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Sensitisation of visible and NIR lanthanide emission by InPZnS quantum dots in bi-luminescent hybrids†

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The synthesis of stable hybrid nanoparticles combining InPZnS@ZnSe/ZnS quantum dots (QDs) and grafted lanthanide complexes has been performed using two different approaches in organic and aqueous media. The final bi-luminescent hybrids exhibit Ln^{III} (Ln = Eu and Yb) centred luminescence upon QD excitation, suggesting that an energy transfer occurs from the QD to the lanthanide.

The lanthanide ions have attracted increasing attention for a broad range of applications from material science to bioanalysis due to their remarkable intrinsic photophysical properties (narrow emission lines, large effective Stokes shifts, high resistance to photobleaching).^{1–3} Intense luminescence and high stability are crucial for the technological applications of lanthanide complexes in the areas of bioanalysis, energy conversion (luminescent dyes or solar concentrators) or in devices such as light emitting diodes.^{4,5} Low energy excitation is also a requirement for these applications, but due to the low molar absorption coefficient of lanthanide transitions (less than 10 M⁻¹ cm⁻¹) it requires the use of suitable chromophores capable of sensitisation of the Ln^{III} emission (antenna effect). Moreover high quantum yields are obtained when Ln^{III} ions are complexed by well-adapted ligands. Most studies have focused on the sensitisation of lanthanide-based luminescence by directly coordinated ligands through the ligand-based triplet excited state, resulting in highly luminescent Eu^{III}^{6–8} and Tb^{III}^{6,9} complexes. d-block and f-block metal complexes are also increasingly used as effective chromophores to sensitise lanthanide luminescence emission both in the visible and near-IR range.^{10–13}

Förster resonance energy transfer (FRET) from visible emitting Eu^{III} and Tb^{III} complexes, as energy donors, to CdSe/ZnS quantum dots (QDs), has been reported and Ln–QD hybrids have proven highly sensitive tools in time-resolved fluoro-immunoassays, and multiplexed diagnostics.^{14–17} Moreover, bi-luminescent Ln–QD hybrids with energy transfer from the lanthanide to the QD can also find applications as light sources in white LEDs.¹⁸

On the other hand, the size-tuneable absorption and emission wavelengths and the large single- and two-photon absorption cross sections make QDs appealing chromophores for the sensitisation of various Ln^{III} ions. However, to date only the luminescence sensitisation of Tb^{III} in doped CdSe and of Eu^{III} in doped InPZnS nanocrystals has been reported.^{19,20} The sensitisation of Ln^{III} emission by QDs has not been achieved so far in Ln–QD organic/inorganic hybrids. Here, we report the synthesis, physical and chemical characterisation of a new series of bi-luminescent hybrid materials. They are based on InPZnS@ZnSe/ZnS core/shell QDs functionalised with podands or self-assembled lanthanide complexes.

Core/shell InPZnS@ZnSe/ZnS QDs with a hydrodynamic diameter of ≈ 5.5 nm were synthesised in a two-step procedure building on our earlier work.²¹ UV-vis absorption, luminescence emission, DLS and TEM analyses (*cf.* ESI†) are consistent with those reported in the literature.²² The QDs used here showed a PL emission maximum in the wavelength range of 525–540 nm and fluorescence quantum yield (QY) of around 40% in organic solvents (**QD-sur**, where sur is a mixture of four lipophilic surfactants used during synthesis, see ESI†). After phase transfer to aqueous solution the QY dropped to around 15% (**QD-pen**, where pen refers to penicillamine coating obtained by replacement of the lipophilic surfactants).

Two different Ln^{III} complexes **1-Ln** and **2-Ln** were grafted onto the QDs according to the procedure shown in Scheme 1. The complexes **1-Ln** (Ln = Eu, Tb, Gd and Yb) were prepared using a multi-step synthesis (ESI,† Scheme S1 and Fig. S1). High thermodynamic stability in water was reported for the closely related [Gd(ebpaten)] complex and similar stability with respect to ligand dissociation is expected for the complexes **1-Ln**.²³ The complexes **1-Eu^{III}** and **1-Tb^{III}** show significant luminescence

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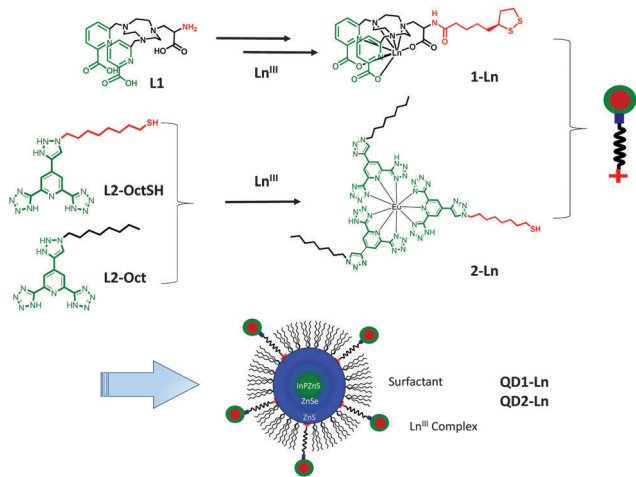
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Scheme 1 Synthesis of the lanthanide complexes **1-Ln** and **2-Ln** and of the hybrids **QD1-Ln** and **QD2-Ln** (Ln = Eu, Tb, Gd and Yb).

quantum yields, (10 and 19% in water, 22 and 40% in D₂O for Eu^{III} and Tb^{III}, respectively). **L2-OctSH** and **L2-Oct** were synthesised from the chelidamic acid following the procedure developed by Di Pietro *et al.*⁶ for **L2-Oct** and a modified procedure for **L2-OctSH** (Scheme S2, ESI[†]). Previous work suggested that the close proximity of the Ln complex to the QD surface can facilitate photo-induced electron transfer from the QDs to the complex resulting in the quenching of QD emission.²⁴ Various spacer lengths (3 to 12 carbons)§ were therefore investigated and a chain of eight carbon atoms was found to be optimum. It leads to a high number of grafted complexes while being short enough to enable QD-to-Ln energy transfer processes, and long enough to favour them over electron transfer. The **L2-Oct** ligands form homoleptic (**L2-Oct**)₃-Ln complexes that are highly stable ($\log \beta_{13} \approx 19$ in methanol).²⁵ Similar results were observed with (**L2-OctSH**)₃-Ln ($\log \beta_{13} \approx 17$ in methanol and $\log \beta_{13} \approx 18.2$ in CHCl₃) and analogous stability is expected for **2-Ln** (Fig. S2, ESI[†]). The (**L2-oct**)₃-Ln complexes showed high luminescence quantum yields in the case of Eu^{III} (70%) and Tb (96%) and a measurable emission for Yb^{III}.⁶

The hybrids **QD1-Ln** (Ln = Eu, Tb, Yb) were synthesised following a previously reported procedure²⁶ *via* the post functionalisation of **QD-pen** by the Ln^{III} complexes **1-Ln** in the presence of a reducing agent. **QD1-Ln** (Ln = Eu, Tb, Yb and Gd) were obtained as pure hybrids after size exclusion column chromatography. The number of complexes per QD (115) was determined by combining two techniques, absorption spectroscopy (QD concentration) and magnetic susceptibility (complex concentration). DLS measurements revealed that the **QD1-Ln** hybrids show a small hydrodynamic diameter of ~9.5 nm and narrow size distribution with polydispersity indices of an average of 0.4 (Fig. 1 and Fig. S4, Table S1, ESI[†]). **QD-pen** exhibits a hydrodynamic diameter, which is 1.5 nm larger than the TEM diameter, corresponding to a 0.75 nm thick ligand shell in accordance with the compact pen-capping. Moreover, the increase of the hydrodynamic diameter of approximately 4 nm from **QD-pen** to **QD1-Ln** is consistent with the successful grafting of the complexes at the QD surface. The formation of the hybrids **QD2-Ln** was

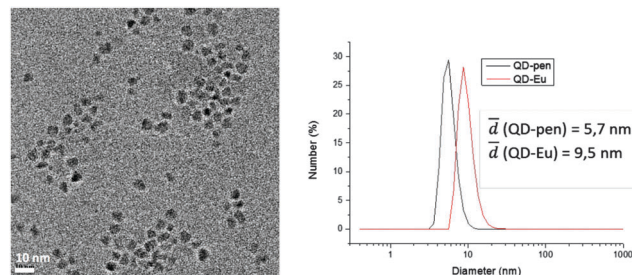


Fig. 1 Left: TEM micrographs of **QD-pen** (mean size: 4.2 ± 0.5 nm). Right: dynamic light scattering data and hydrodynamic diameters of **QD-pen** and **QD1-Eu**.

performed using a novel three-step strategy relying on the well-defined coordination chemistry of the **L2-Oct** ligands enabling the controlled supramolecular build-up of the hybrids. It involves purification by extraction and characterisation by absorption and emission spectroscopy at each stage (ESI[†]). The first step involved a partial exchange in chloroform of the surfactants in **QD-sur** (TEM, Fig. S5, ESI[†]) with **L2-OctSH** to afford the hybrids **QD-L2-OctSH** (Fig. S6, ESI[†]). Reaction of **QD-L2-OctSH** with 1 eq. of Ln(OTf)₃ (Ln = Eu, Tb, Yb) per grafted ligand (**QD-L2-OctSH-Eu**, Fig. S7, ESI[†]), followed by the addition of 2 eq. of **L2-Oct** per metal ion afforded the hybrids **QD2-Ln** (Fig. S8, ESI[†]). Absorption spectroscopy indicates the presence of 200 grafted complexes per QD.

The photophysical properties of **QD1-Ln** (Fig. 2 and Fig. S9–S11, ESI[†]) and **QD2-Ln** (Fig. 3) were then analysed for Ln = Eu, Tb and Yb. After grafting of the ligands or complexes on the surface, the emission QY of the QDs shows a quenching from 40 and 15% for **QD-sur** and **QD-pen** to 5–40% and 1–15%, respectively. Direct excitation of **QD1-Ln** at 273 nm (corresponding to the absorption band of the ligand **L1** but also to the absorption of the QD) resulted in the characteristic Eu(⁵D₀ → ⁷F_j) and Tb(⁵D₄ → ⁷F_j) luminescence emission of the Eu^{III} and Tb^{III} complexes (Fig. 2, left and ESI[†]) through ligand excitation. In addition the emission spectra show a band centred at 525 nm resulting from excitation of the QDs.

The excitation at 273 nm, through the absorption band of the ligand, or at 370 nm of the free Yb^{III} complex did not lead to emission in the NIR region. Notably, the presence of a coordinated water molecule leads to the deactivation of the Yb^{III} centred luminescence. However, the free Eu^{III} complex shows a sizeable

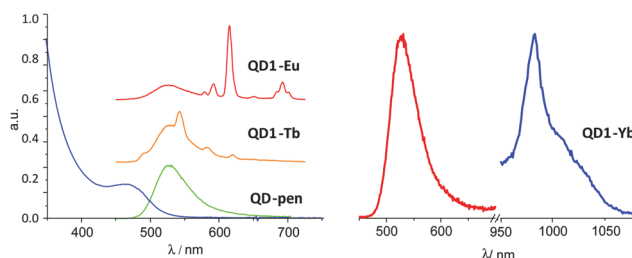


Fig. 2 (left) Normalised absorption of **QD-pen** (blue) and emission ($\lambda_{\text{ex}} = 273$ nm) spectra of **QD-pen** (green), **QD1-Ln** (Tb: orange, Eu: red); (right) normalised emission spectra, ($\lambda_{\text{ex}} = 370$ nm) of **QD1-Yb** in the Vis (red) and NIR range (blue). All measurements were performed in PBS 1× buffer.



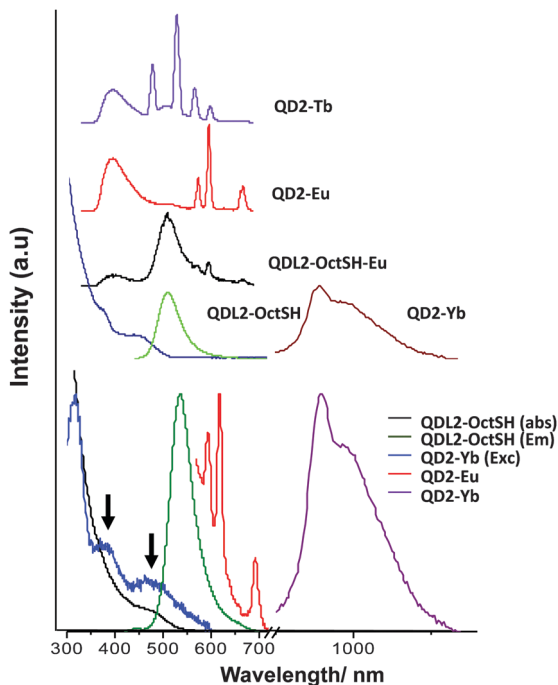


Fig. 3 Photophysical characterisation of **QD2-Ln** (4×10^{-8} M) in CHCl_3 (top) normalised absorption spectrum of **QD-L2-OctSH** (blue) and emission spectra ($\lambda_{\text{ex}} = 325$ nm) of **QD-L2-OctSH** (green), **QD-L2-OctSH-Eu** (black) and **QD2-Ln** (Tb: violet, Eu: red, Yb: brown); (bottom) normalised absorption spectrum of **QD-L2-OctSH** (black) and emission spectra ($\lambda_{\text{ex}} = 400$ nm) of **QD-L2-OctSH** (green) and **QD2-Ln** (Eu: red, Yb: violet). In blue, the excitation spectrum of **QD2-Yb** ($\lambda_{\text{an}} = 978$ nm).

luminescence upon excitation through the ligand at 273 nm but no emission upon excitation at 370 nm (no residual ligand absorption).

When grafted onto **QD-pen**, excitation at 273 (excitation of both ligand and QD) and 370 nm (excitation of QD) of **QD1-Eu** results in a strong and very weak emission of Eu^{III} at 618 nm, respectively. For **QD1-Yb**, excitation at 370 nm gives a weak luminescence emission despite the presence of the coordinated water molecule. The emission spectrum reveals a band at 978 nm (Fig. 2, right), assigned to the ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition and broader vibronic components at longer wavelengths. Excitation at 273 nm of **QD1-Yb** results in the absence of emission, probably due to a weaker efficiency of both the Xenon lamp (low power) and the gratings (tail) in this region compared to 370 nm. The combination of these two factors makes the Yb^{III} NIR luminescence too weak to be detected at 273 nm as observed for **QD1-Eu**. The luminescence emission of the lanthanide ions unambiguously arises *via* excitation of the QDs as no ligand absorption appears at $\lambda > 320$ nm. The presence of the QD-sensitised Eu^{III} and Yb^{III} emission was confirmed by the absence of luminescence when the free complexes **1-Ln** were excited at 370 nm.

Moreover, when the Gd^{III} ion was replaced by Yb^{III} to form **QD1-Yb**, the QD lifetimes decreased (3, 16, and 62 ns) compared to the values (4, 23 and 84 ns) measured for **QD-pen** or **QD1-Gd**, suggesting the presence of an energy transfer from the

QD to the lanthanide ion, associated with a decrease of the QD lifetimes (Table S2, ESI †). For **QD1-Eu**, the decrease of the QD lifetimes is more pronounced (measured values of 1, 6 and 30 ns) while the Eu^{III} emission lifetime measured in the hybrid **QD1-Eu** is similar to the one measured for the free complex in water (0.49 and 0.48 ms, respectively). These data indicate that an energy transfer with additional deactivation pathways occurs in **QD1-Eu** from QD to Eu^{III} . Thus, only a residual emission from the $\text{Eu}({}^5\text{D}_0)$ level is observed, the emission of the QD and the first accepting $\text{Eu}({}^5\text{D}_0)$ electronic level being very close in energy (Fig. S9, ESI †). For **QD1-Tb** (Fig. S10, ESI †), the decrease of the QD lifetimes is significantly less important (3, 19, 72 ns) compared to **QD1-Yb** and **QD1-Eu**, so only a small energy transfer might occur, if possible at all. In this case, the emission of the QD overlaps the $\text{Tb}({}^5\text{D}_4)$ first accepting level with the presence of a back transfer from the $\text{Tb}({}^5\text{D}_4)$ to the QD (Tb^{III} lifetimes = 0.66 and 0.92 ms for **QD1-Tb** and **1-Tb**, respectively, in aqueous buffer). The nullification of these two energetic pathways could explain the absence of luminescence of Tb^{III} in **QD1-Tb**. Furthermore, the values of the QDs quantum yields measured for the hybrids **QD1-Ln**, (1, 5, 10, and 15% for **QD1-Eu**, **-Yb**, **-Tb** and **-Gd**, respectively, Table S2, ESI †) follow a similar trend to the observed decrease of the lifetimes. This trend matches the decrease of both lifetimes and emission of the donor usually associated to an energy transfer.

In the case of **QD2-L2-OctSH** the grafting of the ligands on the surface of the QDs was concomitant with a significant quenching of the QD luminescence emission (decreasing the intensity between 20 and 80% in comparison with a control sample) depending on the quantity of ligand involved in the functionalisation (Fig. 3). The measurements of the QD emission lifetimes (Table S2, ESI †) show a decrease from **QD-sur** (0.3, 17 and 75 ns) to **QD-L2-OctSH** (0.2, 5 and 50 ns). The formation of the complex **QD-L2-OctSH-Eu** leads to a weak luminescence of Eu^{III} , whereas completion of the coordination sphere with **L2-Oct** affording **QD2-Eu** leads to luminescence emission similar to that found for the free complex $[\text{Eu}(\text{L2-Oct})_2(\text{L2-OctSH})]$ and lifetimes for the QD of 0.2, 4 and 31 ns. This suggests that the Eu^{III} coordination environment remains similar to that of the free complex upon grafting at the surface of the QD. The grafting of the **2-Eu** and **2-Yb** results in large quenching of the QD emission suggesting that a partial energy transfer occurs, while no quenching is observed for **2-Tb** (40% QY for **QD2-Tb** and **QD-sur**). Excitation of **QD2-Tb** at 325 nm, (Fig. 3, top), *i.e.* on both the transitions of the ligand and the QD, results in the emission of both the QD and the lanthanide ions. When excitation of **QD2-Tb** was performed at 400 nm (where only the QD is excited), the emission of the metal was not observed. This could be due to the $\text{Tb}({}^5\text{D}_4)$ energy level being too low for an energy transfer or more probably a back-transfer from the $\text{Tb}({}^5\text{D}_4)$ to the QD level as observed in the case of **QD1-Tb**. For **QD1-Ln** and **QD2-Ln** an energy transfer may not be possible by the resonant transfer mechanism due to a lack of absorption/emission overlap. However, phonon-assisted transfer involving energy mismatch and creation and/or annihilation of phonons could occur.



Conversely, the excitation at low energy (400 nm) of **QD2-Eu** and **QD2-Yb**, gave rise to a weak Eu^{III} and a sizeable Yb^{III} luminescence (Fig. 3, bottom). In the Yb^{III} emission spectrum we observe generally one signal in the NIR at approx. 978 nm and a broad component centred at 1040 nm. This is due to an absorption/reemission of the excitation energy by the Yb^{III} energy levels. In addition, the free complexes $[\text{Eu}(\text{L2-Oct})_2(\text{L2-OctSH})]$ and $[\text{Yb}(\text{L2-Oct})_2(\text{L2-OctSH})]$ did not show any measurable luminescence emission when excited at 400 nm, indicating that the excitation through the ligand cannot occur at this wavelength. Moreover, the strong luminescence emission of the Yb^{III} in **QD2-Yb** allowed the measurement of a well-defined excitation spectrum. Thus, the presence of an energy transfer from the QD to the Yb^{III} centre is confirmed by the apparition of two bands at 380 and 450 nm in the excitation spectrum (matching the low-energy band of the absorption spectrum), corresponding to the sensitisation of the complex *via* the QD. This result confirms that the successful population of the lanthanide energy levels was achieved *via* sensitisation of the QD core.

Two new types of **QD-Ln^{III}** organic/inorganic hybrids showing dual luminescence have been prepared and characterised using two different approaches. The QDs and Ln^{III} complexes have been chosen to promote both dual luminescence and energy transfer. A novel self-assembly strategy provides a straightforward and synthetically undemanding route to the synthesis of **QD2-Ln** hybrids that are soluble and stable in organic solutions. These hybrids are potentially useful for the development of new luminescent materials. The use of functionalised, water-stable lanthanide complexes gave access to **QD1-Ln** hybrids with potential application in biological imaging. Overall, the obtained **QD-Ln^{III}** hybrids have allowed the demonstration of the potential of using QDs to sensitise both the visible and NIR emission of lanthanide ions incorporated into QD-grafted complexes, either in organic or aqueous media. Future studies will be directed towards the optimisation of the transfer through an appropriate matching of the Ln and QD energy levels and the thorough investigation of the transfer mechanisms.

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Notes and references

§ Unpublished work: The C_3 spacer was not suitable for the formation of the self-assembly due to the sterically encumbered environment around QD-sur. The C_{12} ligand demonstrates a decrease of the lanthanide sensitisation with respect to the C_8 spacer, which was therefore chosen for all further studies.

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