

PHYSICAL CHEMISTRY SEMINAR



CANCELLED

Prof. Mark W.B. Wilson

*Department of Chemistry
 University of Toronto*

Monday, Oct 11, 2021

4:00 PM

via Zoom

“Understanding the synthesis of PbS quantum dots to achieve nanocrystal-sensitized upconversion photochemistry”



The ability to efficiently up-convert broadband, low-intensity light would be an enabling technology for background-free biomedical imaging, volumetric 3D printing, and sensitizing silicon focal plane arrays to the short-wave infrared. Our approach uses colloidal quantum dots—size-tunable spin-mixing fluorophores—to absorb low-energy photons and sensitize the spin-triplet excitonic states of nearby conjugated molecules.^{1,2} Once there, pairs of these long-lived excitations can combine via triplet fusion (triplet-triplet annihilation) to generate shorter-wavelength fluorescence.

To advance triplet-fusion upconversion, we are using spectroscopy to deepen our understanding of nanocrystal synthesis and probe the movement of energy and charge within and between organic and inorganic semiconductors. For instance, we have uncovered that a pre-nucleation cluster intermediate has historically frustrated efforts to synthesis low-dispersity ensembles of small ($\varnothing < 4$ nm) PbS nanocrystals, and showed that Lewis basic additives can restore one-step growth and yield markedly narrower heterogeneous linewidths in reactions that run to completion.³ We are expanding from this insight to build mechanistic understanding of the synthesis and surface of metal-chalcogenide nanocrystals.

We then harnessed the ultra-small ($\varnothing \sim 1.7$ nm, $h\nu_{\text{peak,abs}} = 2.2\text{eV}$) PbS quantum dots that we can now controllably produce to sensitize ‘red-to-blue’ triplet-fusion upconversion in solution. We show that the long ($> \mu\text{s}$) photoluminescence lifetimes of these particles enable max-efficiency upconversion at lower light intensities ($I_{\text{th}} = 220$ mW/cm²), overcoming a mildly endothermic sensitization scheme that maximizes the anti-Stokes shift ($\Delta E = 1.04$ eV). This architecture facilitates the photo-initiated polymerization of methylmethacrylate using only long-wavelength light ($\lambda: 637$ nm); a demonstration of nanocrystal-sensitized upconversion photochemistry. Finally, from the quasi-equilibrium dynamics of triplet energy transfer, we infer that the chemical potential of photoexcited, ultra-small PbS quantum dots is surprisingly high—completing an advantageous suite of properties for upconversion photochemistry, but reinforcing questions regarding the emissive state.

References:

1. Wu, Congreve, MWBW et al. (Bulovic, Bawendi, Baldo) *Nature Photon.* 10:31 (2016)
2. Huang et al. (Bardeen, Tang) *Nano Lett.* 15:5552 (2015)
3. Green, et al. (MWBW) *Chem. Mater.* 32(9):4803–4094 (2020)
4. Imperiale, et al. (MWBW) *Chemical Science.* (Accepted)

Please contact marla@chem.ucla.edu for additional information.