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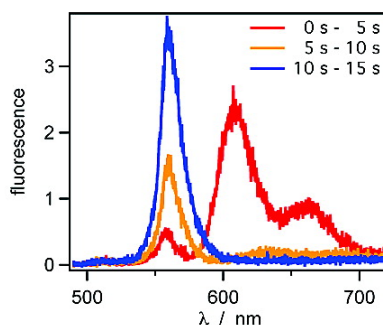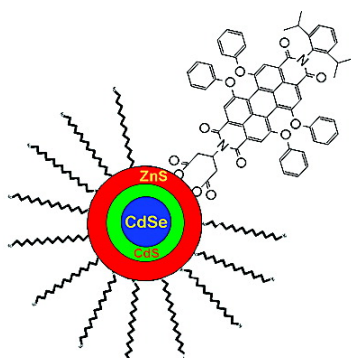
# A Simple and Versatile Route to Stable Quantum Dot#Dye Hybrids in Nonaqueous and Aqueous Solutions

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# A Simple and Versatile Route to Stable Quantum Dot−Dye Hybrids in Nonaqueous and Aqueous Solutions

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Hybrid materials composed of inorganic semiconductor quantum dots (QDs) and $\pi$-conjugated organic molecules (Dye) are being increasingly considered for optoelectronic and sensing applications.[1] Recently, a number of approaches have been developed to prepare Dye/QD conjugates in solution. In early experiments the emission of CdSe/ZnS QDs was completely quenched by unspecific complex formation with a diazaperylene dye.[2] Later on more reliable protocols have been developed in which attachment of dye to QD was mediated by an additional component such as proteins, peptides, or polymers.[3] Other approaches used pyridyl moieties for Dye/QD complex formation or interdigitization of alkylamino chains into the alkyl-capping layer of QDs.[4] In most of these conjugates the QD (Dye) acts as an energy donor (acceptor) and excitation energy transfer (ET) signals complex formation. The modulation of ET efficiency, e.g. by analyte binding, typically provides the basis of the sensing capability. In several instances energy transfer from QD to dye could be satisfactorily modeled in terms of the Förster mechanism (Fluorescence resonance energy transfer: FRET),[5,6] although deviations have also been reported.[4b]

Here, we report a versatile approach to extraordinarily stable Dye/QD hybrids, which uses dicarboxylate anchors[7] to bind rylene dyes to QD. In the example shown in Scheme 1, the starting perylene dye **1**[8a] was partially saponified under basic conditions to give monoanhydride **2**. Imidization of **2** with $\beta$-glutamic acid in NMP affords **3**. Under basic conditions both dyes (**2**, **3**) expose two carboxylate moieties for binding to the QD surface (see below).

Multishell QDs composed of a CdSe core and covered by various layers of CdS and ZnS were synthesized according to existing protocols.[9] Exemplarily, complexes between CdSe/CdS/ZnS QDs and dyes **2** or **3** were formed by sonicating a mixture of dye (in methanol) and QD (in chloroform) after addition of a weak base ($K_2CO_3$) for 4 h.[7] Next, the Dye/QD complexes were precipitated, washed, and redissolved in chloroform yielding clear solutions. The (spectroscopic) observation that after repeated precipitation−dissolution cycles only minor amounts of dye detached from QD, with **3** showing qualitatively a higher binding affinity than **2**, is a first indication of the high stability of the complexes.

In Figure 1a, a series of emission spectra obtained for different Dye **3**/QD ratios is shown. (Similar results have been obtained for **2**, see Supporting Information.) The given ratios are the nominal values of the starting mixtures, and for each ratio the precipitation−dissolution step has been carried out. With increasing dye amounts the QD emission is successively quenched and sensitized dye emission increased, indicating efficient ET in the complexes, which will be analyzed in full detail below. All spectra have been corrected for the small contribution from direct excitation of the dye. Fluorescence decay curves of QDs in the complexes (see Supporting Information) show an additional fast component also corroborating efficient ET.

**Scheme 1.** Rylene Dyes and Dye−QD Binding Model
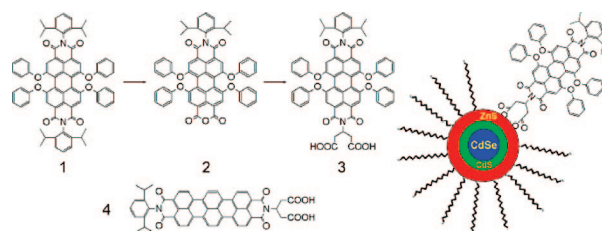


Using dye **1** and going through exactly the same sequence of steps as those described before did not result in any detectable complex formation. These results strongly suggest that dyes **2** and **3** bind specifically via their dicarboxylate groups to QDs, while nonspecific binding of **1** did not occur. Accordingly, we propose a chelate type binding of the bidentate anchors in **2** and **3** to $Zn^{2+}$ ions on the QD surface (Scheme 1). For a given Dye/QD ratio, emission spectra remained almost constant for now up to 9 months corroborating the high stability of the complexes.

So far we have restricted the discussion to perylene derivatives **2** and **3**. Our route for Dye/QD complex formation, however, can be straightforwardly adapted to their terrylene and quaterrylene analogues.[8b] Hence, in combination with QD size quantization, broad color tunability of the complexes can be achieved. Indeed, stable complex formation has been observed, e.g., between terrylene dye **4** (scheme 1) and QDs using the same procedure as that described before. An emission spectrum is presented in Figure 1b clearly showing emission from QDs ($\lambda_{max} \sim 600$ nm) and dye **4** ($\lambda_{max} \sim 670$ nm) after selective excitation of the QDs. Here, multishell QDs with red-shifted emission have been used.

The Dye/QD complexes can be transferred from the organic into the aqueous phase by exchange of the original ligands (oleic acid, oleyl amine) by mercapto-propionic acid (MPA) under basic conditions. Dye **3**/QD and MPA in an isopropanol/chloroform mixture were refluxed under Ar for 5 min. As can be clearly seen in Figure 1c, the aqueous solution contains Dye/QD complexes. An appreciable fraction of **3**, however, has been replaced by MPA, which is known to bind strongly via its thiol group to the QD surface
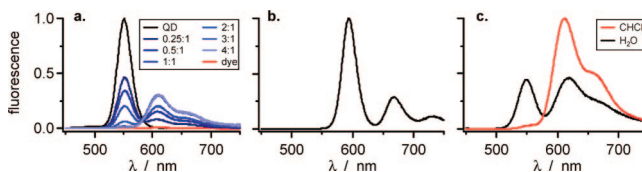


**Figure 1.** Fluorescence spectra of (a) Dye **3**/QD complexes in $CHCl_3$ as function of Dye/QD ratio; (b) Dye **4**/QD complex (ratio 1:1) in $CHCl_3$; (c) Dye **3**/QD complex in $CHCl_3$ and after transfer into water. In all cases the excitation wavelength was 390 nm.
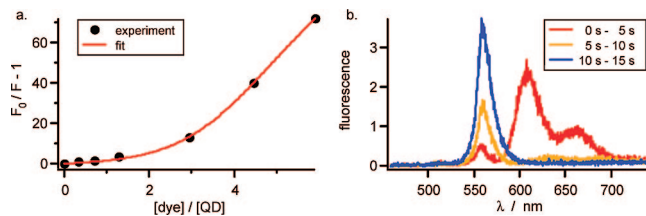
**Figure 2.** (a) Stern−Volmer plot of QD fluorescence quenching in complex with dye **3**. Data were fitted with a model assuming a binomial distribution of the number of dyes bound to QD and an FRET process (see text). (b) Sequence of emission spectra of a single Dye **3**/QD complex in PMMA ($\lambda_{exc} = 488$ nm, details below).

(ZnS).[10] Consequently, the overall ET efficiency in the complex is reduced after transfer into water.

In Figure 2a QD quenching expressed as $F_0/F - 1$ from the series in Figure 1a is plotted versus the Dye/QD ratio where $F_0$ and $F$ are the fluorescence intensity of QDs in the absence and presence of the dye, respectively. As we observed reduced donor emission and sensitized acceptor emission as well as strong spectral overlap between QD emission and dye absorption (Figure S1), the quenching of QD emission is described by the following FRET expression with transfer efficiency $E$ (for details see Supporting Information):

$$\frac{F_0}{F} - 1 = \frac{E}{1-E} \text{ with } E = \sum_{d=0}^{d_{max}} a(d) \frac{d}{d + (r/R_0)^6}$$

where $d$ is the number of dye molecules bound to QD and $a(d)$ is the QD fraction with $d$ bound dye molecules according to a binomial distribution. The ratio ($r/R_0$) is one of the fitting parameters, where $r$ is the donor−acceptor distance and $R_0$ the Förster radius, which for dye **3** is 5.3 nm. The model describes the experimental data of Dye **3**/QD complexes in Figure 2a quite well resulting in ($r/R_0$) = 0.63. Using $R_0 = 5.3$ nm, one obtains $r = 0.63 * 5.3$ nm = 3.4 nm. From our binding model (Scheme 1) we estimate a center-to-center-distance of 3.3 nm. The discrepancy between spectroscopic and geometrical data is quite small and indicates that a Förster approach seems to give a reasonable description of ET in the complexes.

Individual complexes immobilized in PMMA were studied by confocal fluorescence microscopy.[3c,11] In the series of emission spectra shown in Figure 2b, the first spectrum is dominated by the emission of the dye ($\lambda_{max} \sim 600$ nm) while QD emission ($\lambda_{max} \sim 560$ nm) is weak. During recording of this spectrum, the dye bleached, resulting in QD emission only in the second spectrum. The third and all subsequent spectra (not shown) exclusively showed QD emission. The strongly varying emission intensities of QDs in the second and third spectrum are caused by QD blinking.[12] For all cases studied, dye bleaching was more efficient than QD bleaching, which supports the superior photostability of QDs. We found that 45% of the bright spots in the fluorescence images gave rise to mixed Dye/QD emission. The remaining spots were mainly due to QD emission, and in a few cases also dye emission only was found. Statistically, the percentage of complexes containing at least one dye molecule should be 63% for a mean Dye/QD ratio of 1:1 in the reaction solution. The experimental value (45%) is not too far from this number, taking into account that film preparation conditions and rapid dye bleaching in the single particle experiments

will decrease the number of intact complexes. This result, obtained at the single molecule level, is another clear example of the extraordinary stability of our Dye/QD complexes.

In summary, we have established a versatile route for the preparation of extraordinarily stable Dye/QD complexes by furnishing rylene dyes with dicarboxylate anchors. By proper choice of dye and QD components, a broad spectral range from the visible up to the NIR can be covered and additionally the efficiency of ET can be easily tuned. Future work will focus on the selection of more appropriate ligands to optimize transfer of the complexes into the aqueous phase. Furthermore, the time scale of ET will be directly probed by transient absorption measurements. In combination with the capability to vary the Dye−QD distance with, e.g., an increasing number of ZnS layers while preserving the binding geometry, such investigations will give unprecedented insights into the ET mechanism operating in such complexes.

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