

# CORE-CM SEMINAR

## Michigan State University

### Triplet Energy Transfer Across Quantum Dot – Molecular Interfaces

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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.<sup>1</sup> 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 6 orders-of-magnitude.<sup>2</sup> 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.<sup>3</sup> 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. Finally, a curious supramolecular mechanism for the generation of molecular triplets on the surface of PbS nanocrystals will also be presented.<sup>4</sup> These combined nanoparticle/molecular constructs are currently poised to sensitize myriad chemical transformations relevant for fields as diverse as optoelectronics, solar energy conversion, and photobiology.

#### References

- (1) Garakyaraghi, S.; Castellano, F. N. Nanocrystals for triplet sensitization: Molecular behavior from quantum-confined materials. *Inorg. Chem.* **2018**, *57*, 2351-2359.
- (2) Mongin, C.; Garakyaraghi, S.; Razgoniaeva, N.; Zamkov, M.; Castellano, F. N. Direct observation of triplet energy transfer from semiconductor nanocrystals. *Science* **2016**, *351*, 369-372.
- (3) Mongin, C.; Moroz, P.; Zamkov, M.; Castellano, F. N. Thermally activated delayed photoluminescence from pyrenyl-functionalized CdSe quantum dots. *Nat. Chem.* **2018**, *10*, 225-230.
- (4) Garakyaraghi, S.; Mongin, C.; Granger, D. B.; Anthony, J. E.; Castellano, F. N. Delayed molecular triplet generation from energized lead sulfide quantum dots. *J. Phys. Chem. Lett.* **2017**, *8*, 1458-1463.

**THURSDAY, OCTOBER 4, 2018**  
**12:00 NOON \*refreshments at 11:45 am**  
**Room 1400 – Biomedical & Physical Sciences**  
**Professor Rémi Beaulac – Host**