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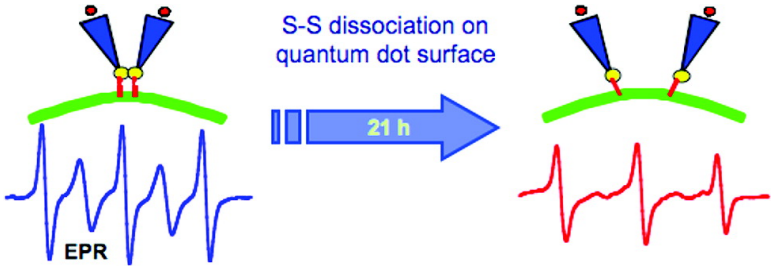


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# Dynamics of the Dissociation of a Disulfide Biradical on a CdSe Nanoparticle Surface

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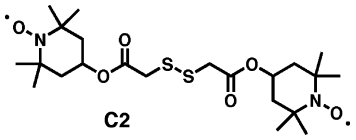
As applications for semiconductor nanoparticle quantum dots (QDs) continue to expand in fields such as biology, imaging, and sensors,[1] it is paramount to have a fundamental understanding of their chemical and electronic interactions. Thiol-stabilized QDs have received considerable attention because they suffer from fewer fluctuations in their properties, and in certain cases their photoluminescence quantum yields show an improvement over trioctylphosphine oxide (TOPO)-capped QDs.[2,3] Further, from the perspective of QDs biological applications, the interaction of RS−H and RS−SR bonds with the surface is of the utmost importance.

As part of our study of the interaction of (TOPO)-capped CdSe QDs with free radicals,[4−6] we have found that binding of disulfide biradical **C2** to the QD surface provides a unique perspective of the mechanism by which disulfide binding evolves on the surface. By probing the system with fluorescence and EPR spectroscopies, we have found that the disulfide linkage is useful for the attachment of species to the surface of CdSe QDs leading to robust, strong chemical bonds to the particle surface and reporting on the dynamics of surface binding and S−S dissociation.




Our study of the interactions between QDs and **C2** was stimulated by earlier work on the interaction of binding and nonbinding nitroxides with CdSe QDs, showing that quenching of QD fluorescence by 4-amino-2,2,6,6-tetramethylpiperidine oxide (4-aT) is several orders of magnitude more efficient than quenching by TEMPO itself,[5,6] indicating that amine binding to the QD surface greatly facilitates fluorescence quenching. The selection of **C2** reflects synthetic convenience, having the disulfide moiety as our potential binding site to the QD surface. Several groups have reported on the binding of amines to CdSe QDs,[2,7] but to our knowledge this is the first in-depth investigation of disulfide interaction with a CdSe QD surface.

As illustrated in the Stern−Volmer (SV) analysis (eq 1) shown in Figure 1, addition of varying amounts of **C2** to green CdSe QDs ($\lambda_{em} = 515$ nm, 5 $\mu$M) resulted in dramatic fluorescence quenching at submillimolar concentrations (expressed as [**C2**] × 2 to account for the number of radical species) after long incubation times (vide infra). We were able to determine the initial slope for fluorescence quenching at low concentrations according to

$$\frac{F_0}{F} = 1 + k_q\tau \times 2 \times [\mathrm{C2}] = 1 + K_{SV} \times 2 \times [\mathrm{C2}] \quad (1)$$

where $F_0$ and $F$ are the emission intensities in the absence and presence of quencher 24 h after mixing (vide infra), $K_{SV}$ is the SV constant equal to the slope of the initial fit, $k_q$ is the quenching rate constant, and $\tau$ is the emission lifetime. The SV plot is nonlinear, (Figure 1); analysis of the steep region yields $K_{SV} = 28\,500\ \mathrm{M}^{-1}$ that, assuming an average lifetime of ca. 40 ns, corresponds to $k_q \approx 7 \times 10^{11}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, which would be significantly faster than the diffusion-limited rate constant in toluene. This indicates that fluorescence quenching is occurring through a static mechanism, as was observed in the case of 4-aT. As in the case for 4-aT, a SV plot shows negative curvature, indicating at least two different modes of quenching. We propose that the initial, steeper portion results from binding to unoccupied Cd surface sites while the less-efficient quenching (giving a characteristic slope of 3700 $\mathrm{M}^{-1}$) reflects slow displacement of weakly bound TOPO ligands once TOPO-free sites are exhausted. Recent work from our group using core and core−shell QDs of various sizes supports this interpretation (see Supporting Information).[8]

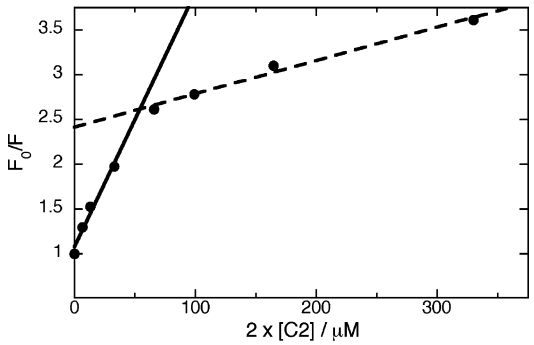



***Figure 1.*** Stern Volmer analysis of the luminescence quenching of 5.0 $\mu$M QDs by addition of **C2**. The downward-curving behavior is indicative of multiple modes of quenching.

The **C2** biradical gives the characteristic EPR spectrum of Figure 2a (initial), where the broad 5-line spectrum is indicative of the two radical centers in each molecule coupling to each other.[9] Upon addition of an excess of QDs (5.0 $\mu$M to 1.7 $\mu$M **C2**), the two visible biradical lines gradually disappear after ∼24 h to the characteristic 3-line spectrum of simple nitroxides ($t = 21$ h).[10] Figure 2b shows EPR spectra when QDs are added to a large excess of **C2** (8.2 $\mu$M QD, 200 $\mu$M **C2**) and 41 h later. Extraction of excess **C2** and any free nitroxide (after 41 h) by toluene evaporation followed by methanol washing and resuspension of the QDs leads to the spectrum of bound **C2** products. The large excess of **C2** is used to maximize the number of radicals bound to the nanoparticles. The disappearance of biradical lines reflects the fact that nitroxide moieties are no longer in proximity to one another once bound to the QD surface, indicative of S−S bond cleavage.

In the EPR studies with **C2**, minor hyperfine splitting from adjacent $CH_2$ groups in positions 3 and 5 only becomes visible following binding to the CdSe surface and loss of the biradical signal (Figure 2b). We believe that the alkane and ester spacers in **C2** increase the length and flexibility from the binding site (S atom) to TEMPO unit such that the majority of the TEMPO moiety is at



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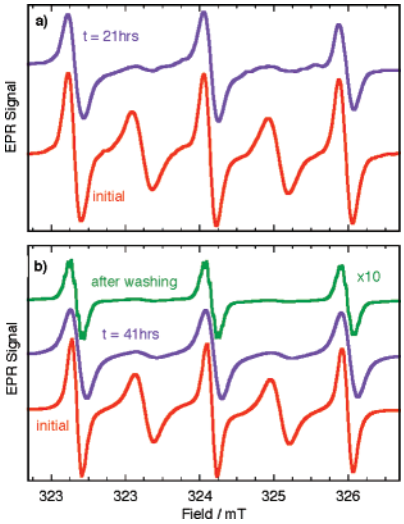


***Figure 2.*** (a) EPR spectra for 1.7 $\mu$M **C2** in toluene after addition of 5.0 $\mu$M QDs recorded immediately after mixing and 21 h later; (b) EPR spectra for 200 $\mu$M **C2** in toluene after addition of 8.2 $\mu$M QDs recorded immediately after mixing, 41 h later, and after extraction. The extraction process leads to significant sample loss (judged by UV absorbance) and a weaker (but better resolved) spectrum. All microwave parameters are kept constant (modulation width = 0.020 mT; time constant = 0.1 s; power = 0.2 mW).

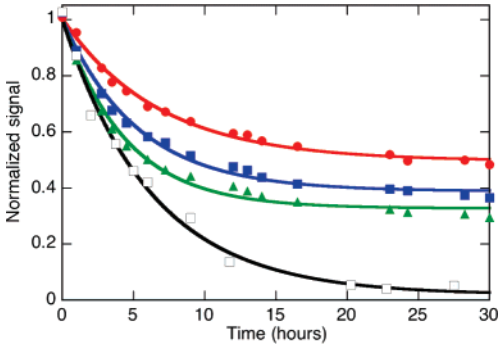


***Figure 3.*** Normalized EPR (□) fluorescence decays in toluene at room temperature under nitrogen. The EPR sample has 2.7 $\mu$M QDs and 1.7 $\mu$M **C2**, while the samples for fluorescence have 2.7 $\mu$M QDs and 17 (●), 34 (■), and 85 (▲) $\mu$M **C2**. The data were fitted with a monoexponential function for convenience, and the data in the plateau region were used for the SV plot of Figure 1. The lifetime derived from EPR is 6.3 h, and that derived from fluorescence are 6.8, 5.3, and 4.4 h for increasing **C2** concentrations.

or near the edge of the TOPO monolayer, where some rotation is allowed; it also is possible that thio-radical head-to-tail trapping (Supporting Information) may also contribute to some rotationally free nitroxide radical and some loss in signal intensity (see 41 h spectrum in Figure 2b).[12]

The dynamics of fluorescence quenching and biradical disappearance are shown in Figure 3. Disappearance of the EPR **C2** biradical signal followed the same trend as fluorescence decrease, though recorded at different **C2** concentrations due to instrumental limitations; the concentrations were still chosen in the low concentration region (compare with Figure 1) where we believe little to no TOPO displacement is required. The correlation between biradical disappearance and fluorescence quenching suggests that thiolate-bound nitroxides from disulfide dissociation are the dominant fluorescence quenchers at long times. Control experiments with an excess of a nonradical analogue of **C2**, with cyclohexyl moieties replacing the TEMPO moieties, were performed and showed no quenching of QD fluorescence, indicating that the radical centers are responsible for the quenching (see details in Supporting Information).

The long incubation times observed suggest an activated adsorption process; the exact magnitude of the barrier that leads to S−S dissociation is not known, but the lifetime[13] of this process is in the neighborhood of 7 h. If we assume that disulfide dissociation can be treated as a simple unimolecular reaction with a pre-exponential factor of $10^{13}$ $s^{-1}$, then the barrier can be estimated as ca. 24 kcal/mol, compared with a typical aliphatic disulfide bond around 70 kcal/mol.[12] Clearly the CdSe surface greatly assists S−S cleavage. Deviations from first-order behavior and lifetimes which vary with **C2** concentration are attributed to the contribution of the two different modes of binding as discussed earlier.

Addition of amines (cyclohexylamine, hexadecylamine) to QDs whose fluorescence had already been quenched by addition and incubation with **C2** did not show any increase in emission intensity, in contrast to the case of 4-aT, suggesting stronger binding by **C2**-derived radicals than in the case of amines. In this system amines are unable to displace thiolate-bound quenchers.

In summary, we report a study of the dynamics of interaction between a CdSe TOPO-coated QD surface and a disulfide using biradical signals combined with fluorescence as a reporter of binding events. The time-dependent nature of the binding event and subsequent fluorescence quenching is determined to be largely due to disulfide bond cleavage on the surface of the QD. Further studies are underway to examine the effect of the aliphatic chain length on electronic interactions affecting fluorescence between the QD surface and adsorbed species. We are also actively investigating the catalytic activity of the CdSe surface in disulfide bond cleavage.

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**Supporting Information Available:** Synthetic details, mechanistic and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) This lifetime in this context refers to the lifetime required for the biradical signal of **C2** to disappear upon QD addition (EPR) or fluorescence intensity of the QDs to stabilize upon **C2** addition.

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