

## Brightening of Quantum Dots via Dot-Dot and Dot-Ligand Interactions

Svetlana Kilina, Levi Lystrom, Naveen Dandu

Chemistry and Biochemistry Department North Dakota State University, Fargo, ND 58102

Due to very high photoluminescence quantum yield and narrow emission line width, colloidal quantum dots (QDs) are near-ideal materials for various lighting technologies, including bio-labels and bi-tags. However, QD's ability to harvest and emit light is extremely sensitive to their complicated surface chemistry. Thus, high sensitivity of their properties to the surface passivation and chemical environment results on "blinking" – fluorescence intermittency – that is disfavorable for many potential applications. Recent experiments on blinking statistics of Si QDs reveal that the close packing of QDs at distances of 1 nm results in a significant increase in "on" time corresponding to the system's state with the high quantum efficiency. However, understanding of physical processes governing this behavior is still incomplete. Using density functional theory (DFT) and time-dependent (TD-DFT) calculations, we investigate the effect of the QD-QD interaction on their morphology and optical properties, specifically focusing on the question how this interaction depends on their surface chemistry. Our calculations suggest that a fast energy transfer between an excited QD to the nearest one provides an additional channel for occupation of long-leaving semi-dark and dark trap states in neighboring QDs forcing the emission to happen from higher-energy optically bright states. This pathway increases 'on' blinking time in aggregates of strongly interacting Si QDs. Also our DFT calculations have explained experimental observations on dramatic increase in quantum yield of CdSe QDs treated with hydrides. Calculations reveal that the hydrides ( $H^-$ ) interacting with the QD's surface result in three main structural effects: the release of hydrogen selenide, reduction of Cd in a form of a metal, and bonding of hydride to surface Cd. The last scenario is the most pronounced in the Cd-enriched QDs and leads to a significant increase of the oscillator strength of the lowest energy transition, as compared to similar QDs ligated by amine ligands. Thus, hydrides efficiently saturate both Cd- and Se-associated dangling bonds and eliminate the hole and electron trap states from the band gap of the QD, resulting in increase in emission. Overall, our calculations provide insights into the surface chemistry of QDs and offering guidance for controlling the optical response of nanostructures by means of surface ligand engineering.