Using Computational Chemistry to Screen Heavy-Atom-Free Sensitizers for Triplet-Triplet Annihilation Upconversion
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Solar panels are a compelling renewable energy alternative to fossil fuels for reducing greenhouse gas emissions and combating global climate change. Mainstream photovoltaic technologies do not effectively utilize photon energies in the near-infrared, a large portion of the solar spectrum. Triplet-triplet annihilation upconversion (TTA UC) provides a method to convert low energy, red and near-infrared photons to higher energy photons to increase the efficiency of solar cells. Previous projects in our lab have shown that a thiosquaraine molecular sensitizer combined with a rubrene emitter produce successful red to yellow upconversion. In this project, we use a combination of theoretical computational chemistry and experimental photoinduced absorption spectroscopy to study the molecular properties of oxo- and thiosquaraines with various arylamine donor moieties. Our goal is to identify properties that lead to near-infrared absorbance, high triplet yields, and efficient intramolecular crossing from the first singlet to first triplet excited state. We report the absorbance energy for squaraines with donor moieties in perpendicular and parallel configurations relative to the molecular axis, as we hypothesize that the dihedral angle of the donor relative to the molecule’s core affects the effective conjugation length of the molecule and its absorbance energy. We also compare the absorbance energy for donor moieties containing different numbers of amine groups, which are correlated with the strength of the donor in the excitation. Using computational chemistry to understand these trends is more efficient than synthesizing each squaraine and will serve as a guide for which donor groups to test experimentally. For example, increasing the number of aromatic rings on the donor redshifts the absorbance energy, indicating that such squaraines may exhibit the properties we want in experiment. We will synthesize and perform photoinduced spectroscopy on the most promising candidate(s) to determine whether they exhibit the desired near-infrared absorbance and high quantum yield.

Nanofabrication of Silica-Shelled Colloidal Quantum Dots as Single-Photon Emitters
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Exhibiting narrowband photoluminescence and tunable surface functionalization, colloidal semiconductor nanostructures are promising candidates for wide-ranging applications from light-emitting technologies to quantum information processing. In recent decades, the syntheses of II-VI and III-V quantum dots, nanorods, and nanoplatelets have been in the spotlight of nanotechnology, whereas the potential of perovskite quantum dots, a zero-dimensional variant, remains to be fully tapped. Boasting fast radiative lifetimes and long optical coherence times, perovskite quantum dots are ideal candidates for coherent single-photon emitters in integrated photonic circuits. Integrated quantum nanophotonics utilize light-matter coupling with embedded light-emitting media to achieve state-of-art engineering processes such as ultralow threshold lasing. However, the scalable integration of single photon emitters in nanophotonic platforms remains a challenge. The subject of this research presents a solution to this problem: giant lead halide perovskite quantum dots for deterministic positioning into optical nanocavities. Owing to the exceptional tunability of their surface chemistry, perovskite quantum dots can be efficiently solution processed with clear...
pathways for deterministic positioning. Size and compositional modulation of these nanomaterials enable optimization of single-photon behaviors, especially high quantum yields and narrow emission linewidths. This investigation enlists a solution-based colloidal synthesis combined with silica encapsulation techniques to afford giant lead halide perovskite quantum dots with desirable sizes, quantum yields, absorption and emission signatures, and narrow photoluminescence linewidths well-suited for single-photon applications. Experiments are designed to 1) reproducibly synthesize photostable and highly luminescent silica-coated perovskite quantum dots, and 2) deterministically position the quantum dots on silicon nitride nanobeam cavities. All products are analyzed using UV-vis and fluorescence spectroscopies, along with transmission electron microscopy. The outcome of this study also paves the way for understanding the robust single-photon properties of perovskite quantum dots in optical cavities, thereby providing insights into the design of colloidal single-photon emitters in other morphologies.

**Water Detection in MAPbI₃ Perovskite Photo-Oxidative Degradation**

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Perovskite materials have promising power conversion efficiency for use in efficient and inexpensive solar panels but are handicapped by material degradation. The degradation of methylammonium lead tri-iodide (MAPbI₃) occurs in the presence of heat, illumination, hydration, and oxygen. The fastest degradation is via the reaction with oxygen and water under illumination (water accelerated photo-oxidation, WPO). The exact mechanism for degradation with oxygen under illumination (dry photo-oxidation, DPO) is unknown, but the most commonly proposed reaction includes net water production, which would allow transitioning to accelerated degradation by WPO even without water initially present. Previous degradation experiments in our group have been conducted with perovskite thin films at steady state with flowing gas delivering reactants and removing products. The degradation products in the gas phase are challenging to collect in sufficient concentrations to characterize. We develop a novel experimental strategy to determine the stoichiometry of MAPbI₃ degradation focusing on the possibility of water production. We simulate atmospheric perovskite degradation using MAPbI₃ crystals suspended in o-dichlorobenzene with saturated dissolved oxygen and water for easy and accurate characterization of degradation products. The liquid samples are collected for analysis by gas chromatography-mass spectrometry and ultraviolet-visible spectroscopy measurements following degradation with heat, illumination, oxygen, water, and combinations of the four. These measurements determine the types and amounts of components produced, allowing for conclusions on the overall stoichiometry of DPO and WPO isolated from other, parallel processes. Importantly, we find that water is not produced from DPO and net consumed by WPO. These findings allow for developing novel degradation mechanisms that will lend essential understanding in engineering methods to counteract degradation and move perovskite solar panels towards full-scale viability.

**Supramolecular Cages as Redox Mediators for Organic Electrosynthesis**

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Given the harsh impact of climate change and industrial pollution on the planet, it is imperative that we lower the energy consumption of chemical synthesis and reduce hazardous byproducts. As many organic reactions involve oxidation and reduction, electrocatalysis has been solidified as a promising route toward cleaner, more energy-efficient redox reactions. However, high energy barriers for charge transfer between electrodes and dissolved reactants can serve as a critical obstacle. We propose the use of supramolecular cages with redox-active ligands as electrocatalysts to address this challenge. Supramolecular cages are compounds formed from the self-assembly of organic ligands and metal ions, with large, open cavities that could act as hosts for reactive species. Electro catalysts are compounds that reversibly transfer charge from electrodes to dissolved reactants, lowering the overall energy barrier. Specifically, we are targeting a giant electroactive Fe₂⁺ cage with perylene-bisimide ligands as an electrocatalyst for the reduction of vicinal dihalides, perfluoroalkyl iodides, and aldehydes. We have made significant progress in the five-step synthesis of the perylene-bisimide ligand required for cage assembly and have conducted preliminary cyclic voltammetry experiments for the vicinal dihalide reduction. Ultimately, our goal is to use this supramolecular cage to establish new electrocatalytic pathways for the synthesis of industrially relevant compounds and chemical feedstocks.

**Toward Heptazine-based Organic Photocatalysts for Practical Application in Proton-Coupled Electron Transfer Reactions**

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Proton-coupled electron transfer (PCET) has been studied extensively, with the anticipation that it could enable applications in energy storage and conversion. We have previously studied 2,5,8-tris(4-methoxyphenyl)-1,3,4,6,7,9,9b-heptaazaphenalene (TAHz), a derivative of carbon nitride, as
a promising organic photocatalyst. This is because the heptazine core of TAHz is composed entirely of carbon and nitrogen, while most photocatalysts comprise rare transition metal centers. Additionally, TAHz has been spectroscopically shown to form excited-state complexes with hydroxylic species. However, practical organic synthesis using TAHz as a photocatalyst has proven difficult due to its low solubility. Thus, we synthesized heptazine-based molecules with better solubility and more electron-withdrawing functionalities so future photochemical reactions can be more practically carried out. As a future direction, we plan to explore these new derivatives in the direct oxidative C-H amidation of the model substrates N-methylindole and N-methyl-para-toluenesulfonamide by PCET. This model reaction may improve upon previous catalytic methods in that the photocatalytic mechanism with heptazines replaces the need for heavy-metal photocatalysts and stoichiometric oxidants. Demonstrating the efficacy of this reaction may also present new opportunities for larger-scale application of heptazine derivatives to energy storage devices.

Synthesis and Characterization of Acid Site Distributions in Conventional and Core-Shell MFI Zeolite Catalysts
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The conversion of hydrocarbons (alkanes, alkenes) found in natural and shale gas resources is an important strategy to generate chemicals and fuels en route to a more sustainable energy future. The catalytic reactivity of zeolites for alkane and alkene conversion depends on the distribution of Bracid sites (H⁺) generated from the replacement of Si⁴⁺ ions with Al³⁺ ions in the crystalline framework. Synthesis methods have been explored to design core-shell MFI zeolitic materials with differing Si/Al ratios between the core and shell regions to alter mass transport limitations and enhance product selectivity. Namely, surface passivation of a ZSM-5 (i.e, Si and Al-containing MFI zeolite) crystallite can be achieved through the heterogeneous nucleation of a catalytically-inert Silicalite-1 (i.e, Si-only MFI zeolite) shell whose pores align with those of the core zeolite. We synthesized ZSM-5@Silicalite-1 (core@shell) samples under varied conditions of core annealing time and Silicalite-1 growth solution composition. We characterized the core and core-shell zeolites using powder X-ray diffraction (XRD), inductively coupled plasma – optical emission spectroscopy (ICP-OES), scanning electron microscopy (SEM), and nitrogen adsorption-desorption isotherms (77 K). Characterization data obtained on these zeolitic materials provided insight into their elemental composition, crystallinity, micropore volume, shell thickness, and shell coverage. An accurate assessment of such structural properties is essential to probe their influences on catalytic behavior, to provide a basis for comparison with core-shell zeolites prepared by other synthetic routes, and to design catalysts that are tailored for industrial functions. Experimental results indicated that increased core annealing times and relative molar concentrations of tetraethyl orthosilicate (TEOS) in the Silicalite-1 growth solution contributed to the formation of thicker Silicalite-1 shells. These observed trends will guide future efforts to tailor the shell thickness of ZSM-5@Silicalite-1 core-shell zeolites for catalytic applications.