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Efficient Quenching of TGA-Capped CdTe Quantum Dot Emission by a Surface-Coordinated Europium(III) Cyclen Complex

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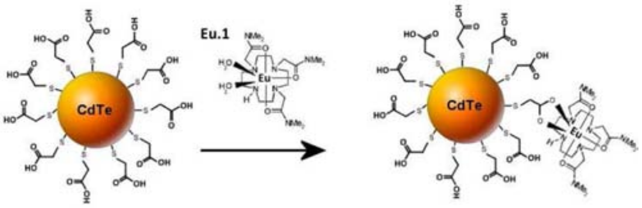
Supporting Information

ABSTRACT: Extremely efficient quenching of the excited state of aqueous CdTe quantum dots (QDs) by photoinduced electron transfer to a europium cyclen complex is facilitated by surface coordination to the thioglycolic acid capping ligand. The quenching dynamics are elucidated using steady-state emission and picosecond transient absorption.

Scheme 1. Formation of the Eu.1-CdTe Conjugate



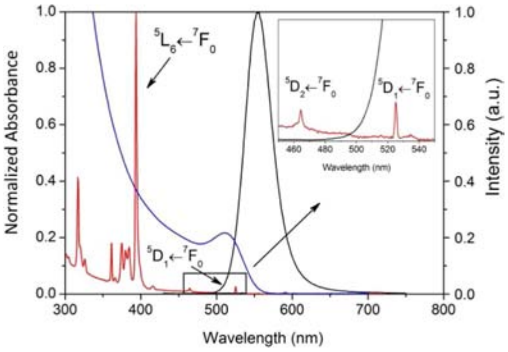


Figure 1. Absorption spectrum of 0.1 M **Eu.1** and 1.29×10^{-5} M TGA-CdTe QDs in water and emission spectrum (λ_{ex} = 450 nm) of QDs. Spectra have been normalized for the sake of comparison.

The luminescent properties of cadmium chalcogenide quantum dots (QDs), which include narrow emission band and high quantum yields, render them attractive for a range of applications including optoelectronics, light-harvesting, biological imaging and biosensing.[1−7] In general, excitation of QDs generates exciton (electron−hole pair) excited states, which can subsequently recombine through a number of processes. These occur over various time scales with fast carrier trapping known to happen on the picosecond time scale, while electron−hole recombination occurs over longer times.[8] Surface states play an important role in these processes, and consequently QDs are highly sensitive to surface modifications.[9] In particular, the binding of suitable molecules at the surface can facilitate efficient charge[10] or energy transfer[11] (both are typically signaled by changes in luminescence). Lanthanide complexes have been used extensively for sensing and imaging due to their long-lived excited states (ms) and well spaced, line-like emission in the visible {Eu(III), Tb(III)} and near infrared {Yb(III), Nd(III)} regions.[15] Recently, the sensing capacity of a lanthanide complex attached to gold nanoparticles for biologically relevant species has been demonstrated.[13] However, combining the properties of Lanthanide and QD systems offers the potential to achieve enhanced optical properties.[12] In this work, we investigate the properties of aqueous lanthanide-CdTe systems formed by the coordination of a caged europium complex **Eu.1** to the terminal COOH groups of the thioglycolic (TGA) capped CdTe QDs as shown in Scheme 1 and compare these results to the system formed in the presence of the uncaged Eu(III) triflate salt.

Water-soluble TGA-CdTe QDs were prepared using the method developed by Gaponik et al.[15] The steady-state absorption spectrum in water shows a band at 510 nm, which is assigned to the first excitonic transition (1Se−1Sh) (Figure 1). From this, the diameter of the particles was determined to be 2.3 nm, which was corroborated by high-resolution transmission electron microscopy; see Figure S1 in the Supporting Information (SI).[16] The presence of negatively charged COO^- surface groups was confirmed by ζ-potential measurements (−48 mV); see Figure S2 in the SI. Excitation of the QDs at 450 nm resulted in band-edge photoluminescence centered at 550 nm with a QY of 22% measured against Rhodamine 6G. The **Eu.1** complex was synthesized according to literature procedures.[12] The strongest transition in the visible spectrum of **Eu.1** occurs at 394 nm and has a molar extinction coefficient of just 2 M^{-1} cm^{-1}, see Figure 1, (the small value is due to a combination of strongly forbidden f−f electronic transitions of Eu^{III} and the nature of the

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cyclen ligand). Therefore, accurate concentrations of Eu.1 were determined using a displacement titration (see Figures S3−S5 in the SI).[12,13]

The addition of **Eu.1** to QDs resulted in no significant change in the UV−visible absorption at 510 nm but had a dramatic effect on the steady-state emission of the QDs (see Figure 2a).

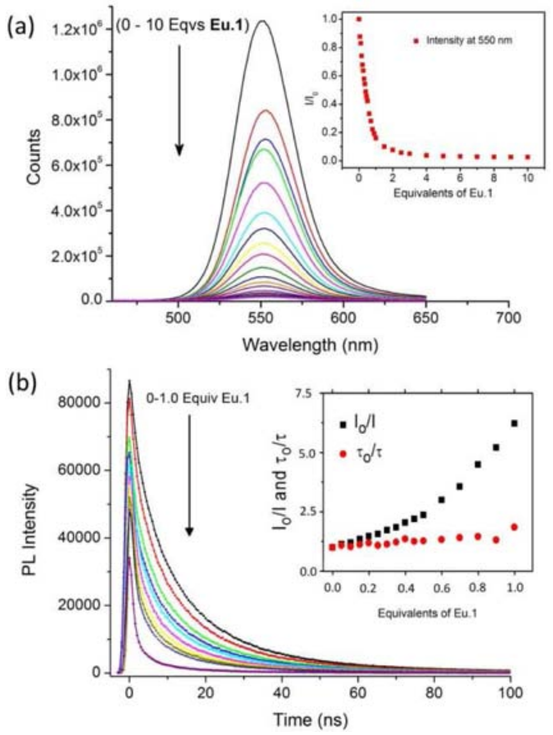

Figure 2. Changes in (a) the PL intensity (λ_{ex} = 450 nm and (b) the ns fluorescence decay profiles of TGA-CdTe QDs (3.7×10^{-6} M) in the presence of **Eu.1** [$(0-3.7) \times 10^{-5}$ M].

Strong (80%) quenching occurred upon titration of 1 equiv, and almost complete quenching (∼96%) was reached with 2 equiv (Figure 2a). If quenching was treated as a dynamic process, the Stern−Volmer analysis yielded a bimolecular quenching constant of 1.9×10^{13} M^{-1} s^{-1}. This is orders of magnitude greater than the diffusion-limited value of 1.0×10^{10} M^{-1} s^{-1} predicted for aqueous solutions and suggests a dominant role of static quenching.[17] The role of static quenching is also supported by a decrease in the initial amplitude of the decay profiles (Figure 2b). In the absence of **Eu.1**, biexponential behavior was observed with τ values of 6 ns (25%) and 20 ns (75%), respectively. Successive additions of **Eu.1** result only in a small reduction in the average emission lifetime, from 18 to 14 ns upon the addition of 1 equiv of **Eu.1**.

Recently, it was reported that strong surface interactions can result in a preferential decrease in one component of the QD emission, which manifests as a reduction in the average lifetime.[18] Furthermore, the same efficient quenching behavior was also observed for a much weaker (100 nM) solution of QDs (see Figure S6 in the SI). This contrasts with studies that employ hole and electron trapping, where the reagents would have to be in large excess for such low concentrations of QDs.[10] The strong quenching at low equivalents is attributed to the significant driving force for **Eu.1** to bonds to the surface TGA, which results in the release of two water molecules.[19] Taken together, these results strongly indicate that the europium complex is able to quench a precursor to the exciton by subnanosecond processes that are too fast to measure with the SPC instrument.

Picosecond transient absorption (ps-TA) spectroscopy was performed using excitation energies below ca. 0.56 mJ cm^{-2} to minimize multiphoton effects. The ps-TA spectrum of QDs following excitation at 400 nm (50 fs) is shown in Figure 3a.[20]

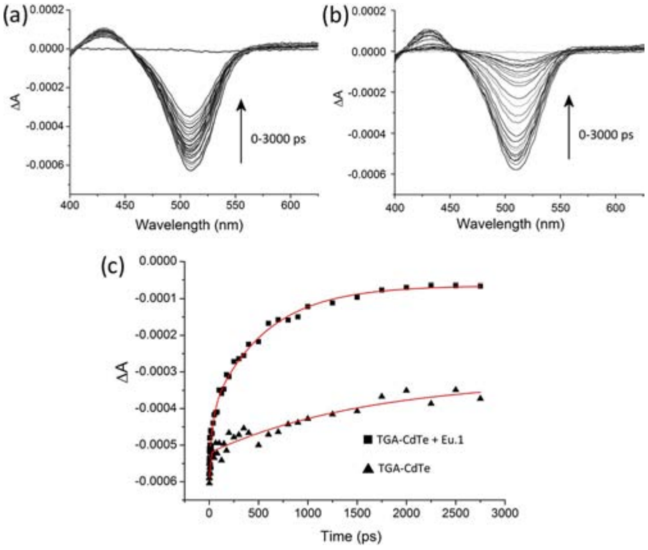

Figure 3. Transient absorption spectra following 400 nm (50 fs) excitation of 3.7×10^{-6} M TGA-CdTe QDs in the absence (a) and presence (b) of **Eu.1** (3 equiv). (c) Comparison of the kinetics for recovery of bleach in TGA-CdTe QDs upon the addition of **Eu.1**.

The dominant feature is that of a strong bleached band that corresponds to the depletion of the ground state. Multicomponent analysis was needed to determine the kinetics of recovery of this band, and assuming a biexponential model, lifetimes of 8 ± 3 ps (22%) and 1.6 ± 0.5 ns (34%) were found; the latter state results in incomplete recovery (44%) of the bleach on the time scale of the experiment (Figure 3c). These values are in agreement with recent ps-TA observations for similar QDs.[21]

Figure 3b shows the transient absorption of TGA-CdTe recorded in the presence of 3 equiv of **Eu.1**. In this case, we see almost complete signal recovery of the bleached band, which is more clearly visible in Figure 3c. Biexponential analysis of the recovery kinetics, for the bleach, yielded lifetimes of 16 ± 4 ps (22%) and 475 ± 42 ps (72%) and a small amount of longer-lived species (ca. 6%). Thus, in the presence of **Eu.1**, a 475 ps component dominates. This indicates that the principal recovery pathway is due to surface interactions.[22]

Next we considered the mechanism of quenching. The possibilities of energy and electron transfer were investigated because both processes would affect the excited-state lifetimes. Energy transfer was ruled out because of the absence of any Eu^{III}-based phosphorescence from the **Eu.1-CdTe** sample. This is not unexpected because of the extremely small overlap between the absorption of **Eu.1** and emission of the QDs. However, the close proximity of the surface-coordinated **Eu.1** can facilitate photoinduced electron transfer from the QDs to the complex.[10] The importance of the chemical headgroup through which the electron acceptor adsorbs at the QD surface has recently been highlighted in the case of electron transfer from the QD to a ruthenium metal cluster.[23] If electron transfer from the QDs to **Eu.1** is responsible to some extent for quenching of the QD emission, then a similar behavior should be observed when simple europium(III) salts are used as the redox component; i.e., the Eu^{III} ion is also present.

The addition of europium(III) triflate was indeed found to quench the CdTe emission very effectively (see Figure S7 in the SI), similar to what was reported recently for $EuCl_3$ by Hong et al.[24] However, contrary to the latter study, the triflate salt caused precipitation of the QDs from solution in the experimental conditions used (see Figure S8 in the SI). In contrast, the QDs were found to be stable to aggregation in the presence of **Eu.1**. This is attributed to the entrapment of the Eu^{III} ion within the cyclen cage. Having observed efficient quenching for both europium species (salt and complex), we considered the quenching ability of a terbium triflate salt for which electron transfer is prohibited (the standard redox potential values of couple Ln^{3+}/Ln^{2+} are $E = -0.34$ V and -3.7 V vs SHE for Ln = Eu^{III} and Tb^{III}, respectively).[25] The addition of $Tb(CF_3SO_3)_3$ did not result in efficient quenching (see Figure S9 in the SI) and also induced some particle aggregation. This result was taken to further confirm that quenching arises due to electron transfer from the QDs to **Eu.1**.

In summary, a thorough photophysical investigation of a hybrid lanthanide QD system has been undertaken using steady-state emission and ps-TA spectroscopy. The europium triflate salt was found to quench the QD emission, but this was accompanied by precipitation of the sample. Extremely efficient quenching was also observed for **Eu.1** without compromising the QD stability. The highly stable and robust QD system is attributed to the caged nature of **Eu.1**. The quenching behavior was also observed for low equivalents of **Eu.1** at nanomolar concentrations of QDs in water. The coordination of **Eu.1** to a carboxylate at the surface is seen as a key driver for highly efficient quenching. Transient absorption indicated that surface binding of the europium complex resulted in removal of the nanosecond decay component, which dominates deactivation in the parent TGA-CdTe particles, and this occurs principally through static electron transfer. We believe that such lanthanide QD systems have great potential as electron-transfer components for sensing and signal applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details for experimental methods and additional titration data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(19) On the basis of the surface area of 16.6 nm^2 calculated for a 2.3 nm spherical particle and the thiol footprint of 0.22 nm^2, the maximum number of surface TGA molecules was estimated to be approximately 75.

(20) The low absorption of **Eu.1** at 394 nm does not influence the transient spectrum obtained using fs laser excitation at 400 nm.

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