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

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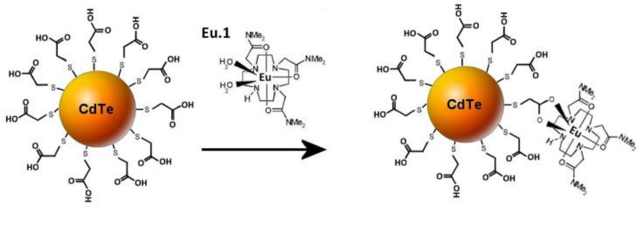
Supporting Information Placeholder

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 ps-transient absorption.

The unique properties of cadmium chalcogenide quantum dots have positioned them as rivals to traditional organic dyes.[1] In particular their highly luminescent nature, render them attractive for a range of applications including optoelectronics, 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 varying timescales with fast carrier trapping known to happen on the picosecond timescale while electron-hole recombination occurs over much 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 signalled by changes in luminescence), which can be used for imaging, sensing, and light harvesting applications. 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.



Scheme 1. Formation of **Eu.1-CdTe** conjugate.

CdTe QDs are attractive for fluorescence based applications as they possess a single narrow emission band, display high quantum yields (QY) and highly stable particles can be prepared in aqueous solution.[12,13] Lanthanide complexes possess long-lived excited states (ms) and well spaced, line-like emission (~10 nm) in the visible {Eu(III), Tb(III)} and near infrared {Yb(III), Nd(III)} regions; properties that have been employed widely for sensing and imaging.[14] Thus lanthanide-nanoparticle hybrids have potential to display enhanced optical properties.[15] One recent example of this is the sensing capacity of a lanthanide complex attached to a gold nanoparticle surface for the purpose of detection of biologically relevant ions or drugs.[16]

Water soluble TGA-CdTe QDs were prepared according to a method developed by Gaponik *et al.*[12] The steady state absorption spectrum in water shows a band at 510 nm which is assigned to first excitonic transition (1Se-1Sh), see Fig. 1. From this the diameter of the particles was determined to be 2.3 nm, which was corroborated by high resolution transmission electron microscopy (HRTEM), see Fig. S1.[17] The presence of negatively charged COO^- surface groups in water was confirmed by zeta potential measurements (-48 mV) see Fig S2. Excitation of the TGA-CdTe 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 using a tri-acetamide substituted cyclen ligand according to literature procedures.[14] The molar absorption coefficient of **Eu.1** (due to a combination of strongly forbidden f-f electronic transitions of Eu(III) see Fig. 1, and the nature of the cyclen ligand) is very small. The strongest transition in the visible spectrum occurs at 394 nm and has a molar extinction coefficient of just 2 M^{-1} cm^{-1}. This necessitated the use of a displacement titration to determine the accurate concentration of **Eu.1** (see Fig. S3-5 ESI†).[14, 16]

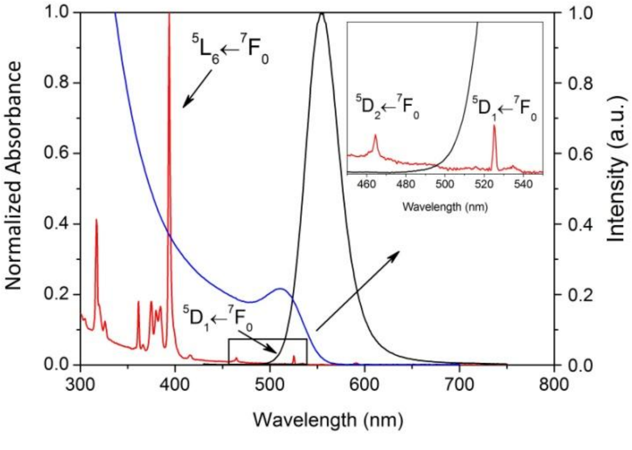


Figure. 1 Absorption spectrum of 0.1 M $Eu(ClO_4)_3$ and 1.29×10^{-5} M TGA-CdTe QDs in water and emission spectrum ($\lambda_{ex} = 450$ nm) of TGA-CdTe QDs; spectra have been normalized for sake of comparison.

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 Fig. 2a).

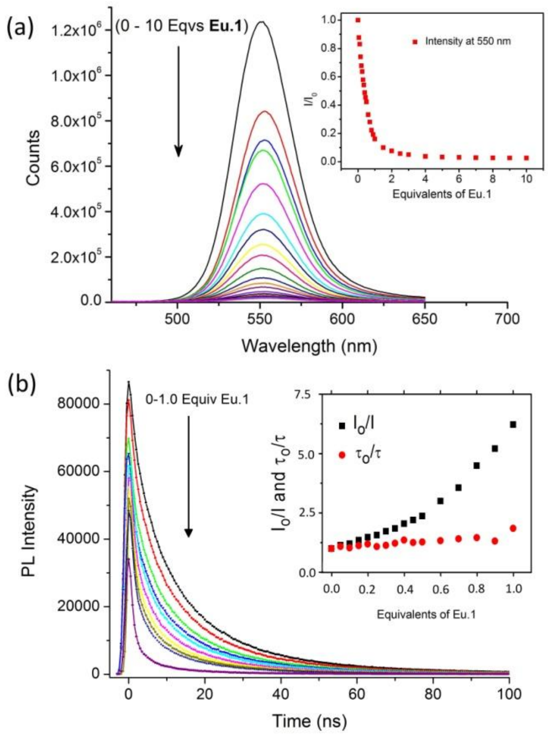


Figure. 2. Changes in (a) the PL intensity (λ_{ex} = 450 nm and (b) the ns fluorescence decay profiles of TGA-CdTe QDs (3.7×10^{-6} M) in the presence of increasing concentration of **Eu.1.** (0-3.7 $\times10^{-5}$ M).

Strong (80 %) quenching occurred upon titration of one equivalent and almost complete quenching (~96%) was reached with two equivalents, Fig. 2a. If the 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.[18] The role of static quenching is also supported by the decrease in the initial amplitude of the decay profiles, Fig. 2b. In the absence of **Eu.1** biexponential behaviour 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 addition of one 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.[19] Furthermore, the same efficient quenching behaviour was also observed for a much weaker (100 nM) solution of QDs (see Fig. S6 ESI†). 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 quantum dots.[10]. The strong quenching at low equivalents is attributed to the significant driving force for **Eu.1** to form bonds with the QD surface TGA carboxylate groups, present in large numbers, which results in the release of two water molecules.[20] Taken together these results strongly indicate that the europium complex is able to quench a precursor to the exciton by sub-nanosecond processes which are too fast to measure with the SPC instrument.

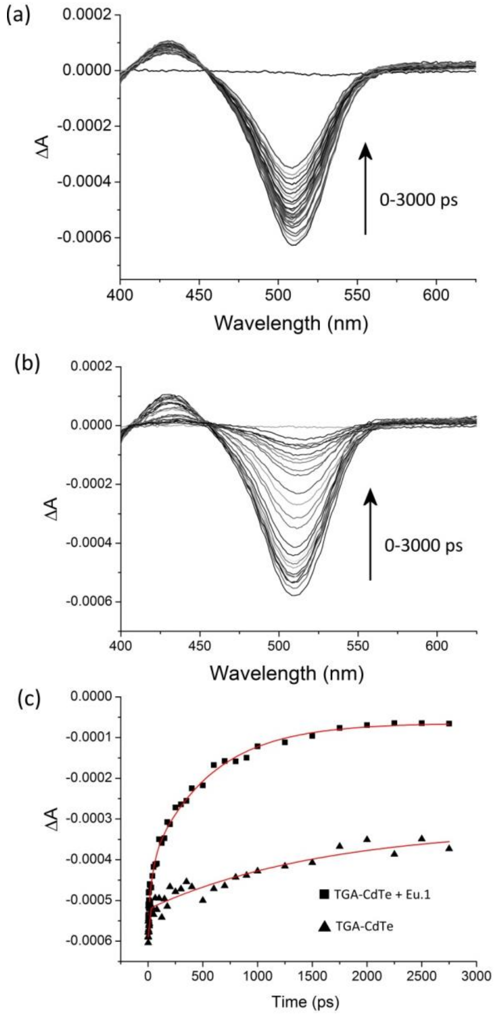


Figure. 3 Transient absorption spectra following 400 nm (50 fs) excitation of 3.7 μM TGA-CdTe QDs in the absence (a) and presence (b) of **Eu.1** (3 eq.), (c) comparison of kinetics for recovery of bleach in TGA-CdTe QDs upon addition of **Eu.1**.

Picosecond transient absorption spectroscopy was performed using excitation energies below *ca.* 0.56 mJ cm^{-2} to minimize multiphoton effects. The ps-transient absorption spectra of TGA-CdTe QDs following visible excitation at 400 nm (50 fs) is shown in Fig. 3a.[21] The dominant feature is that of a strong bleached band which corresponds to the depletion of the ground state. Multicomponent analysis was needed to determine the kinetics of recovery of the bleach 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 timescale of the experiment, Fig. 3c. These values are in agreement with recent ps-TA observations for similar QDs.[22]

Figure 3b shows the transient absorption of TGA-CdTe recorded in the presence of three equivalents of **Eu.1**. In this case we see almost complete signal recovery of the bleach band, which is more clearly visible in Fig. 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.[23]

Next we considered the mechanism of quenching. The possibilities of energy and electron transfer were investigated as both processes would affect the excited state lifetimes. Energy transfer was ruled out due the absence of any Eu(III) based phosphorescence from the **Eu.1-CdTe** sample. This is not unexpected due to the extremely small overlap between the absorption of **Eu.1** and the emission of the TGA-CdTe QDs. However, the close proximity of the surface coordinated **Eu.1** can facilitate photoinduced electron transfer from the QD to the complex.[10] The importance of the chemical headgroup through which electron acceptor adsorbs at the QD surface has very recently been highlighted in the case of electron transfer from the QD to a ruthenium metal cluster.[24] If electron transfer from the QDs to **Eu.1** is responsible to some extent for the quenching of the QDs emission, then similar behaviour should be observed when simple Eu(III) salts are used as the redox component, *i.e.* the Eu(III) ion, is also present.

The addition of Eu(III) triflate was indeed found to quench the CdTe emission very effectively (see S7 ESI†), similarly to what was reported recently for $EuCl_3$ by Hong *et al.*[25] However, contrary to the latter study, the triflate salt caused the precipitation of the QDs from solution in the experimental conditions used (see Fig. S8 ESI†). 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 europium ion within the heptadentate cyclen cage as one single carboxylate is sufficient to complete the Eu(III) first coordination sphere. Having observed efficient quenching for both europium species (salt and complex) we considered the quenching ability of 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 and Tb, respectively).[26] The addition of $Tb(CF_3SO_3)_3$ did not result in efficient quenching (see Fig. S9 ESI†) and also induced some particle aggregation. This result was taken to further confirm that the quenching arises due to electron transfer from the TGA-CdTe QDs to **Eu.1**.

In summary, thorough photophysical investigation of a hybrid lanthanide QD system has been undertaken using steady state emission and ps-transient absorption 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 the **Eu.1**. The quenching behaviour was also observed for low equivalents of **Eu.1** at nanomolar concentration of QDs in water. The coordination of **Eu.1** to a carboxylate at the surface is seen as a key driver for the highly efficient quenching. Transient absorption indicated that surface binding of the europium complex resulted in removal of the ns decay component, which dominates deactivation in the parent TGA-CdTe particles, and this occurs principally through static electron transfer. We believe that such lanthanide quantum dot systems have great potential as electron transfer components for sensing and signal applications.

ASSOCIATED CONTENT

Supporting Information

Electronic Supplementary Information (ESI) available: 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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20 Based on the surface area of 16.6 nm^2 calculated for a 2.3 nm spherical particle and the thiol foot print of 0.22 nm^2 the maximum number of surface TGA molecules was estimated to be approximately 75.

21 The Eu(III) absorption at 394 nm (Fig. 1), corresponding to the $^5L_6 \leftarrow {}^7F_0$ transition, has a very low molar absorption coefficient (ε_{394} = 2 M^{-1} cm^{-1}) and thus is not influencing the transient spectrum obtained using fs laser excitation at 400 nm.

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SYNOPSIS TOC (Word Style "SN_Synopsis_TOC").

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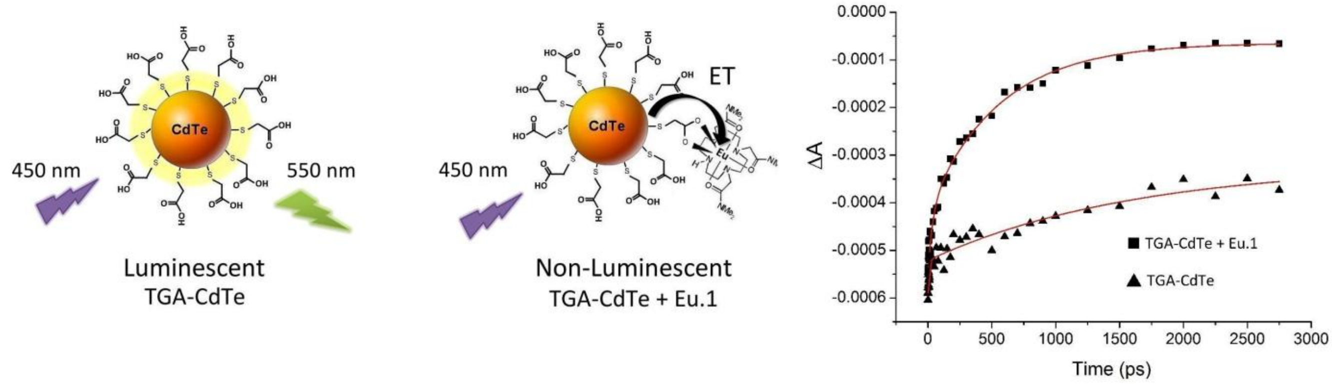

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