Fluorescence Quenching of Colloidal Quantum Dots by Paramagnetic Quenchers

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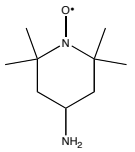
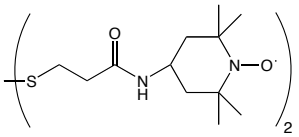
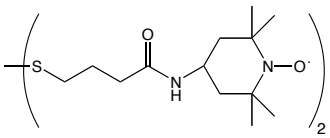
Nanocrystalline quantum dots (QDs) have been the subject of intense research for over a decade now because of their interesting properties and their potential in development of nanodevices and technology. TOPO-coated CdSe QDs have become one of the most studied QD systems because of their easily-tunable emission wavelengths and highly desirable properties. It has been shown that CdSe fluorescence is quenched non-linearly by TEMPO, a nitroxide radical species, but at very low efficiency. The present study focused on the effects of tethering nitroxide molecules to the surface of the QDs using amino or disulfide moieties. The quenchers utilized are show in the figure below.



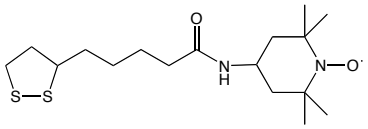
4-amino-TEMPO



C3 Disulfide Radical



C4 Disulfide Radical



C7 Disulfide Radical

It was shown that tethering the nitroxide molecule to the QD surface dramatically increased the quenching efficiency of the quenchers. It was also found that as in the case of TEMPO, all other quenchers showed a quenching efficiency that was QD size dependent: Smaller QDs were quenched more efficiently than larger QDs. To explain such a phenomenon, a "reverse Perrin" model was proposed.

In addition, it was found that tether length also drastically affected quenching efficiency. Concentrating only on the disulfide series of compounds, quenching efficiency was in the order C3>C4>C7. The results once again corresponded nicely to the "reverse Perrin" model. The magnitude of the effect ruled out the possibility of an energy-transfer quenching mechanism, which led us to propose either 1) an induced intersystem crossing mechanism or 2) the nitroxide radicals acting as surface traps. Further work is currently underway to determine the correct mechanism.