi.uu.se

"Far Red photochemistry in Photosystem II"



Jim McCusker

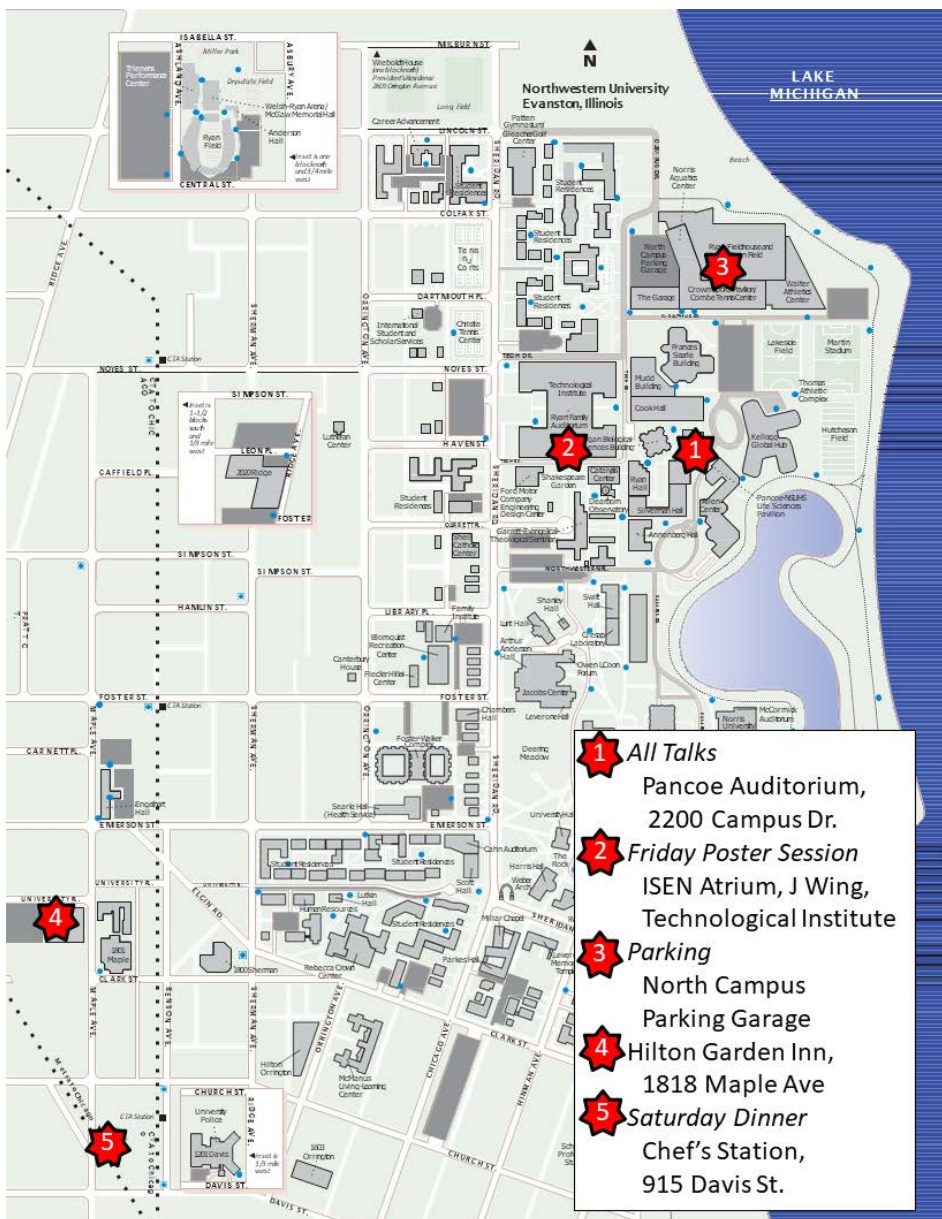
Professor, Michigan State University

jkm@chemistry.msu.edu

"Using Spin to Control Excited-state Reactivity"

Abstract: Electron spin is a fundamental property of Nature. Although many of the more common physical observables linked to spin are well documented, the degree to which spin helps to define the chemistry of molecular systems is not as clear. This question constitutes the conceptual underpinning of our research effort. Specifically, we are interested in the design of donor-acceptor molecular assemblies that will allow us to probe the extent to which spin and spin-polarization manifests in their physical and photophysical properties. Previous work from our lab demonstrated that the concept of conservation of angular momentum is a necessary consideration for dipolar energy transfer. We have now extended this concept to demonstrate that one can leverage this idea to differentiate between competing energy and electron transfer reaction pathways following photoexcitation of a donor-acceptor assembly. This presentation will describe the synthesis and characterization of new compositional platform that we have developed based on a dimensional reduction of our previously published work that allows for the creation of systems amenable to both electron and energy transfer from an initially formed MLCT excited state. Time-resolved emission and absorption data will be described that reveal selectivity for excited-state electron transfer to Co(III) despite favorable conditions for dipolar energy transfer due to the introduction of a spin restriction for energy transfer. The possibility of generalizing this approach to more complex systems will also be discussed.

Event Map





Michael R. Wasielewski received his PhD from the University of Chicago and was a postdoctoral fellow at Columbia University. He began his career at Argonne National Laboratory, where he advanced to Senior Scientist and Group Leader. In 1994, he joined the faculty of Northwestern University, and from 2001-2004 served as Chair of the Department of Chemistry. He is currently the Clare Hamilton Hall Professor of Chemistry, Executive Director of the Institute for Sustainability and Energy at Northwestern (ISEN), Director of the Center for Light Energy Activated Photoredox Processes (LEAP), and Executive Director of the Solar Fuels Institute (SOFI), a global consortium of energy research centers. His research has resulted in more than 560 publications, focusing on light-driven processes in molecules and materials, artificial photosynthesis, molecular electronics, molecular spintronics, ultrafast optical spectroscopy, and time-resolved electron paramagnetic resonance spectroscopy.

Thank you to our generous sponsors!



Northwestern
DEPARTMENT OF CHEMISTRY



INSTITUTE FOR
SUSTAINABILITY AND ENERGY

WEINBERG COLLEGE
OF ARTS & SCIENCES