

# NC PhotoChem 2020



## The 2020 North Carolina Photochemistry Symposium

October 8<sup>th</sup> – 9<sup>th</sup>, 2020

Co-sponsors:

**UNC Charlotte, NC State University, Appalachian State  
University, UNC Chapel Hill, Wake Forest University,  
University of South Carolina, and AIP Publishing**

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## SCHEDULE

***Thursday – October 8th***

### **Session 1**

**1:00 PM** – Welcome

**1:10 PM** – Natalia B. Shustova – *University of South Carolina* – “Photophysics and Electronic Structure of Metal-Organic Frameworks”

**1:35 PM** – Steven Lopez – *Northeastern University* – “Photodynamics simulations towards explosive materials”

**2:00 PM** – Breakout/break #1 (check out student posters on [Flipgrid](#) – 30 minute break)

### **Session 2**

**2:30 PM** – Elham Ghardiri – *Wake Forest University* – “Nanomaterials Ultrafast Photochemistry for Energy and Medicine”

**2:55 PM** – Kristin Wustholz – *William & Mary* – “Harnessing Single-Molecule Emission Dynamics for Photocatalysis and Multicolor Imaging”

**3:20 PM** – (2x 5 minute student talks)

**3:30 PM** – Closing

***Friday – October 9th***

### **Session 3**

**1:00 PM** – Welcome

**1:10 PM** – Shunji Egusa – *UNC Charlotte* – “Luminescent protein-metal complexes”

**1:35 PM** – Frank Leibfarth – *UNC Chapel Hill* – “Upcycling through Polymer C–H Functionalization Methods”

**2:00 PM** – Breakout/break #2 (check out student posters on [Flipgrid](#) – 30 minute break)

#### **Session 4**

**2:30 PM** – Pamela Lundin – *High Point University* – “Synthesis of Organic Molecules with Interesting Photoproperties”

**2:55 PM** – Amanda Morris – *Virginia Tech University* – “Dizzy Photochemistry: The Role of Spin (Forbidden) Processes in MOF Energy Transfer

**3:20 PM** – (2x 5 minute student talks)

**3:30 PM** – Awards Ceremony

## **1. Photophysics and Electronic Structure of Metal-Organic Frameworks**

**Natalia Shustova**

University of South Carolina

Tailoring the photophysical properties of chromophores without their derivatization but as a function of their confined environment is a viable solution for developing novel materials with a tunable optoelectronic profile. This concept can be realized through utilization of a confined environment of metal-organic frameworks, molecular cages, or covalent-organic frameworks. In this talk, we will discuss a variety of methods that provide the new pathways for photophysics modulation of frameworks with coordinatively and non-coordinatively immobilized chromophores. In particular, the correlation between the confined scaffold environment and the chromophore molecular conformation will be discussed utilizing the pore aperture and time as variables. Furthermore, correlation between material photophysical profile and changes in an electronic structure of hybrid frameworks will be considered. Thus, systematic investigation of confined environment effects on the photophysical and structural properties of incorporated guest molecules could provide a pathway for the development of novel materials with tunable photophysics properties.

## 2. Photodynamics simulations towards explosive materials

Steven A. Lopez

Northeastern University

Sunlight is a renewable energy source that can be stored in chemical bonds using photochemical reactions. The synthesis of exotic and strained molecules is especially attractive with photochemical techniques because of the associated efficient and mild reaction conditions. The seminar describes how we have used computations to understand the photophysics and subsequent photochemistry of a possible cubane precursor tricyclo[4,2,0,0,2,5]octa-3,7-diene (TOD). We have used complete active space self-consistent field (CASSCF) calculations with an (8,7) active space and the ANO-S-VDZP basis set to understand the. The energies were corrected with a second-order perturbative correction CASPT2(8,7)/ANO-S-VDZP. The  $S_0 \rightarrow S_1$  vertical excitation energy of 1 is 6.25 eV, whose nature is  $\pi \rightarrow \pi^*$  excitation. The minimum energy path from the  $S_1$  Franck-Condon point leads directly to a  $4\pi$ -disrotatory electrocyclic ring-opening reaction to afford bicyclo[4,2,0]octa-2,4,7-triene. The 2D potential energy surface scan located a rhomboidal  $S_1/S_0$  minimum energy crossing point that connects 1 and cubane, suggesting that a cycloaddition is theoretically possible. We used fewest switches surface hopping non-adiabatic molecular dynamics to enumerate the photochemical reaction pathways of this reaction: 85% of 1,722 trajectories relaxed to 8 products; the major products are bicyclo[4,2,0]octa-2,4,7-triene (30%) and cycloocta-1,3,5,7-tetraene (32%). Only 0.4% of trajectories undergo a [2+2] cycloaddition to form cubane.

### **3. Nanomaterials Ultrafast Photochemistry for Energy and Medicine**

**Elham Ghardiri**

Wake Forest University

We integrate Ultrafast spectroscopy and microscopy techniques to study the time-resolved photochemical processes in nanomaterials and their interfaces. The photochemical/photophysical processes occur in time frames of femtosecond to milliseconds. These photochemical studies are relevant to integrating nanomaterials-based devices for solar energy conversion, including solar cells, and biomedical applications.

#### **4. Harnessing Single-Molecule Emission Dynamics for Photocatalysis and Multicolor Imaging**

**Kristin Wustholz**

William & Mary

The conversion of solar energy into electricity within dye-sensitized solar cells (DSSCs) or renewable fuels in dye-sensitized photocatalysis (DSP) requires the efficient utilization of absorbed photons in charge transfer events as well as the minimization of unwanted losses. There is a substantial literature precedent for time-resolved spectroscopy studies of dye-semiconductor interfaces, which have revealed many important details about the average dynamics occurring in these systems. However, the reported kinetics are complex, multiphasic, and vary widely, a likely consequence of substantial environmental heterogeneity. Advancing DSSC and DSP technologies requires determining the extent and origin of kinetic dispersion at the dye-semiconductor interface, which is difficult to determine using traditional ensemble-averaged methods. Here, we use single-molecule spectroscopy (SMS) to probe the heterogeneous excited-state dynamics of organic-dye-sensitized  $\text{TiO}_2$ . Using a combination of SMS measurements, robust statistical analysis, and Monte Carlo simulations, we demonstrate that so-called “universal” power laws do not represent the electron-transfer dynamics of xanthene-sensitized  $\text{TiO}_2$ . Instead, the data is lognormally distributed, consistent with the Albery model for dispersive electron transfer. For heavy-atom-containing photosensitizers such as eosin Y (EY), both triplet-state decay and dispersive electron transfer are operative. These results provide new mechanistic insights that are relevant to the design of next-generation materials for DSSCs and DSP. In the process of these investigations, we observed that EY exhibits striking single-molecule emission dynamics that can be differentiated from the dynamics of other xanthene dyes, revealing new opportunities in multicolor single-molecule imaging.

## 5. Luminescent protein-metal complexes

**Shunji Egusa**

UNC Charlotte

I will discuss new findings on the red luminophore in the bovine serum albumin (BSA)-gold (Au) compound, initially described by Xie *et al.* (*J. Am. Chem. Soc.* **2009**, *131*, 888-889) as neutral Au<sub>25</sub> nanoclusters. We identified multiple specific Au(III) binding sites in BSA. Static structures are known for many proteins, but the dynamic characters of proteins are often overlooked. The red luminophore formation was a dynamic process, which was consistent with the pH-induced equilibrium transition between the conformations of BSA. Notably, the kinetic rate of the fluorophore formation was not dependent on the concentration of Au(III). We propose a new mechanism of the red luminophore formation based on Langmuir-type adsorption of Au(III) to BSA, as an alternative to the single-site nucleation model of a neutral Au<sub>25</sub> nanocluster.

## 6. Upcycling through Polymer C–H Functionalization Methods

**Frank Leibfarth**

UNC Chapel Hill

Plastics are the largest synthetic consumer product in the world, with an annual production of over 360 million metric tons annually. Despite the structural diversity enabled by modern advances in polymer synthesis, greater than 60% of world plastic production remains dominated by polyolefins. These high-volume, low-cost engineering thermoplastics are made from a small sub-set of petroleum derived monomers and demonstrate diverse thermomechanical properties, attractive chemical resistance, and excellent processability. Creating sustainable materials that compete with the performance and value proposition of polyolefins is a grand challenge for the field of polymer science. The goal of research in the Leibfarth group is to develop synthetic methods that transform readily available starting materials into functional and sustainable thermoplastics with molecular-level precision. This goal informs our work developing synthetic methods that leverage chemo- and regioselective C–H functionalization of commodity polymers to discover new material properties and upcycle plastic waste. Often, the unique reactivity afforded by photocatalysis provides advantages over other approaches. These concepts have resulted in platform synthetic methods that enhance the thermomechanical and adhesion properties of synthetic polymers while also uncovering mechanistic insights that broadly inform synthetic method development.

## **7. Synthesis of Organic Molecules with Interesting Photoproperties**

**Pamela Lundin**

High Point University

Our laboratory is collaborating with groups at High Point University and DePaul University with spectroscopy expertise to study novel organic molecules with interesting photoproperties. In one project, we have synthesized dimers of the dye rhodamine B behave with linkers of varying rigidity. Using UV-vis absorption spectroscopy, fluorometry, and fluorescence correlation spectroscopy, we have compared how these dimers behave as a function of their linker. In our second project we are synthesizing conjugated small molecules that serve as model donor and acceptors for a single-component active layer in an organic photovoltaic. I will discuss the synthesis of these model components and preliminary transient absorption spectroscopy results.

## **8. Dizzy Photochemistry: The Role of Spin (Forbidden) Processes in MOF Energy Transfer**

**Amanda Morris**

Virginia Tech University

The finite supply of fossil fuels and the possible environmental impact of such energy sources has garnered the scientific community's attention for the development of alternative, overall carbon-neutral fuel sources. The sun provides enough energy every hour and a half to power human civilization for an entire year. However, two of the remaining challenges that limit the utilization of solar energy are the development of cheap and efficient solar harvesting materials and advances in energy storage technology to overcome the intermittent nature of the sun. In the seminar, the research projects to be discussed focus on the development of an artificial photosynthetic array for solar energy storage. Photosynthetic systems consist of light harvesting arrays and redox mediators that can funnel the electrochemical potential stored in molecular excited states to catalytic centers to drive the oxidation of water and the reduction of CO<sub>2</sub> to sugars. Many artificial approaches to this chemistry have been reported. In the Morris group, we investigate metal organic frameworks (MOFs) as both light harvesters and high surface area catalysts as photosynthetic mimics. I will discuss our work in the understanding of energy transfer through MOF arrays. Our fundamental work with metal polypyridyl doped frameworks has provided support for a Förster-type energy transfer mechanism between formally triplet excited states. Additionally, we have determined that alignment of the chromophores in 3D space enables long-range energy transfer. The application of MOFs in photon upconversion and photovoltaics will be discussed.

## **1. Synthesis of Rhodamine B Amide Dimers**

**Elizabeth A. Riser**, Pamela Lundin, Keir Fogarty

High Point University

Rhodamine B is an organic dye that gives off a bright pink, often fluorescent, color. Through the carboxylic acid functional group in rhodamine B, it can be modified with new functional groups such as amines to then create amides. These derivatives can adopt different structures as a function of pH and have been explored for fluorescent sensing applications. Our group has synthesized a library of rhodamine B amides, including dimeric structures based on diamine linkers. We have utilized both aromatic and alkyl amines. In this presentation, we will outline the synthesis of these targets and compare their behavior.

## **2. Synthesis and Characterization of Polyhedral Oligomeric Silsesquioxane Porphyrin Conjugates for Photodynamic Therapy**

**Zaneta Zhin**, Paolo Siano, Alexis Johnston, Paula Loman-Cortes, Juan Vivero-Escoto

UNC Charlotte

Polyhedral Oligomeric Silsesquioxane (POSS) is a unique nanoparticle silica popularly used in biomedical treatments such as drug and gene delivery and, above all, anti-cancer therapy to target cancer cells. In particular, POSS have been used to enhance the outcome of photodynamic therapy (PDT). The photosensitizer (PS) in PDT plays its role initiating the activation in selection of destroying cells. However, PS makes an impact on insolubility in aqueous media leading to self-quenching, aggregation and decreased phototoxicity that has lower chance of targeting cancer cells. In this project, POSS molecules containing porphyrin (POSSP) are synthesized and characterized with various functional groups such as isobutyl, phenyl, aminopropyl and methylated aminopropyl. The effect of the functional groups favorably enhanced the singlet quantum yields of POSSPs. In addition, the phototoxicity of POSSPs was evaluated against cancer cells showing similar PDT effect trend as the singlet oxygen quantum yield. We have shown that by tuning the functional groups on POSSPs the PDT effect can be improved.

**3. Determination of quantum yield and molar attenuation coefficient of Dibutoxyphenyl Thiazolothiazole**

**David Diaz**, Carly Kwiatkowski, Abhishek Shibu, Dr. Michael Walter

UNC Charlotte

All images that we see on our displays are a ratio of three main colors: red, green, and blue. Although we have excellent red and green emitters, there is a dearth of solution-processable blue organic emitters. Herein, we report a novel solution-processable organic blue molecular semiconductor- Dibutoxyphenyl Thiazolothiazole. We have studied its absorption and photoluminescence emission spectra in the solution phase and established its quantum yield and molar attenuation coefficient. The crystals emit in the blue region which leads us to believe that this material could be used for blue OLED applications.

**4. Synthesis of redox-active organometallic backbone MOFs by phosphine-carbene ligand exchange with metal-sulfur cubanes**

**Jonathan H. Gillen**, Christopher Bejger

UNC Charlotte

The primary focus of this proposal is to use synthetic transition metal-sulfide cubanes as tetrahedral building blocks in the synthesis of porous, crystalline, supramolecular frameworks. The stronger carbene-metal bond in combination with a ridged network should allow for enhanced charged cluster stability while maintaining and allowing tuning of the cluster redox activity. Such clusters as the Fe<sub>4</sub>S<sub>4</sub> cubane are integral as electron transfer pathways and redox-active centers in biological systems. Mimicking such structures outside the protein in heterogeneous and porous architectures may lead to industrially relevant biomimetic catalyst for electro and photochemical processes relevant to solar fuels.

## 5. Photophysical Properties of Donor-Acceptor Thiazolothiazolium

Nikolas A. Sayresmith, Jackson Mower, Krista Tang

UNC Charlotte

Spectrophotometric acid titrations of a donor-acceptor, asymmetric thiazolothiazole (a-TTz) and its symmetric counterparts were carried out using trifluoroacetic acid in chloroform to study the reactivity of the TTz core across different substitution patterns and probe the photophysical properties of thiazolothiazolium. We report that donor groups activate the nitrogen centers of the TTz core while acceptor groups deactivate them, thus giving the nitrogen centers of donor-acceptor a-TTzs intermediate reactivity compared to their symmetric analogues. Additionally, we synthesized and characterized mono- and tri-alkylated donor-acceptor thiazolothiazoliums to improve water solubility. Along with their ease of synthesis and enhanced water solubility, the photophysical properties of these donor-acceptor thiazolothiazoliums make them attractive for applications involving biological and environmental sensing.

## **6. Effect of growth parameters on Si nanowire morphology and distribution**

**Esha Thakur**, Tang Ye, Haitao Zhang, Yong Zhang, Michael G. Walter

UNC Charlotte

One dimensional silicon nanowires (Si NWs) possess unique optoelectronic properties with significant light trapping and efficient charge carrier separation. Si NWs have a high aspect ratio, high mobility, enhanced light absorption, stability, and flexibility. Owing to these properties, Si NWs have been used in various device applications like solar cells, batteries, photodetectors, and Field-Effect Transistors. One of the most versatile methods that are used for the epitaxial growth of Si NWs is Vapor-Liquid-Solid (VLS) mechanism using chemical vapor deposition. Herein, the Cu seed layer was used for Si NW growth in a CVD reactor at atmospheric pressure using silicon tetrachloride as a precursor and Ar as a carrier gas. The effect of various growth parameters like substrate position and growth conditions on Si NW morphology, size, and distribution was investigated. The growth yield and Si NW morphology were observed to be dependent on the growth conditions and substrate position in the reactor.

## **7. Confinement-Driven Photophysics in MOFs and Cages: Experimental and Theoretical Perspective**

**Anna Berseneva, Natalia B. Shustova**

University of South Carolina

Tailoring the photophysical properties of chromophores without their derivatization but as a function of their confined environment is a viable solution for developing novel materials with a tunable photoluminescence profile. This concept can be realized through the integration of chromophores inside metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), and molecular cages. In this presentation, we will discuss the relationship between chromophore structure and their photophysical response inside rigid frameworks using the 5-(benzylidene)-2,3-dimethyl-3,5-dihydro-4H-imidazol-4-one (BI) chromophore family. Comprehensive analysis of the confinement geometry and photophysical response of integrated BI-chromophore allowed us to establish a photophysics-Àconfinement relationship. To shed light on the structure-photophysics correlation, the framework confined environment was truncated to a molecular cage, thus resulting in utilization of crystallography, spectroscopy, and time-dependent density functional theory calculations to reveal the effect a confined space has on the chromophore,Àôs molecular conformation and any associated changes on a photophysical response. Overall, systematic investigation of confined environment effects on the photophysical and structural properties of incorporated guest molecules could provide a pathway for the development of novel materials with tunable photophysics properties.

**8. From blight to bright: Detecting single point mutations with fluorescent nucleic acid biosensors**

**Morgan Chandler**, Martin Panigaj, Brandon Roark, Jenna A. Tan, Mathias Viard, M. Brittany Johnson, Brian Lynch, Ho Shin Kim, Ian Marriott, Joseph Tracy, Marcus Jones, Yaroslava G. Yingling, Kristin L. Wustholz, Kirill A. Afonin

UNC Charlotte

Nucleic acids coupled with quantum dot (QD) fluorescence blinking can be utilized as a biosensing strategy to report the presence of a target molecule. By measuring QD blinking, a single particle phenomenon which is obscured when several QDs lie within the detection volume of a confocal microscope, this method is readily applicable to a wide range of target species. Using DNA and RNA as scaffolds, QDs are programmed to aggregate into lattices when they encounter a particular target such as the oncogene Kras and the subsequent observation of quasi-continuous emission indicates the presence of the target with a low limit of detection. Nucleic acids can be designed to facilitate different strategies of dynamic assembly and allow for conditionally activated therapeutics such as the release of Dicer Substrate RNAs for gene silencing in human breast cancer cells. QD lattices can also be functionalized with aptamers for diseased cell recognition. The intracellular activity and immunostimulation of QD lattices, confirmed by various gel techniques, microscopy, and predictions by computational modeling, offer a rapid strategy for RNA to be utilized in diagnostic and therapeutic applications.

## **9. Using Photo Catalysts as a Sustainable Synthetic Route for Azobenzene Compounds**

**James D. Sitter**, Aaron K. Vannucci

University of South Carolina

Azobenzene derivatives account for approximately 70% of dyes used in industries worldwide. Unique for their photo-induced isomerization, there is also growing interest and applications in optical storage, medical applications, and in the material industries. The utilization of traditional oxidative or reductive synthesis routes to manufacture these compounds lead to massive amounts of energy waste and waste in waterways. Additionally, traditional methods of azobenzene synthesis can present potential hazards due to the substrate, its volatility and instability. It is imperative to develop renewable routes of azobenzene synthesis without producing massive quantities of hazardous waste. This presentation will present the characteristics that make azobenzene compounds desirable and traditional synthesis methods of these compounds. A new synthesis route for the synthesis of azobenzene derivatives will be presented utilizing renewable energy sources and an environmentally friendly synthesis route.

**10. Synthesis of Urea-tethered Halogenated Triphenylamines to Study the Influences of the Halide Atoms on Photogenerated Radicals**

**Muhammad S. Hossain**, Ammon J. Sindt, Dustin W. Goodlett, Dylan Shields, Colin J. O'Connor, Aleksandra Antevska, Stavros G. Karakalos, Mark D. Smith, Sophya Garash-chuk, Thanh D. Do, Anna D. Gudmundsdottir, and Linda S. Shimizu

University of South Carolina

Persistent organic radicals are important for establishing functional materials with magnetic, optical, and electronic properties. In particular, para-substituted triphenylamines (TPAs) have applications in organic magnetic materials and are also commonly incorporated in the hole transporting layer of photovoltaic cells. Fully para-substituted TPAs are typically capable of generating much more stable radical cations than their partially substituted counterparts. Herein we investigate the effects of halide substituents on assembly, charge transfer, and stability of TPA radical cations. A series of urea tethered halogenated TPAs were synthesized where one of the phenylamine moieties was halogenated in the para-position. In solution, these compounds quickly degrade once TPA radicals are generated. Mass spectrometry provides evidence of radical cation formation as well as insight into degradation pathways. However, in the solid-state these compounds afford persistent photogenerated radicals that have a half-life ranging from one week to less than a day. Time-dependent density functional theory (TD-DFT) calculations suggest the stability of TPA radical cations depends on initial photoinduced charge separation. The nonhalogenated, as well as the chloro and bromo substituted urea tethered TPAs form the charge separated state between the two TPA moieties whereas the iodo derivative forms a charge separated state between a TPA and the methylene urea. Transient absorption spectroscopy can help identify charged species and provides kinetic traces for bromo substituted TPA with a lifetime of ~80 ns. Observed fluorescence quenching supports a plausible charge transfer event after initial charge separation. We hypothesize that the urea assembly motif helps delocalization of charge and delays the charge recombination step. Finally, these understandings can help in the design of next generation organic photonic and magnetic materials.

**11. An Iridium Molecular Photoelectrocatalyst for H<sub>2</sub> Evolution at an Electrochemical “Underpotential”**

**Bethany M. Stratakes**, Alexander J. M. Miller

UNC Chapel Hill

Molecular photoelectrocatalysis is an emerging approach to the synthesis of solar fuels, in which a complex capable of photochemical H<sub>2</sub> generation can be regenerated electrochemically to creating a closed catalytic cycle. A major limitation of current systems is the lack of bona fide energy storage, which can only occur at or below the thermodynamic potential, at negative electrochemical overpotentials ( $\eta < 0$ ). Here, we investigate an iridium photoelectrocatalyst,  $[\text{Cp}^*\text{Ir}(\text{bpy})(\text{NCCH}_3)]^{2+}$ , that undergoes electrochemical reduction at potentials less negative than the thermodynamic potential for proton reduction, forming a metal hydride. Illumination with visible light leads to photochemical H<sub>2</sub> evolution, a thermodynamically uphill process, resulting in net energy storage. Careful tuning of the reaction media leads to catalytic proton reduction at negative overpotentials ( $\eta < 0$ ), with a Faradaic efficiency of 90.6% at  $\eta = -40$  mV. Catalysis was observed as low as  $\eta = -90$  mV, with approximately 4 kcal/mol of photon energy stored.

## **12. Side chain engineering of conjugated polymer incorporating nucleobases: Direct arylation polymerization and fluorescence ion-sensing**

**Sina Sabury**, S. Michael Kilbey II

University of Tennessee Knoxville

Functional groups at the terminus of the side chains of conjugated polymers are used to enhance their functionality, or to improve their morphological or photophysical properties. Here we use direct arylation polymerization (DAP), which is atom efficient and proceeds under mild conditions, to synthesize a nucleobase (adenine) functionalized, alkyl thiophene-based alternating copolymer. To accomplish this, competing side reactions between adenine and catalyst are overcome through Boc-protection of the adenine-functionalized thiophene monomer. In addition, solubility issues are surmounted by introducing additional side chain and backbone flexibility using the comonomer 3,3',3'',4'-tetrahexyl-2,2':5',2''-terthiophene (abbreviated as tT4h). This design change makes the deprotected, alternating copolymer, TAd-tT4h, soluble in the common organic solvents. Relative to the non-functionalized homologue (T-tT4h), thermal analysis shows a ~57 °C increase in the glass transition temperature of the adenine-containing polymer, which is attributed to interbase hydrogen bonding interactions and an increase in main chain stiffness. The ability of adenine functionality TAd-tT4h to complex with metal ions is exploited for fluorescence ion-sensing. In the presence of Cu<sup>2+</sup>, there is strong fluorescence quenching, as high as 91%, which can be recovered upon washing with disodium EDTA solution. These results show that DAP provides an effective route to nucleobase-functionalized polythiophenes, which may find utility in sensing and diagnostic applications, as well as in organic electronics.

### **13. Electronic Properties and Photophysics of Photochromic Frameworks**

**Corey Martin**, Natalia B. Shustova

University of South Carolina

Stimuli-responsive materials have gained esteem in the advancing technology sensor due to their dynamic behaviors under applied stimuli. Modulated by temperature, pressure, pH, applied voltage, or light; chromic materials have found application in "smart" windows or sensors, self-healing coatings, optoelectronic switches, and controlled drug delivery systems. We have recently reported examples of metal-organic frameworks (MOFs) as a tool to study the fundamental changes in photophysical and electronic properties of photochromic molecules upon their embedment into porous scaffolds. In this presentation, we disclose our findings of photoisomerization kinetics for a series of photochromic MOFs including spiropyran and diarylethene units. In particular, we established a correlation of the changes in photophysical profile and electronic structure as a function of excitation wavelength. By a combination of UV-vis and diffuse reflectance spectroscopies, pressed-pellet and single-crystal conductivity measurements, X-ray photoelectron spectroscopy, and theoretical modeling, we determined the photoswitch-invoked control of materials properties that opens new avenues for technological applications.

## 14. Excited-State Processes of Cyclometalated Dinuclear Platinum (II) Complexes Bridged by N<sup>^</sup>O Ligands

Subhangi Roy, Arnab Chakraborty, James E. Yarnell, Chelsea M. Taliaferro, Felix N. Castellano\*

North Carolina State University

Dinuclear Pt(II) complexes with various bridging ligands have seen an increased interests due to the search for new materials for light harvesting and understanding of fundamental excited state properties of metal-metal interactions. For this class of dimer complexes, bridging ligands play a significant role in tuning the Pt-Pt interaction in the excited state. A series of Pt(II) dimers were synthesized using N<sup>^</sup>O bridging ligands 2-hydroxy-6-methylpyridine (MePyO), 2-hydroxy-6-phenylpyridine (PhPyO) and 8-hydroxyquinoline (8HQ) along with phenyl pyridine (ppy) and 7,8-benzoquinoline (bzq) as cyclometalating ligands. Unlike previously reported N<sup>^</sup>N (pyrazolate) bridged dimer complexes these N<sup>^</sup>O bridged complexes are isolated exclusively as anti isomers. These dimers feature high thermal and photochemical stability and high solubility in both coordinating and non-coordinating solvents. Whereas for MePyO and PhPyO the lowest excited state was localized on triplet metal-metal-to-ligand charge-transfer (MMLCT) state, in case of 8HQ a triplet ligand-centered (LC) lowest excited state was observed. The rigidochromic blue shift measured in case of MePyO and PhPyO was larger compare to 8HQ bridged dimer consistent with a CT state and a LC state respectively. Interestingly for hydroxypyridine bridged complexes the CT is directed to the cyclometalating ligand but for 8HQ based complexes it is towards bridging ligand. All these studies provide broader insight towards the role of these N<sup>^</sup>O ligands and can be valuable for future development of new dimeric complexes.

**15. Assembled bis-urea Macrocycles: Photodriven electron transfer from host to guests**

**Md Faizul Islam**, Md Faizul Islam, Ammon J. Sindt, Mark D. Smith, Sophya Garashchuk, Linda S. Shimizu

University of South Carolina

Triphenylamines (TPA) are excellent electron donor molecules which are used in organic magnetic materials and organic dyes due to their ability to form radical cations. Recently, our group has examined the incorporation of TPAs as covalent C-shaped spacers within bis-urea macrocycles to assemble into columnar structures that contain the solvent of crystallization bound within the channels. Heating the crystals lead to the removal of the solvent and activates the crystal for guest exchange by single-crystal-to-single-crystal transformations. Herein, we study how encapsulation of different acceptors inside the channels of the activated host molecule modulates the electron transfer process from the host (donor) to guest (acceptor) through space. Photoinduced electron transfer was initiated by exciting the host molecules with 365 nm LED. Photophysical study shows sign of a charge-transfer complex followed by potential electron transfer event in the host:guest complex. Computational study further provides evidence for the formation of a charge separated state in their excited state. Currently, we are working on further probing the electron transfer event by time-resolved spectroscopy. These Donor-Acceptor materials have the potential to find their application in magnetic and conductive materials.

**16. Visible Light-Induced Homolysis in Chlorobis(2,9-dimethyl-1,10-phenanthroline)copper(II)**

**Remi Fayad**, Sebastian Engl, Evgeny Danilov, Cory Hauke, Oliver Reiser, Felix Castellano

North Carolina State University

Developments in the field of photoredox catalysis that leveraged the long-lived excited states of Ir(III) and Ru(II) photosensitizers to enable radical coupling processes paved the way for explorations of synthetic transformations that would otherwise remain unrealized. While first row transition metal photocatalysts have not been as extensively investigated, valuable synthetic transformations covering broad scopes of olefin functionalization have been recently reported featuring photoactivated chlorobis(phenanthroline) Cu(II) complexes. In the present work, the photochemical processes underpinning the catalytic activity of  $[\text{Cu}(\text{dmp})_2\text{Cl}]\text{Cl}$  (dmp = 2,9-dimethyl-1,10-phenanthroline) were studied. The combined results from static spectroscopic measurements and conventional photochemistry, ultrafast transient absorption, and electron paramagnetic resonance spin trapping experiments strongly support blue light ( $\lambda_{\text{ex}} = 427$  or 470 nm)-induced Cu-Cl homolytic bond cleavage in  $[\text{Cu}(\text{dmp})_2\text{Cl}]^+$  occurring in  $\sim 100$  fs. On the basis of electronic structure calculations, this bond-breaking photochemistry corresponds to the Cl to Cu(II) ligand-to-metal charge transfer transition, unmasking a Cu(I) species  $[\text{Cu}(\text{dmp})_2]^+$  and a Cl atom, thereby serving as a departure point for both Cu(I)- or Cu(II)-based photoredox transformations. No net photochemistry was observed through direct excitation of the ligand-field transitions in the red ( $\lambda_{\text{ex}} = 785$  or 800 nm), and all combined experiments indicated no evidence of Cu-Cl bond cleavage under these conditions. The underlying visible light-induced homolysis of a metal-ligand bond yielding a one-electron-reduced photosensitizer and a radical species may form the basis for novel transformations initiated by photoinduced homolysis featuring in situ-formed metal-substrate adducts utilizing first row transition metal complexes.

## 17. Highly Efficient Photochemical Upconversion Using a Zr(IV) Sensitizer

Mo Yang, Yu Zhang, Carsten Milsmann, Felix N. Castellano

North Carolina State University

Photochemical upconversion via triplet-triplet annihilation (TTA-UC) represents a regenerative approach for converting lower energy incident light into higher energy photons. While a variety of TTA-UC compositions have been well established for numerous promising applications including solar cells, bioimaging and photodynamic therapy, the most prevalent sensitizers have been confined to earth-rare and precious transition metals, such as Ru, Ir, Re and Pd. As the 4th most earth-abundant transition metal, zirconium represents an attractive candidate for scalable yet cost-efficient sensitizers, however it has rarely been studied in this context. Here, a highly efficient TTA-UC leveraging of a newly-conceived Zr(MesPDPPH)<sub>2</sub> complex as the photosensitizer is presented. This Zr(IV) sensitizer exhibits thermally activated delayed fluorescence (TADF) featuring exceptionally long-lived LMCT excited state (350 microseconds) and high quantum yield photoluminescence (QY=45%). The extended lifetimes induced by TADF is ideally suited for diffusional bimolecular photochemistry, as required in solar energy applications. The current photochemical upconversion composition demonstrated that the selective wavelength excitation of Zr(MesPDPPH)<sub>2</sub> with both coherent and non-coherent photons generated upconverted fluorescence of 9,10-diphenylanthracene (DPA) with the upconversion quantum efficiency of ~42% and 20%, respectively, better-performing the most common transition metal based sensitizers. Coherent photons down to the order of mW/cm<sup>2</sup> was sufficient to generate TTA-UC utilizing only micromolar concentrations of acceptor. Additionally, linear incident light power dependence in the low power density region suggested that bimolecular TTA process was highly efficient even on the order of mW/cm<sup>2</sup>. TTA-UC processes were confirmed using a variety of spectroscopic measurements including static and dynamic photoluminescence as well as transient absorption spectroscopy. The triplet energy transfer and TTA rate constants were near the diffusion limit. The transient absorption kinetic analysis of the DPA triplet decay suggested that over 80% of the DPA triplets decay occurred through the bimolecular TTA channel. The current investigation highlights the potential of earth-abundant transition metal photosensitizers featuring TADF for the development of new UC-TTA compositions.

**18. Blue light photochemistry in the curious case of cyclobutadiene formation at a zirconium center****P. Minh N. Do**, Carsten Milsmann

West Virginia University

Reduced early transition metal (TM) compounds are inherently reactive and undergo distinct transformations compared to late TM analogs. This divergence is advantageous for designing new and complementary stoichiometric and catalytic reactions. State-of-the-art synthetic routes toward low-valent early TM complexes often involve strong chemical reductants or thermal activation of high-valent organometallic precursors. For organozirconium compounds, alternative photochemical means are attractive but mostly confined to high energy UV light or broad-spectrum light source. Our prior work with zirconium complexes containing electron-rich pyridine monopyrrolate (PMP) ligands explored the importance of ligand-to-metal charge transfer (LMCT) bands for visible light excitation that facilitates C-C bond formation by formal reductive elimination at zirconium. These studies prompted the synthesis and photochemical investigation of  $(\text{MePMPMe})_2\text{ZrBn}_2$  (MePMPMe = 3,5-dimethyl-2-(2-pyridyl)pyrrolide, Bn = benzyl) as a precursor to low-valent intermediates. Absorption spectroscopy in benzene showed one strong band in the visible region with a maximum at 417 nm ( $\mu = 12\ 300\ \text{M}^{-1}\ \text{cm}^{-1}$ ). Time-dependent density functional theory (TD-DFT) calculations revealed the hybrid nature of the absorption band: LMCT/ligand-to-ligand charge transfer (LLCT). Ligand contribution came from either MePMPMe or Bn. Within minutes being exposed to a 462-nm LED, the bibenzyl coupling product was formed and opened the coordination sphere for further reactivity. Photolysis in the presence of diphenylacetylene lead to the unexpected half-sandwich complex  $(\text{MePMPMe})_2\text{Zr}(4\text{-C}_4\text{Ph}_4)$ , confirmed by X-ray crystallography. Under the same reaction condition,  $(\text{MePMPMe})_2\text{ZrBn}_2$  and 4-methylbenzyl bromide generated  $(\text{MePMPMe})_2\text{ZrBr}_2$ . Bibenzyl by-products were identified by GC-MS and various NMR experiments. The presence of bibenzyl, 4-methylbibenzyl and 4,4-dimethylbibenzyl suggested a radical mechanism.

**19. Photophysics, Electronics, and Redox-Activity of Well-Defined Donor-ÀAcceptor Fulleretic Covalent-Organic Materials****Gabrielle A. Leith**, Natalia B. Shustova

University of South Carolina

Crystalline covalent-organic frameworks (COFs), made solely from organic building blocks, offer the unique opportunity for material engineering due to nearly no limitations in the choice of organic linker. Taking advantage of COF modularity and tunability, we probed the effect of donor-acceptor alignment using crystalline (purely organic) scaffolds with covalently bound tetracyanoquinodimethane- (TCNQ) and fullerene-acceptors. Integration of strong electron-acceptors inside the insulating porous scaffolds provided an opportunity to tune electronic properties resulting in circa 100,000,000-fold conductivity enhancement, one of the largest increases reported for COFs to date. In addition, the first studies towards estimation of charge transfer rates as a function of acceptor stacking support the experimentally observed drastic, eight-fold conductivity enhancement. Moreover, the porosity of the prepared crystalline hybrids was maintained providing a pathway to re-enforce semi-conducting behavior in typically insulating porous materials (for example, covalent-organic (COFs)). The buckyball and TCNQ-covalently bound materials also exhibited redox-active behavior. The prepared purely organic acceptor-based material has undergone comprehensive characterization and photophysical studies such as powder X-ray diffraction, steady-state and time-resolved photoluminescence, X-ray photoelectron, Fourier transform infrared spectroscopies, thermogravimetric, cyclic voltammetry, and gas sorption analysis. The presented studies not only demonstrate the possibility to merge the intrinsic properties of strong electron-acceptors with the versatility of hierarchical scaffolds, but also provide a blueprint for the development of electroactive and conductive multidimensional and multifunctional D-A crystalline materials.

**20. Aqueous Thiazolothiazole Derivatives for Electrochromic, Electrofluorochromic, and Photochromic Multifunctional Devices**

**Tyler Adams**, Andrew R. Brotherton, Jordana A. Molai, Natasha Parmar, Jon Palmer, Kristin A. Sandor, Michael G. Walter

UNC Charlotte

Electrochromic and photochromic materials can be used for a variety of applications including windows and eyeglasses and electrofluorochromic materials can be used for sensors or displays. Few materials have the potential to contain all three properties, especially while in an aqueous medium. Dipyridinium thiazolothiazole (TTz) derivatives show prominent color change and fluorescence reduction with the application of a low voltage or light illumination while in a simple FTO glass/hydrogel/FTO glass device. The hydrogel used contains 5 mM TTz and 10 mM 1,1'-ferrocenedimethanol in a 4% aqueous PVA/borax slime. These simple water-based devices show high color contrast, high fluorescence contrast, fast turn-on speeds, and excellent cyclability/reversibility. They also darken from a transparent yellow to a dark purple/blue with 15 min of light exposure. One of these devices, when cycling on and off 1.8 V every 20 s, has a light transmittance contrast of 62% after 250 cycles. Similar devices have also shown fluorescence contrast up to 80%, all while being made from inexpensive, aqueous materials.

**21. Study on emission decay rates and molecular assembly of metallated carboalkoxyphenyl porphyrins**

**Abhishek Shibu**, Carly Kwiatkowski, Camilla Middleton, Dr. Meesha Kaushal and Dr. Michael Walter

UNC Charlotte

Porphyrins are heterocyclic structural analogs of chlorophyll and can be tuned to fabricate nature inspired solar cells. In solar cells however, excess of long-lived triplet states could yield deleterious effects as it results in polaron formation and subsequent degradation of materials and interfaces. Therefore, a molecular design approach that could reduce excited state lifetimes will increase the device stability and power conversion efficiency. Herein, we report successful reduction of lifetime of the excited-state by inserting a Zn atom in the porphyrin complex. We compare the emission lifetimes of four carboalkoxyphenylporphyrins to their metallated counterparts: Zinc-tetra(4-carbobutoxyphenyl)-porphyrin (Zn-TCB4PP), Zinc-tetra(4-carbohexoxyphenyl)-porphyrin (Zn-TCH4PP), Zinc-tetra(4-carbo-2-ethylhexoxyphenyl)-porphyrin (Zn-TCEH4PP), Zinc-tetra(4-carbooctoxyphenyl)-porphyrin (Zn-TCO4PP). We have also studied the absorption properties of the metallated porphyrins and juxtaposed the solution phase spectra with those of thin films. We comment on the molecular organization in thin films and their dependency on the peripheral alkyl chains. We have found that molecules with longer alkyl chain length have extended lifetimes implicating a decrease in porphyrin-porphyrin affinity. This could result in a decrease of non-radiative electronic transitions. This work will be important to understand exciton diffusion in metallated thin films and facilitate discussion on directed charge transfer in heterojunction solar cells.

**22. Optical Properties of Gold Nanostars in Chitosan and Agar Gels  
Matrices**

**Casey Folks**

UNC Charlotte

Compared to the colloidal solutions of nanoparticles, plasmonic nanoparticles embedded in solid supports are preferred in sensing applications due to their enhanced stability, convenience in handling, and ability to offer more consistent plasmonic response. In this work, we studied gold nanostars (GNS) loaded in organic gel polymers of agar and chitosan to identify how the variations of the matrix (chitosan or agar) concentration affect the optical properties of the nanocomposites and thus their potential application as a SERS platform. GNS particles were either embedded in the polymer gel by bulk-mixing or surface deposition.

### **23. Synthesis of Thiazolo[5,4-d]thiazole Derivatives For Use as Fluorescent Probes**

**Jared C. Meadows**

UNC Charlotte

The long-term goal of this project is to synthesize novel highly fluorescent, solvatochromic thiazolo[5,4-d]thiazole (TTz) -derived molecular sensors for use as probes to conduct an in vitro analysis of the antibiotic target enzyme undecaprenyl pyrophosphate synthase (UPPS). UPPS is a cis-prenyltransferase that is critical in the synthesis of lipid carriers for peptidoglycan synthesis in bacteria, and catalyzes 8 consecutive condensation reactions by which 8 units of isopentenyl pyrophosphate (IPP) are covalently bound to a single molecule of farnesyl pyrophosphate (FPP) to form the 55-carbon bactoprenyl pyrophosphate (BPP).<sup>1</sup> BPP is an essential lipid carrier which forms the anchor in the plasma membrane of bacteria on which surface polysaccharides are synthesized. Asymmetric TTz derivatives have been shown to exhibit very strong excited-state dipoles, resulting in highly solvatochromic properties.<sup>2</sup> Several fluorescent probes have been used to study this enzyme,<sup>3</sup> but the solvatochromic properties of these TTz compounds can potentially provide more insight into the UPPS mechanism due to their characteristically high sensitivity to their chemical environment. Using TTz compounds as fluorescent probes, we will mimic the natural FPP substrate and monitor the fluorescence changes to learn more about the mechanism by which UPPS releases its substrate.

## 24. Multiconfigurational Calculations and Nonadiabatic Molecular Dynamics Explain Tricyclooctadiene Photochemical Chemoselectivity

Jingbai Li, Steven A. Lopez

Northeastern University

Sunlight is a renewable energy source that can be stored in chemical bonds using photochemical reactions. The synthesis of exotic and strained molecules is especially attractive with photochemical techniques because of the associated efficient and mild reaction conditions. We have understood the photophysics and subsequent photochemistry of a possible cubane precursor, tricyclo[4,2,0,0,2,5]octa-3,7-diene (1) with complete active space self-consistent field (CASSCF) calculations with an (8,7) active space and the ANO-S-VDZP basis set. The CASSCF energies were corrected with a second-order perturbative correction CASPT2(8,7)/ANO-S-VDZP. The S0  $\rightarrow$  S1 vertical excitation energy of 1 is 6.25 eV, which is a  $\pi \rightarrow \pi^*$  excitation. The minimum energy path from the S1 Franck-Condon point leads to a 4 $\pi$ -disrotatory electrocyclic ring-opening reaction to afford bicyclo[4,2,0]octa-2,4,7-triene. The 2D potential energy surface scan located a rhomboidal S1/S0 minimum energy crossing point connecting 1 and cubane, suggesting that a cycloaddition is theoretically possible. We used the fewest switches surface hopping to study the photodynamics of this cycloaddition: 85% of 1722 trajectories relaxed to eight products; the major products are bicyclo[4,2,0]octa-2,4,7-triene (30%) and cycloocta-1,3,5,7-tetraene (32%). Only 0.4% of trajectories undergo a [2 + 2] cycloaddition to form cubane.

## 25. Various Light-Harvesting Materials for Dye-Sensitized Solar Cells

Dillip K. Panda, Monica A. Gordillo, Sourav Saha

Clemson University

In this research work, we highlight the fabrication and characterization of low-cost, high efficiency, durable, and stable two kinds of solar cells, such as multichromophoric supramolecular dye-sensitized solar cells (DSSCs), and Metal-organic Framework (MOF) sensitized solar cells. In order to increase the efficiency of DSSCs, a photoanode prepared either using multichromophoric self-assembled zinc-porphyrin-peryleneimide dyad / zinc-phthalocyanines-peryleneimide. The surface coverage of the two dyes on the same thickness of the TiO<sub>2</sub> surface is different confirmed through UV-Vis spectra of dye-coated TiO<sub>2</sub> (that affect the electron injection into the Fermi-energy level of the conduction band of TiO<sub>2</sub> that affect significantly upon the IPCE observed for each device. This dyad on TiO<sub>2</sub> films displays more efficient light-to-electrical energy conversion than DSCs, based on individual dyes. The higher efficiencies of dyad based DSSCs can be attributed to co-sensitization along with the vectorial electron transfer that leads to better charge separation. For Metal-organic Framework (MOF) sensitized solar cells, photoanodes were prepared by a solvothermal technique using pillared porphyrin framework (PPF-11) films featuring vertically aligned Zn-tetrakis (4-carboxyphenyl) porphyrin (ZnTCPP) walls horizontally aligned 2, 2,4,4'-dimethyl-4, 4'-bipyridine beams attached to ZnO/FTO glass substrate. The photovoltaic performances of all assembled solar cells are evaluated both in the dark and under standard light conditions (100 mW/cm<sup>2</sup>, air mass 1.5 G). The incident-photon- to-current efficiency (IPCE) is determined measured at various electrolyte filling and also examined the sensitization effect of the chromophore. The electrochemical impedance spectroscopy (EIS) technique was employed to measure the charge-transfer resistances (RCT) at each electrode/electrolyte interface over a frequency range of 10<sup>6</sup>–10<sup>1</sup> Hz both under light and dark condition. The interfacial charge-transfer resistance values are calculated by fitting the Nyquist plots of EIS data using an appropriate equivalent circuit diagram. The structural and optical properties of the photoanode also investigated by various spectral techniques (XRD, XPS, Raman, FTIR, and UV-Vis-DRS). The surface morphology and roughness of each photoanodes examined using SEM, SEM-EDXA (SEM-Energy Dispersive X-ray Analyzer), and AFM.

**26. TIPS-Pentacene Triplet Exciton Generation on PbS Quantum Dots  
Results from Indirect Sensitization**

**Christopher Papa, Felix N. Castellano**

North Carolina State University

PbS quantum dots (QDs) of variable size and band-edge exciton energy (ranging from 1.15 to 1.54 eV) were post-synthetically modified with a carboxylic acid-functionalized TIPS-pentacene derivative (TPn) to serve as the molecular triplet acceptor for transient absorption studies. Selective excitation of the PbS NCs at 743 nm leads to QD size-dependent formation of an intermediate with time constants uncorrelated to the PbS QD valence band potential. However, the experimentally-determined rate constants for the delayed formation of the TPn triplet excited state markedly increase with increasing PbS conduction band energy, displaying a possible parabolic Marcus free energy dependence in the normal region. These observations provide evidence of an indirect triplet sensitization process, which is inconsistent with a concerted Dexter-like energy transfer process. The collective data are consistent with the generation of an intermediate resulting from hole trapping of the initial PbS excited state, followed by sluggish formation of the TPn triplet excited state, whose rate constant and yield increases with decreasing quantum dot size.

## **27. Rational Design of Multi-Electron Electrolytes Using Redox Non-Innocence**

**Mitchell R. Anstey**, Ellen Warner, David Choi, Claudia Hernandez Brito, Aislinn Whalen, David Blauch, Neil Tomson, Michael Gau, Patrick Carroll

Davidson College

DOE OE's core mission is to support "efforts to ensure a resilient, reliable, and flexible electricity system." Among the many ways in which this is achieved, OE has placed redox flow batteries among the three core R&D technologies that can provide this new electrical grid. Our work focuses on new chemistry that can improve stability, cyclability, and energy density. Redox flow batteries predominantly rely on molecular electrolytes for charge storage. In all cases, the redox-active component must be vetted in all of the relevant oxidation states (charged and discharged) to ensure the system will function over its lifetime while providing some level of optimization of energy density. Electrolyte stability and energy density enhancements for redox flow batteries are tackled by our research team using a single strategy: redox non-innocence. In one sense, this is the confinement of electrons to a specific portion of a larger molecule. We have identified molecules with multiple electron "bins" that are designed to survive repeated cycling. This poster will describe the most recent results of this work as it relates to a molecular scaffold based on dihydroxyphenoxazine.

## 28. Multiconfigurational Computations and Time-resolved Spectroscopy Describe the Chemoselective Photoisomerization of Hexafluorobenzene

Jordan Cox, Mike Kellogg, Matthew Bain, Stephen Bradforth, Steven A. Lopez

Northeastern University

Photochemical reactions grant molecules access to higher energy intermediates than typical thermal reactions, and as such are critical tools for the synthesis of natural products and energy dense materials. Computational methods utilizing a single electron configuration (e.g. density functional theory) cannot accurately describe the nonadiabatic processes typical of photochemical reactions. Instead, multiconfigurational methods like complete active-space self-consistent field (CASSCF) and complete active space perturbation theory (CASPT2) are required to account for the strong coupling between degenerate or near-degenerate electron configurations near electronic state crossings. We have performed extensive CASSCF and CASPT2 computations and nonadiabatic dynamics simulations to fully describe the photochemical isomerization reaction in hexafluorobenzene, including the first reported optimization of a conical intersection for this system. Benzene photochemistry is wavelength-dependent while the photochemical isomerization of hexafluorobenzene is chemoselective for hexafluoro-Dewar-benzene. Hexafluorobenzene also exhibits an atypical broad, featureless emission spectrum which is strongly red-shifted from the absorption onset. The perfluoro effect, a selective stabilization of the  $\sigma^*$  and  $\pi^*$  orbitals, is thought to play a role in this unique behavior, but this role is not well understood. We have performed CASSCF and CASPT2 computations at the XMS-CASPT2/aug-cc-PVDZ//CAS(6,7)/aug-cc-PVDZ level and transient absorption spectroscopy to determine the potential energy surface in the vertical excitation region and along the reaction coordinate. We have also performed nonadiabatic dynamics simulations with the fewest-switches surface hopping algorithm at the CAS(6,7)/aug-cc-PVDZ level to determine the excited state lifetime and quantum yield for this reaction. We have determined that the red-shifted emission band is not the product of a low-lying, weakly-absorbing state, as previously suggested, and is instead caused by a strong structural distortion in the excited state. Our characterization of the S<sub>0</sub>/S<sub>1</sub> branching space for benzene and hexafluorobenzene reveal that the differences in reactivity between these two systems are largely due to an increase in the asymmetry of the branching space upon fluorine substitution. The origin of this asymmetry and its effects on the relative reaction dynamics will also be discussed.

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