

## NON-LINEAR EFFECTS IN THE QUENCHING OF FLUORESCENT SEMICONDUCTOR NANOPARTICLES BY PARAMAGNETIC SPECIES

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Semiconductor nanoparticles have received much attention due to their exceptional luminescent properties. Controlled quenching of fluorescent Q-dots may be the first step in the development of functional sensors. We have examined the quenching of fluorescent CdSe quantum dots by the persistent free radicals TEMPO and 4-Amino-TEMPO in toluene solutions. We used quantum dots of 2.4 nm (green,  $\lambda_{\max}$  525 nm), 3.2 nm (orange,  $\lambda_{\max}$  575 nm) and 6.7 nm (red,  $\lambda_{\max}$  630 nm), in diameter. Stern-Volmer plots for fluorescence quenching by TEMPO are characterized by major deviations from linearity; typical Stern-Volmer plots are linear, and deviations from linearity are frequently attributed to quenching of more than one electronic state, or to a combination of static and dynamic quenching. In the case of quantum dots the changes in slope with TEMPO concentration are too large to be accommodated within this model. The data show an exponential dependence with quencher concentration, of the type  $I_0/I = \exp(\alpha[Q])$ . Interestingly, the values of  $\alpha$  show remarkable size dependence. For example the values are 13.7 and 1.6 M<sup>-1</sup> for quantum dots of 2.4 and 6.7 nm in diameter, respectively. These values indicate that small Q-dots are quenched much more efficiently than large ones. For example, in the presence of 0.6 M TEMPO 35% of the emission persists for 6.7 nm nanoparticles, but only 0.1% in the case of 2.4 nm nanoparticles. The nature of the molecular interactions leading to this unusual behavior will be presented.

Association constants for the interaction of TEMPO with CdSe quantum dots are small; however, the equilibrium constants are much larger in the case of 4-amino-TEMPO, with extensive binding with micromolar concentrations. A size dependent quenching of the fluorescence is also observed. A comparison of steady state and time-resolved fluorescence data with ESR parameters for the nitroxide leads to a better understanding of the interactions involved.

We have also examined the interactions of quantum-dots with paramagnetic species in photonic crystal fibers (PCFs), where the non-linearity mentioned above leads to unusual time dependent fluorescence, as monitored by fluorescence microscopy. The potential of quantum-dot filled PCFs in the design of functional materials, such as multichannel sensors will be discussed.