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Colloidal Metal Chalcogenide Quantum Dots as Photo-Redox Catalysts for
Model Reactions Relevant to the Formation
of Liquid Fuels

Weiss, Emily
NORTHWESTERN UNIVERSITY
633 CLARK
EVANSTON, IL, 60208
USA

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Annual Report for:

Colloidal Metal Chalcogenide Quantum Dots as Photo-Redox Catalysts for Model Reactions Relevant to the Formation of Liquid Fuels

Emily A. Weiss, Department of Chemistry, Northwestern University

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PRINCIPAL INVESTIGATOR: Emily A. Weiss (e-weiss@northwestern.edu)

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Objective: The objective of this research program is to demonstrate and describe, quantitatively and mechanistically, the photocatalysis of a set of basic chemical reactions relevant to the production of liquid fuels by colloidal metal-chalcogenide quantum dots (QDs). Many reactions that produce, or facilitate the production of, fuels – such as the reduction of CO₂ to methanol or methane – require multiple reductions or oxidations, or both, of small-molecule substrates. These “redox” reactions can be conducted even more sustainably by powering them with sunlight, through the use of a photo catalyst. **The long-term objective of this research** is to develop metal-chalcogenide QDs into multi-active-site, colloidal photo catalysts that surpass the performance of homogeneous and heterogeneous catalysts for the sustainable, solar-powered production of liquid fuels.

Abstract: Our work on this project focused on quantum dot (QD)-photocatalyzed chemoselective and stereoselective organic reactions, namely demonstrating how adsorption of molecules to the surface of QDs can be used to provide microenvironments that promote enhanced photophysical processes and enhanced selectivity of chemical reactions. We show that colloidal QDs serve as visible-light chromophores, photocatalysts, and reusable scaffolds for homo- and hetero-intermolecular [2+2] photocycloadditions of unprecedented regioselectivity and diastereoselectivity for the previously minor *syn*-cyclobutane products, including the *syn*-head-to-tail cyclobutane, which has never before been accessed as the major product of a heterophotocycloaddition. This work produced series of pioneering, high-impact publications that provide fundamentally new strategies for challenging organic reactions.

Accomplishments

The first installment of this work is published in *Nature Chemistry* (2019). Direct coupling of alkenes into cyclic molecules through photocycloaddition is a shortcut for forming complex molecules with cyclic cores and various substituents, particularly tetrasubstituted cyclobutanes, which are common components of bioactive compounds and precursors for many natural products. Effective photochemical strategies for forming tetrasubstituted cyclobutanes must be chemoselective, regioselective, and stereoselective. We designed nano-photocatalysts to drive triplet-mediated [2+2] photocycloadditions of chalcone and stilbene derivatives by QD-to-

molecule triplet energy transfer. Self-assembly of molecules on the QD surface enables extrinsic control of the configuration of the cyclobutane (diastereoselectivity and regioselectivity) that counters the stereo-electronic preferences of the substrates. This strategy has great potential to enhance any reaction that proceeds through a triplet excited state, including metal complex-catalyzed reactions. This work is also the first example of catalysis triggered by triplet-triplet energy transfer from a QD.

The second installment of this work is published in the first issue of *Chem Catalysis*. The use of visible-light photosensitizers to power [2 + 2] photocycloadditions that produce complex tetrasubstituted cyclobutanes, as demonstrated in our previous work and by others, is a true success of photochemistry, but the scope of this reaction has been limited to activated α,β -unsaturated carbonyls. Our work demonstrates selective intermolecular homo- and hetero-[2 + 2] photocycloadditions of terminal and internal aryl-conjugated dienes—substrates historically unsuited for this reaction because of their multiple possible reaction pathways and product configurations—through triplet-triplet energy transfer from CdSe QD photocatalysts to generate valuable and elusive *syn-trans* aryl vinylcyclobutanes. We realized that the negligible singlet-triplet splitting of nanocrystals' excited states allows them to drive the [2 + 2] pathway over the competing [4 + 2] photoredox pathway, a chemoselectivity not achievable with any known molecular photosensitizer. We again used reversible tethering of the cyclobutane product to the nanocrystal surface to obtain stereoselectivity, here near-quantitative yield of the *syn-trans* product. This work is significant in that it expands the scope of selective photochemical [2 + 2] cycloadditions to coupling of conjugated dienes.

The third part of this work, published in *J. Am. Chem. Soc.*, we greatly expanded the scope of QD-photocatalyzed intermolecular [2 + 2] cycloadditions – namely, to freely diffusing substrates (no anchoring groups) – with the aid of polyaromatic energy shuttles that act as noncovalent adsorption sites for substrates on the QD surface. These QD–shuttle complexes photocatalyze homo- and heterointermolecular [2 + 2] photocycloadditions of benzalacetone, chalcone and its derivatives with up to 94% yield; the yields for all reactions are comparable to those achieved by $\text{Ir}(\text{ppy})_3$ but with the advantages of a factor of 2.5 lower catalyst loading, superior stability, and the ability to recover the catalyst by simple centrifugation and reuse it for multiple reaction cycles.

Much of the work done with this grant is compiled in a Perspective article for *J. Am. Chem. Soc.* on triplet-mediated photoreactions that I believe will serve as a guide to the field in this exciting new area.