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Highly luminescent water-soluble lanthanide nanoparticles through surface coating sensitization†

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Water-soluble $La_{0.95}Eu_{0.05}F_3$·AEP (AEP = aminoethylphosphate) nanoparticles (NPs) were shown to react with 6-carboxy-5′-methyl-2,2′-bipyridine ($bipyCOO^-$) in water, resulting in an increase of more than two orders of magnitude of the europium centred emission upon excitation at 305 nm. Nanoparticles coated by the $bipyCOO^-$ ligands were prepared by surface ligand exchange in water, isolated and characterized by infrared spectroscopy, transmission electron microscopy, energy dispersion X-ray analysis and dynamic light scattering. These analyses compared to those of the genuine NPs sample confirmed the partial replacement of AEP by $bipyCOO^-$, with retention of the original morphology of the particles. The photo-physical properties of the isolated $La_{0.95}Eu_{0.05}F_3$·$bipyCOO^-$ NPs were measured in water by absorption, steady-state and time-resolved luminescence spectroscopies and revealed that the large increase of the luminescence of the NPs is due to a surface generated antenna effect where coated $bipyCOO^-$ moieties efficiently absorb light and transfer the energy to the emitting europium atoms of the NPs.

Introduction

Analytical procedures based on fluorescence detection are among the most sensitive and user friendly techniques. These advantages make the search for new luminescent materials a field of broad creativity, boosted by the emergence of fluorescent semiconducting nanoparticles like quantum dots (Q-dots).[1] These exceptionally bright emitters display unrivalled properties such as size-dependent absorption and emission characteristics, very large absorption cross sections, and high photostability, and have already found applications in areas such as fluorescence microscopy, *in vivo* imaging and fluoroimmunoassays.[2] However, due to their shape anisotropy and size distribution, their fluorescence lifetimes are often multi-exponential and rather short,[3] preventing their use in time-gated or time-correlated luminescence applications. Furthermore, Q-dots most often contain heavy metal elements that might be toxic to cells or living organisms and generate environmental hazards regarding their synthesis and storage.

Despite their attractive characteristics in both aqueous and non-aqueous media,[4] luminescent lanthanide nanocrystals (LnNCs) and nanoparticles (LnNPs) have received less attention as emitters. However, their emission spectra display sharp bands characteristic of the lanthanide f–f electronic transitions, covering the whole visible and near-infrared spectral window, with excited-state lifetimes ranging from micro- to milli-seconds, depending on the nature of the lanthanide.[5] The design of functionalized water-soluble LnNPs has been successfully applied to biological systems,[5,6] and offers the possibility of energy upconversion, of particular interest for *in vivo* fluorescence applications.[7] However, LnNCs, in contrast to Q-dots, do not benefit from any quantum confinement effect on their absorption properties and in fact show very weak absorption that dramatically decreases their brightness and restricts their applications to the use of high power excitation sources.

The drawback of weak absorption by lanthanide cations has been cleverly bypassed in coordination chemistry by the development of the "antenna effect".[8] It consists in the use of absorbing chromophoric units able to efficiently absorb light and sensitize the lanthanide emission. It is well known that energy transfer to lanthanide cations in LnNPs can occur from the anions present in the bulk structure of NPs such as in phosphate- and vanadate-based NPs,[9] and a recent example also showed the possibility of energy transfer from surface passivating shells in SiO_2 coated NPs.[10] But to the best of our knowledge, there exists only one report on LnNPs with chromogenic ligands for antenna effect in DMSO.[11] The capping antenna would allow for a large increase of the luminescence intensity through indirect excitation, and for the possibility to tune the absorption cross section into regions were NPs did normally not absorb.

We here demonstrate that a very efficient sensitization of Eu can be obtained in Eu-doped LaF_3 NPs through surface functionalisation with an adequate tridentate coordinating ligand, 6-carboxy-2,2′-bipyridine, $bipyCOO^-$ (Chart 1), and

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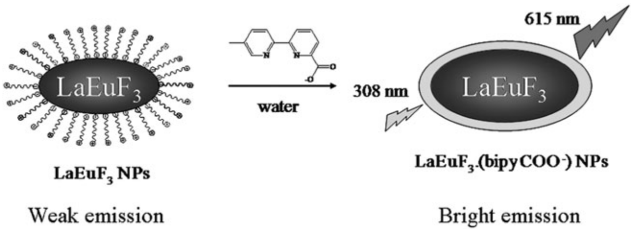

Chart 1

that the isolated surface functionalised NPs display very large improvements of their photo-physical properties and in particular of their brightness.

Results and discussion

Synthesis and characterization of the LaEuF$_3$·AEP NPs

LnNPs were obtained according to literature procedure,[12] by dropwise addition of a 95 : 5 mixture of hydrated La(III) and Eu(III) salts in water to an aqueous solution of sodium aminoethylphosphate (AEP) containing sodium fluoride, with aqueous ammonia used to maintain the pH at 7.0. In addition, the nanoparticles were dialysed against pure water with a 6000–8000 Da cut-off dialysis-bath to remove any residual small molecular aggregates and unbound ligands. ^{1}H and ^{31}P NMR spectra of the LaEuF$_3$·AEP nanoparticles were in excellent agreement with those described in the literature.[12]

The X-ray powder diffraction diagram of these NPs displayed peaks characteristic of the LaF$_3$ structure (Fig. 1),[13] with broad peaks indicative of a low crystallinity of the sample probably due to the low-temperature synthesis. Infrared spectroscopy (Fig. 2) showed intense absorption bands due to the phosphate groups at 1076 cm^{-1}, as well as a broad band around 3080 cm^{-1} assigned to N–H stretching vibrations, and a medium-intensity band at 1637 cm^{-1}, characteristic of LaEuF$_3$ NPs.[13]

C, H, N elemental analysis of the LnNPs showed the particles to be composed of 24% AEP in weight. Dynamic light scattering analysis (DLS, Fig. S1, ESI†) revealed a major component (94%) with an average hydrodynamic radius of 232 nm and a dispersion of ±65 nm, pointing to a large polydispersity of such NPs. Transmission electron microscopy confirmed the particle distribution and associated energy dispersive X-ray analysis (EDX) established a large phosphorus content, as expected for a coating of the LnNPs by the AEP ligands (Fig. 3).

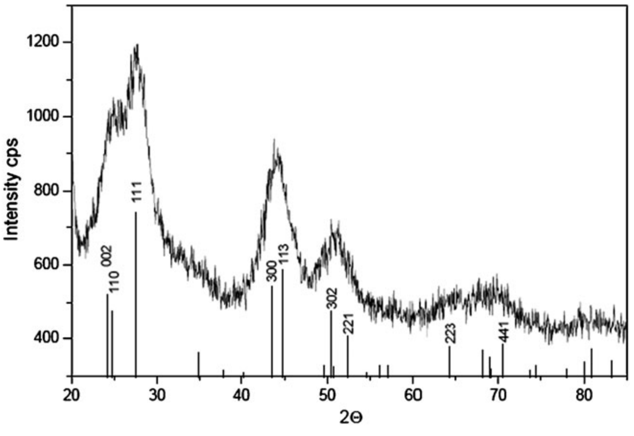

Fig. 1 X-Ray powder diffraction pattern of LaEuF$_3$·AEP LnNPs.

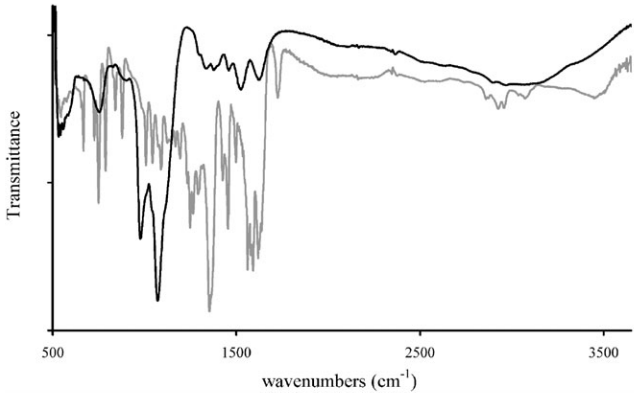

Fig. 2 Infrared spectra of the LaEuF$_3$·AEP (black) and of surface functionalized LaEuF$_3$·bipyCOO$^-$ (grey) NPs.

Titration experiment with the bipyCOO$^-$ ligand

Buffered (TRIS/HCl, 0.01 M, pH = 7.0) aqueous solutions of the LaEuF$_3$·AEP NPs produced very weak emission bands characteristic of the Eu $^5D_0 \rightarrow {}^7F_J$ (J = 0 to 4) electronic transitions[14] upon excitation in the 250–400 nm. Addition of aliquots of a 10^{-3} M solution of 5-methyl-6-carboxy-2,2′-bipyridine (bipyCOO$^-$)[15] in the same buffer to the solution of the LnNPs led to a spectacular increase of the Eu centred emission (Fig. 4, λ_{exc} = 305 nm).

To remove spurious signals due to light scattering and fluorescence of unbound ligands, it was convenient to measure the emission spectra in the gated mode[16] after a 50 μs delay. Maximum amplification of the emission was obtained after 2 to 3 h of equilibration time, as shown by monitoring the time dependence of the emission or absorption after each addition (Fig. S2, ESI†). The equilibrium emission intensities show an asymptotic dependence on the amount of bipyCOO$^-$ added,

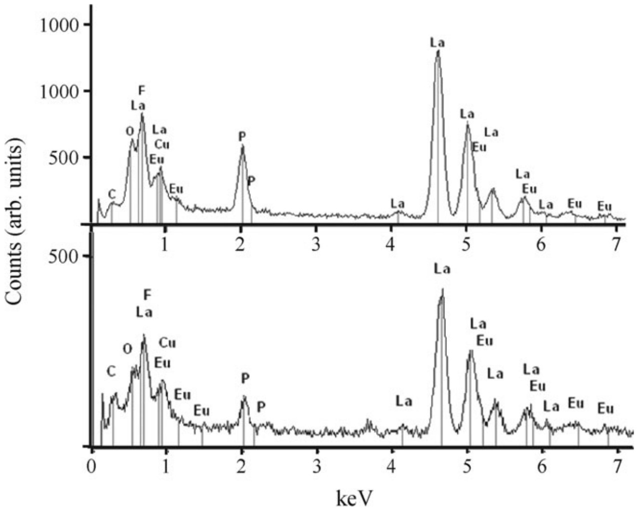

Fig. 3 Energie dispersion X-ray analysis of LaEuF$_3$·AEP (top) and of surface functionalized LaEuF$_3$·bipyCOO$^-$ (bottom) NPs.

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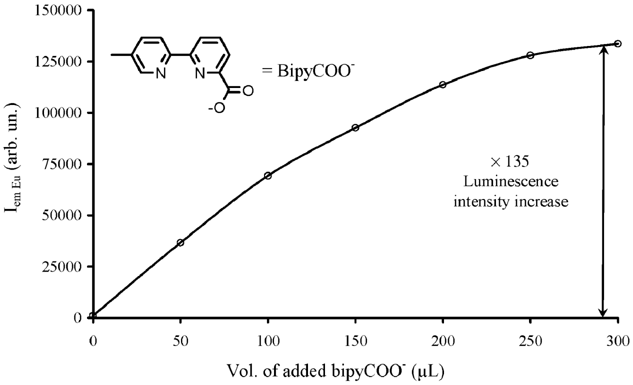

Fig. 4 Evolution of the time-gated Eu-centred emission intensity (λ_{exc} = 305 nm, 550 nm < λ_{em} < 730 nm, delay = 50 μs) of a 2 mL solution of $LaEuF_3$·AEP (35.2 mg L^{-1}) in buffered water (TRIS/HCl, 0.01 M, pH = 7.0) upon addition of a 1.0 × 10^{-3} M solution of $bipyCOO^-$.

with enhancement by at least a factor of 135 being readily obtained. For large excess of added ligand, a plateau is obtained (Fig. S3, ESI†) and the intersection of the region of climbing intensities with the constant region led to a break point corresponding to a stoichiometry of one AEP replaced by two $bipyCOO^-$ units.

Interestingly, the absorption spectra measured at different points of a titration (Fig. 5) showed that the absorption maximum attributed to the π–π* excitation of the bipy moiety appeared at 305 nm, indicating a *cis* configuration of the diaza substituents, unlike the *trans* configuration, giving an absorption maximum at 288 nm, found in the free ligand.[17] Furthermore, the excitation spectra for Eu emission at 615 nm matched the absorption spectra, clearly pointing to the coordination of $bipyCOO^-$ in a tridentate mode, a conformation highly favourable for energy transfer from the ligand to the Eu centres. Additionally, such a coordination mode has been assessed in coordination complexes by X-ray diffraction analysis on single crystals.[18]

Synthesis and characterization of the $LaEuF_3$·$bipyCOO^-$ NPs

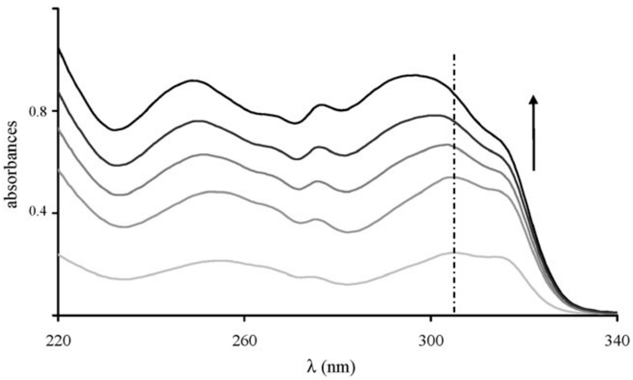

Fig. 5 Absorption spectra of a 2 mL solution of $LaEuF_3$·AEP (103 mg L^{-1}) in buffered water solution (TRIS/HCl, 0.01 M, pH = 7.0) upon addition of 40, 100, 135, 165 and 205 μL of a 1.0 × 10^{-3} M solution of $bipyCOO^-$.

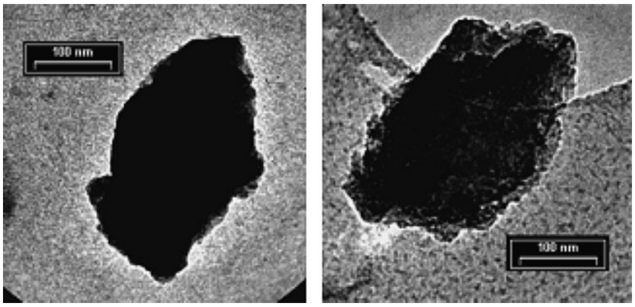

Fig. 6 TEM micrographs of $LaEuF_3$·AEP (left) and $LaEuF_3$·$bipyCOO^-$ NPs (right).

$LaEuF_3$ nanoparticles functionalized by $bipyCOO^-$ were then prepared by dissolving $LaEuF_3$·AEP in water containing bipyCOOH previously neutralized to pH = 8.0–9.0 with Et_3N. After treatment, concentration of the aqueous solution under reduced pressure resulted in the precipitation of a white solid. Since the pure AEP NPs are highly soluble in water, the precipitation observed upon ligand exchange is a strong evidence that important changes had occurred in the physico-chemical properties of the particles. The isolated particles were analyzed by TEM (Fig. 6) and comparison of the energy dispersive X-ray analyses of the AEP precursors and $bipyCOO^-$ functionalized NPs showed the relative phosphorus content to be greatly decreased, as expected for partial ligand exchange (Fig. 3).

The infrared spectrum confirmed the ligand exchange (Fig. 1), showing a large decrease of the phosphate bands of AEP and the presence of new absorption bands characteristic of $bipyCOO^-$,[18,19] such as ν_{COO^-} at 1624 cm^{-1} and ν_{CHarom} at 2962 and 2938 cm^{-1}.

DLS analysis revealed a hydrodynamic radius of 201 nm, very similar to that observed for the genuine AEP NPs (Fig. S1, ESI†).

All these analysis pointed to a partial displacement of AEP molecules at the surface of the NPs with retention of the overall morphology of the NPs.

The photo-physical properties of the $LaEuF_3$·$bipyCOO^-$ NPs were measured in pure water solution. The UV-Vis absorption spectra (Fig. 7) confirmed the presence of the $bipyCOO^-$ ligand with a strong absorption band at 305 nm,

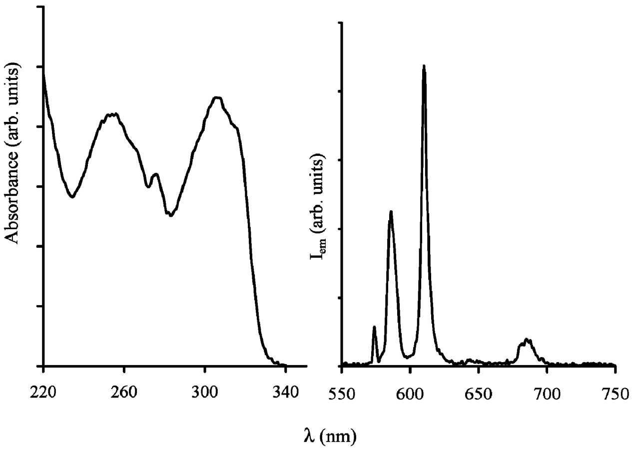

Fig. 7 Absorption (left) and time-resolved emission (right, λ_{exc} = 307 nm) spectra of $LaEuF_3$·($bipyCOO^-$) in pure water.

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a region devoid of absorption in the genuine $LaEuF_3$·AEP precursor. Excitation in this absorption band resulted in an intense europium emission as a result of ligand to europium energy transfer (Fig. 7). Upon ligand excitation, the europium centred excited state lifetime was monitored at 615 nm ($^5D_0 \rightarrow {}^7F_2$ transition). The intensity decay was conveniently fitted with a single mono-exponential curve and gave an excited-state lifetime of 125 μs. The luminescence quantum yield was measured relative to $[Ru(bipy)_3]Cl_2$ in water (Φ = 2.8%),[20] showing an overall yield of 1.85 ± 0.28%. Considering the low Eu-doping ratio (5%) and the poor degree of crystallinity of the as-synthesized LnNPs, this value appears promising for future improvement of luminescence properties.

Conclusion

In summary, we have demonstrated that the antenna effect can be observed for lanthanide-based nanoparticles in water, Eu luminescence being enhanced by up to two orders of magnitude by very efficient light harvesting from surface-bonded $bipyCOO^-$ ligands. The isolated NPs display a broad absorption in the near UV domain and their brightness is largely improved as a result of the ligand to europium energy transfer, with a corresponding long-lived excited-state lifetime. Future developments will be directed toward the synthesis of new coating ligands containing activated functions as well as the extension to other Ln emitters and LnNPs precursors. These dual organic/inorganic nanoparticles may find interesting applications in numerous fields based on fluorescence detection, such as fluorescence microscopy[21] or time-resolved fluoro-immunoassays.[22]

Experimental

BipyCOOH[15] was synthesized according to a literature procedure and the NPs were obtained with modifications of the published procedure.[12] Dialysis were performed using Cellu Sep T2 © (Membrane Filtration Products, USA) tubular membrane of 6000–8000 nominal molecular weight cut off. Infrared spectra were recorded as solids on a Perkin Elmer Spectrum One. X-Ray diffraction patterns were obtained on a Siemens D500 spectrometer. Transmission electron micrographs and energy dispersion X-ray analysis were obtained on a Jeol 2100FCs microscope. UV-Vis absorption spectra were measured on a Uvikon 933 spectrophotometer. Steady-state and time-resolved fluorescence spectra were acquired on a Perkin Elmer LS 50B and a PTI QuantaMaster spectrometers. Luminescence quantum yields were measured on the Perkin Elmer LS50B apparatus working in the phosphorescence mode using a 0 μs delay and a 10 ms integration window. Measurement were realized with optically diluted samples (d.o. <0.05) according to conventional procedures.[23] Luminescence lifetimes were measured on the PTI system using 400 integration canals for a total integration time greater than at least five lifetimes.

Synthesis of $La_{0.95}Eu_{0.05}F_3$·AEP NPs

A 40 mL solution of water containing AEP (140 mg) was adjusted to pH 7.0 with dilute NH_3 (aq). NaF (130 mg) was added and the temperature was raised to 37 °C before dropwise addition of a mixture of $La(NO_3)_3·6H_2O$ (537 mg, Alfa Aesar, 99.99%) and $Eu(NO_3)_3·5H_2O$ (33 mg, Aldrich, 99.9%) in 2 mL water. A light turbidity formed which disappeared upon stirring for 72 h. The solution was concentrated to *ca.* 3 mL, filtered over a cotton pad, and 20 mL of acetone were added, resulting in the formation of a voluminous precipitate, which was isolated by centrifugation (3000 rpm, 20 min). The solid was dissolved in 3 mL water and dialyzed against water (3 × 300 mL). The dialyzed solution was evaporated to dryness and dried under vacuum to give 273 mg of a white powder. IR (cm^{-1}): 3080 (m, br), 1631 (m), 1530 (m), 1464 (m), 1389 (m), 1350 (m), 1074 (s), 982 (s), 762 (m).

Synthesis of $La_{0.95}Eu_{0.05}F_3$·$bipyCOO^-$ NPs

To a solution of $LaEuF_3$·AEP (75 mg) dissolved in 5 mL water was added bipyCOOH (16 mg) and Et_3N (15 μL). The solution was agitated for 2 h at RT. The solution was evaporated to dryness and the solid was triturated and sonicated with 20 mL MeOH. The solid was dissolved in 5 mL water and slowly concentrated by slow evaporation of the solution heated at 40 °C until a precipitate formed. The solution was cooled to RT and the solid isolated by centrifugation (3000 rpm, 20 min) and dried under vacuum to give 16 mg of a white powder. IR (cm^{-1}): 3468 (w, br), 3088 (w), 2962 (w), 2933 (w), 2870 (w), 1730 (m), 1620 (s), 1589 (s), 1566 (s), 1454 (m), 1429 (m), 1364 (s), 1298 (w), 1267 (m), 1246 (m), 1195 (w), 1092 (m), 1045 (m), 1008 (m), 879 (m), 790 (m), 753 (m).

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