



Luminescence enhancement of nanosized ytterbium and europium fluorides by surface complex formation with aromatic carboxylates



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ABSTRACT

Ytterbium 2,6-naphthalenedicarboxylate (Yb₂(nda)₃·4H₂O) and ytterbium 9-anthracenecarboxylate (Yb(ant)₃) were obtained for the first time, and it was shown that both of them exhibit ligand sensitized ytterbium luminescence. Anions ant⁻ and nda²⁻ were tested for the nanoparticle surface modification of YbF₃ and model EuF₃. The surface modification of the size uniform toroid-like EuF₃ nanoparticles with K₂(nda) and octahedron-like YbF₃ nanoparticles with K(ant) results in the significant luminescence enhancement due to lanthanide carboxylate formation on the particle surface. Such a surface modification leads to the particle size decrease, while their shape remains the same.

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1. Introduction

Luminescent lanthanide(III)-containing functional nanosized materials have recently attracted increasing attention, for example, as luminescent probes for cell imaging and medical diagnostics due to their unique optical properties such as well-characterized and intense line-like emission, constant position of luminescence bands, long lifetimes of the excited state and high Stokes shift [1–4]. Such lanthanide materials, emitting in the near-infrared (NIR) range are especially important for both bioanalyses and bioimaging, since NIR range has a few interferences with biomaterials so that photons can penetrate deeply into biological samples, cells and tissues.

The luminescent nanosized materials, necessary for bioimaging, may be based on purely inorganic materials, such as quantum dots or metal oxides or fluorides, as well as on metal-organic frameworks [5–7]. Lanthanide fluorides are known to be easily obtained in the form of nanoparticles with narrow size distribution. Besides the highest intrinsic quantum yield equal to 100% was reported for NIR-emitting LaF₃:Er material [8]. However, pure lanthanide fluorides and their materials have low absorbance and efficient antenna is needed to enhance their luminescence.

One of the approaches to solve this problem can be surface modification of nanosized lanthanide fluorides via complex formation with organic antenna-ligands. An example of the successful realization of this approach was shown recently in Ref. [9], where by

the impregnation, sorption or mechanochemical treatment surface modification of EuF₃ toroid-like particles with 1,10-phenanthroline and dibenzoylmethanate-anion was fulfilled, and luminescence enhancement via these ligands was achieved. Similar approach was realized in Ref. [10] where such a luminescence enhancement was achieved for lanthanide doped SnO₂. To the best of our knowledge, no such experiments were conducted to produce NIR-emitting surface modified nanoparticles. In the current work following the methodology utilized in Ref. [9] we have studied the influence of post-synthesis surface modification of the NIR-emitting YbF₃ nanoparticles on Yb³⁺ luminescence. As antenna ligands 2,6-naphthalenedicarboxylate (nda²⁻) and 9-anthracenate (ant⁻) were chosen for their high affinity to rare earth ions. Though aromatic carboxylates are well-known to sensitize lanthanide luminescence [11–14], they are for the first time used for surface modification of nanosized lanthanide luminescent materials. Anion nda²⁻ possesses rather low triplet state energy (18,300 cm⁻¹ [11]) and should therefore be able to sensitize Yb³⁺ luminescence. Lanthanide complexes with ant⁻ are unknown, though because of higher conjugation degree its triplet state energy should be even lower than that of nda²⁻. Nanoparticles of EuF₃ were added as model objects for which the effect of luminescence enhancement can be easily detected in the visible spectral range. Besides the luminescent complex Eu₂(nda)₃·4H₂O has been already described in Ref. [11]. Here both ytterbium and europium complexes with the selected ligands nda²⁻ and ant⁻ were synthesized in powder form to ensure the presence of sensitized luminescence. Nanoparticles YbF₃ and EuF₃ were prepared according to Safronikhin et al. [9] and used for surface modification.

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2. Results and discussion

2.1. Synthesis and characterization

The powder samples of $\text{Ln}_2(\text{nda})_3 \cdot 4\text{H}_2\text{O}$ and $\text{Ln}(\text{ant})_3$ ($\text{Ln}=\text{Eu}$, Yb) were synthesized via ligand exchange reaction between the

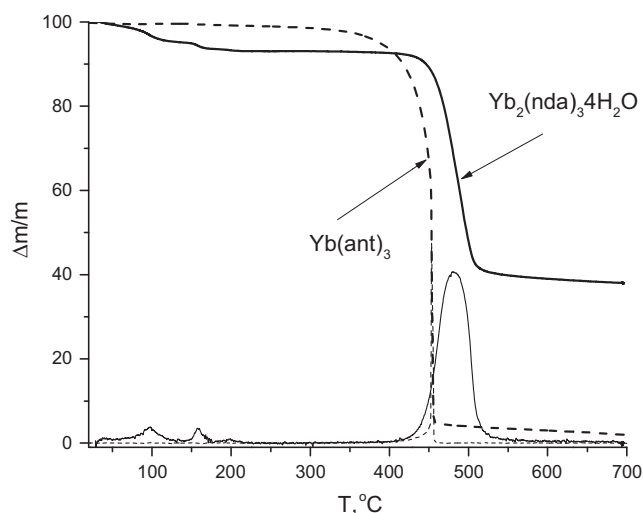


Fig. 1. TGA curves of $\text{Yb}(\text{ant})_3$ and $\text{Yb}_2(\text{nda})_3 \cdot 4\text{H}_2\text{O}$.

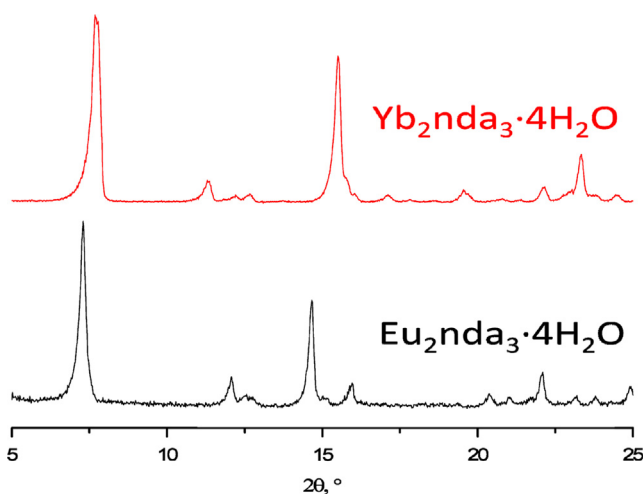


Fig. 2. Powder XRD patterns of $\text{Eu}_2(\text{nda})_3 \cdot 4\text{H}_2\text{O}$, $\text{Yb}_2(\text{nda})_3 \cdot 4\text{H}_2\text{O}$.

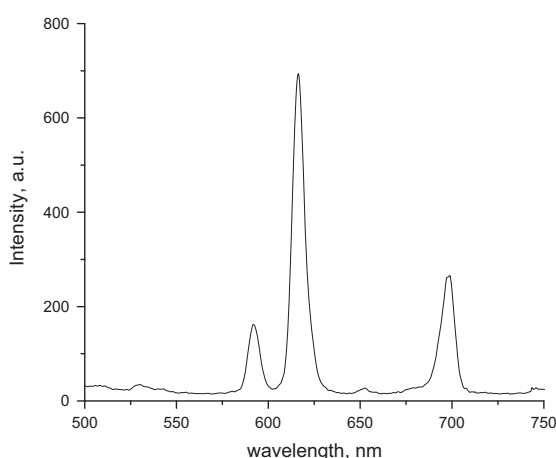
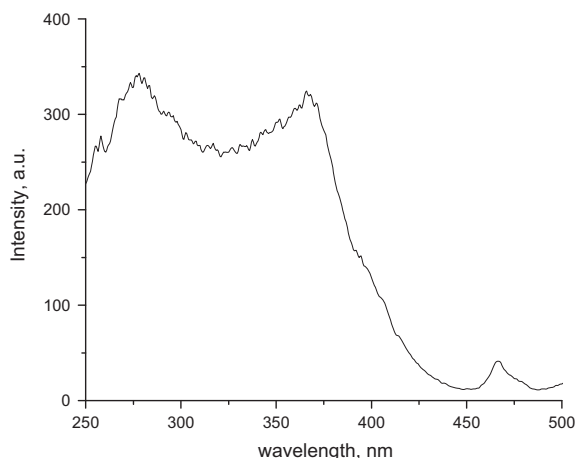


Fig. 3. Excitation and luminescence spectra of $\text{Eu}_2(\text{nda})_3 \cdot 4\text{H}_2\text{O}$.

corresponding lanthanide nitrate and the potassium carboxylates in water [15] and characterized by the elemental analysis and the TGA data. The TGA data have shown that $\text{Eu}(\text{ant})_3$ and $\text{Yb}(\text{ant})_3$ were formed in dehydrated form and were stable up to $\sim 350^\circ\text{C}$ in Ar (Fig. 1). The complex $\text{Yb}_2(\text{nda})_3 \cdot 4\text{H}_2\text{O}$ loses four water molecule in the temperature range of $100\text{--}160^\circ\text{C}$ with formation of $\text{Yb}_2(\text{nda})_3$, which was thermally stable up to $\sim 400^\circ\text{C}$ (Fig. 1). TGA curve of $\text{Yb}_2(\text{nda})_3 \cdot 4\text{H}_2\text{O}$ coincided with that of $\text{Eu}_2(\text{nda})_3 \cdot 4\text{H}_2\text{O}$ [11].

X-ray powder diffraction (Fig. 2) method was used to prove the isostructurality of $\text{Yb}_2(\text{nda})_3 \cdot 4\text{H}_2\text{O}$ to europium analog $\text{Eu}_2(\text{nda})_3 \cdot 4\text{H}_2\text{O}$ by coincidence of their XRD patterns.

To examine luminescent characteristics of the synthesized aromatic carboxylates, photoluminescence (PL) spectra, excitation spectra and the lifetime of the excited state were measured for $\text{Eu}_2(\text{nda})_3 \cdot 4\text{H}_2\text{O}$ (Fig. 3), while new complex $\text{Eu}(\text{ant})_3$ did not demonstrate ionic luminescence.

Fig. 3 shows the luminescence and excitation spectra of $\text{Eu}_2(\text{nda})_3 \cdot 4\text{H}_2\text{O}$. Four typical Eu^{3+} bands at 592, 616, 635 and 698 nm, corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j=1,2,3,4$), are observed in PL spectrum, their intensity ratio is given in Table 1. Two bands in the excitation spectrum at 280 nm and 380 nm correspond to the Eu^{3+} excitation through organic ligands, while the low intensity band at 480 nm corresponds to the direct europium excitation.

The sensitization efficiency (η_{sens}) of the anionic ligands for nanoparticle surface modification should be high enough ($> 50\%$). The η_{sens} value can be calculated as the ratio of the external and internal quantum yields

$$\eta_{\text{sens}} = \frac{Q_{\text{Ln}}^{\text{L}}}{Q_{\text{Ln}}^{\text{In}}} \times 100\%$$

The external quantum yield Q_{Ln}^{L} of $\text{Eu}_2(\text{nda})_3 \cdot 4\text{H}_2\text{O}$ was measured using the integration sphere to be 3.8%. The internal quantum yield was calculated from the spectral data

$$Q_{\text{Ln}}^{\text{In}} = \frac{\tau_{\text{obs}}}{\tau_{\text{rad}}} \times 100\%,$$

$$\frac{1}{\tau_{\text{rad}}} = 14,65\text{s}^{-1} \times n^3 \times \frac{k_{\text{tot}}}{I_{0-1}},$$

where τ_{obs} and τ_{rad} are the observed and radiative lifetimes respectively, n is the refraction index, which equals approximately 1.5 for the most of solids, and k_{tot} and I_{0-1} are the total integral intensity of europium luminescence and the intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition respectively.

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