Tunable and purified luminescence *via* energy transfer and delamination of LRH (R = Tb, Y) composites with 8-hydroxypyrene-1,3,6-trisulphonate

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Abstract

This work demonstrates tunable and purified luminescence *via* one-step delamination of HPTS/OS-LRH composites (HPTS is trisodium 8-hydroxy-pyrene-1,3,6-trisulphonate, OS is sodium salt of 1-octane sulfonic acid, LRH is layered rare-earth hydroxide, R = Tb, Y) along with energy transfer. The $\text{HPTS}_x\text{OS}_{1-x}\text{-LTb}_y\text{Y}_{1-y}\text{H}$ composites presented varied luminescence behaviour depending on their physical state. In solid state, dual-color luminescence was observed: blue-dominant emissions (437 nm) for $\text{HPTS}_x\text{OS}_{1-x}\text{-LTbH}$, and blue- (437 nm) to green-dominant (516 nm) luminescence for $\text{HPTS}_{0.02}\text{OS}_{0.98}\text{-LTb}_y\text{Y}_{1-y}\text{H}$. In delaminated state in formamide, purified luminescence was present: pure blue emission (440 nm) for $\text{HPTS}_x\text{OS}_{1-x}\text{-LTbH}$ and $\text{HPTS}_{0.02}\text{OS}_{0.98}\text{-LTb}_y\text{Y}_{1-y}\text{H}$ ($y \geq 0.5$), while pure bluish-green emission (498 nm) for $\text{HPTS}_{0.02}\text{OS}_{0.98}\text{-LTb}_y\text{Y}_{1-y}\text{H}$ ($y \leq 0.3$). Both the delamination of the composites and energy transfer from layer Tb^{3+} to HPTS contributed to the blue luminescence. The intriguing energy transfer process between photoactive inorganic hosts and organic guests can be utilized to fabricate hybrid materials with superior luminescence property.

Keywords: Layered materials; LRH composites; luminescence property; energy transfer

1. Introduction

Nowadays, organic-inorganic hybrid luminescent materials have attracted comprehensive attention because of their superior physicochemical properties which arise from the synergetic interactions of the inclusive components [1, 2]. The organic guests especially those with chromophores are mainly responsible for the optical properties, while the inorganic host matrixes protect the organic components and thus provide adequate stability of such hybrid materials. Layered double hydroxides (LDHs) and layered rare-earth hydroxides (LRHs) are unique classes of layered compounds comprising positively-charged host layers and negatively-charged interlayer species. Numerous studies of the LDH-chromophore hybrids [3-6] revealed their superlative functionalities, such as, higher photo-stability and enhanced luminescence over their individual components [7, 8]. Previously, our group has reported different kinds of anionic guest intercalated LDH composites and their applications in luminescence and environmental remediation [9-14]. In contrast to LDHs, LRHs compounds are a newly emerging family of layered materials [15-18], on account of the unique ability to combine the useful properties of rare earth ions with various gallery guests. However, with regard to luminescent property of LRHs, most of the investigations focused mainly on layer ions such as Eu^{3+} , Tb^{3+} and Dy^{3+} [17, 19-24], and less attention was given on the luminescence arising from the interlayer organic guests or synergetic interactions of the organic species with host layers.

For LRHs, due to the coordination of the layered lanthanides with the hydroxyl groups and water molecules, emissions of layered ions are normally weakened, which limits their practical application in optical devices. To enhance the emissions of layered ions, organic

sensitizers were introduced into the inter layer gallery [16, 25, 26], as we did on the intercalation of organic species into Eu^{3+} -containing LRHs [27-29]. To achieve luminescent hybrids of LRHs, fluorescent molecules can be introduced into the interlayers. As is known, when the emission and excitation spectrum of the inclusive components have certain overlaps, energy transfer may occur [24, 30, 31] between photoactive layer ions and interlayer organics. Such energy transfer brings novel luminescence properties, however, there have been a lack of studies focusing on this area. We previously reported the LEuH composites with the fluorescent molecule of 8-hydroxy-pyrene-1,3,6-trisulphonate (*abbr.* HPTS) and anion surfactant of 1-octane sulfonic acid sodium (*abbr.* OS) can achieve facile delamination which led to novel luminescence property [32]. We also combined coumaric acids with LRH layers ($\text{R} = \text{Eu/Gd, Tb/Y}$) to fabricate delaminated composites [33, 34], all of which presented versatile luminescence due to the energy transfer.

In this work, for intensive investigation of the luminescence behavior and synergetic energy transfer effect of this kind of LRH composites, we synthesized the composites involving Y:LTbH layers and HPTS/OS guests. Color-tuning luminescence was present for the composites in solid state and delaminated state, depending on the varied ratios of HPTS/OS and $\text{Tb}^{3+}/\text{Y}^{3+}$. Purified luminescence can be achieved *via* delamination of the composites and energy transfer from layer ions to HPTS species.

2. Experimental

2.1. Preparation of NO_3 -LRH precursor.

Tb_4O_7 (99.9%) and Y_2O_3 (99.9%) were obtained from Nonferrous Metal Research Institute Rare Earth New Materials Co., Ltd. Hexamethylenetetramine (HMT) was purchased from Xi

Long Chemical Co., Ltd. OS and HPTS were purchased from Beijing HWRK Chemical Co., Ltd. $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were prepared by dissolving $\text{Tb}_4\text{O}_7/\text{Y}_2\text{O}_3$ in a small amount of $\text{HNO}_3/\text{H}_2\text{O}$ mixture with a volume ratio of 1:1, followed by drying.

The $\text{NO}_3\text{-LTb}_y\text{Y}_{1-y}\text{H}$ ($y = 1, 0.9, 0.7, 0.5, 0.3, 0.1$ and 0) precursors were synthesized *via* hydrothermal reactions of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ using HMT as the hydrolysis reagent [27]. The total amount of Tb^{3+} and Y^{3+} was fixed to be 1.0 mmol, where the molar ratios of Tb^{3+} were set to be 1, 0.9, 0.7, 0.5, 0.3, 0.1 and 0, respectively. Aqueous solutions (de-ionized water, 80 mL) of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}/\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with the above Tb/Y ratios, HMT (1 mmol), and NaNO_3 (13 mmol) were heated at 90 °C for 12 h in a Teflon autoclave. The obtained products were filtered, washed with de-ionized water, and then vacuum dried at 40 °C for 24 h.

2.2. Preparation of composites of OS-LTbH, $\text{HPTS}_x\text{OS}_{1-x}\text{-LTbH}$ and $\text{HPTS}_{0.02}\text{OS}_{0.98}\text{-LTb}_y\text{Y}_{1-y}\text{H}$.

The composites were synthesized by an ion exchange method. For the synthesis of OS-LTbH, 3 mmol (0.649 g) OS was firstly dissolved in 80 ml de-ionized water, then 0.43 mmol (~ 0.1 g) $\text{NO}_3\text{-LTbH}$ powder was dispersed into this solution. The reaction was conducted at 70 °C for 24 h in a Teflon-autoclave. The resulting precipitates were collected by filtration, washed with de-ionized water, and vacuum dried at 40 °C for 24 h.

For $\text{HPTS}_x\text{OS}_{1-x}\text{-LTbH}$ composites, different proportional HPTS/OS were firstly mixed to generate corresponding solutions (~ 80 mL). The total amount of OS and HPTS was fixed to be 3 mmol, with only varying the molar ratios of $\text{HPTS}_x\text{OS}_{1-x}$ as $x = 0.02, 0.05, 0.10, 0.15$ and 0.20 . Taking $\text{HPTS}_{0.05}\text{OS}_{0.95}\text{-LTbH}$ ($x = 0.05$) as an example, 0.15

mmol (0.079 g) HPTS was dissolved in 80 mL de-ionized water to obtain a green solution, then 2.85 mmol (0.616 g) OS was added. Afterwards, 0.43 mmol (~0.1 g) of NO₃-LTbH powder was dispersed into the above solution. The reactions were conducted at 70 °C for 24 h in Teflon-autoclaves. The precipitates were collected by filtration, washed with deionized water, and vacuum dried at 40 °C for 24 h.

For preparation of HPTS_{0.02}OS_{0.98}-LTb_yY_{1-y}H ($y = 1, 0.9, 0.7, 0.5, 0.3, 0.1$ and 0), taking the HPTS_{0.02}OS_{0.98}-LTb_{0.1}Y_{0.9}H as an example, firstly, 0.06 mmol (0.032 g) HPTS was dissolved in 80 mL de-ionized water to obtain a green solution, then 2.94 mmol (0.636 g) OS was added. After that 0.43 mmol (~0.078 g) of NO₃-LTb_{0.1}Y_{0.9}H powder was dispersed into the above solution. In the preparation of other composites, the moles of HPTS, OS and NO₃-LTb_yY_{1-y}H were kept constant but only changed the mass of the NO₃-LTb_yY_{1-y}H based on their molecular weight. The reaction temperature and other subsequent procedures are the same as above.

For delamination of the as-prepared composites, 0.05 g powders of the composites were dispersed into 20 mL formamide (*abbr.* FM) followed by mechanical shaking of 2 h, to form translucent colloidal suspensions.

2.3. Synthesis of Gd(III) complex of HPTS (Gd-HPTS).

Firstly, 0.6 mmol (0.271 g) Gd(NO₃)₃·6H₂O was dissolved in 3 mL H₂O, then the solution was mixed with 5 mL methanol solution containing 0.6 mmol (0.315 g) HPTS. The as-obtained solution was evaporated by heating until the rest of the solution is ~1 mL. After by cooling, the Gd-HPTS complex was precipitated out, and vacuum dried at 40 °C for 24 h.

2.4. Characterization Techniques

The powder X-ray diffraction (XRD) patterns were collected by using a Phillips X'pert Pro MPD diffractometer with Cu-K α radiation at room temperature, with a step size of 0.0167°, scan time of 15 seconds per step, and 2θ ranging from 4.5 to 70°. The generator setting was 40 kV and 40 mA. For the small degrees, the XRD patterns were measured at room temperature with step size of 0.008°, scan time of 30 seconds per step. Fourier transformed infrared (FT-IR) spectra of the samples were recorded on a Nicolet-360 Fourier-Transform infrared spectrometer by the KBr method. Scanning electron microscope (SEM), elemental distribution mapping, and energy dispersive spectroscopy (EDS) measurements were performed on a Hitachi S-4800 microscope. Luminescence spectra of samples at liquid state were obtained on a Cary Eclipse spectrofluorimeter, while the solid luminescence spectra were performed in the PerkinElmer-LS55 spectrofluorimeter. The phosphorescence spectra of the HPTS-Gd complex were measured at 77 K in a methanol on a Hitachi F-7000 FL Spectrophotometer. The fluorescence lifetimes of samples in FM with concentrations of $\sim 10^{-6}$ mol/L were detected on a FLS920 lifetime and steady state spectrometer (Edinburgh Instruments LTD).

The metal ion contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jarrel-ASH, ICAP-9000) after the solids were dissolved in a 0.1 M HNO₃ solution. C, H and N contents were determined by using an Elementar vario EL elemental analyzer. The chemical formulas of the products were determined based on the results of ICP-AES and CHN analyses.

3. Results and discussion

3.1. Structure and morphology of the as-prepared composites.

XRD patterns of the $\text{NO}_3\text{-LTbH}$ precursor and composites of OS-LTbH , $\text{HPTS}_x\text{OS}_{1-x}\text{-LTbH}$ and $\text{HPTS}_{0.02}\text{OS}_{0.98}\text{-LTb}_y\text{Y}_{1-y}\text{H}$ were presented in Fig. 1. The $\text{NO}_3\text{-LTbH}$ (Fig. 1A-a) has a series of strong (00 l) reflections at 0.83, 0.42 and 0.27 nm as characteristics of a layered phase, demonstrating a basal spacing (d_{basal}) of 0.83 nm, identical to previously reported values for Cl-LTbH [34]. The sharp and symmetric diffractions suggest the high crystallinity of the $\text{NO}_3\text{-LTbH}$. Fig. 1A-c-f showed the composites by ion-exchange of $\text{NO}_3\text{-LTbH}$ with different proportions of HPTS/OS, for which enlarged d_{basal} values of 2.00-2.06 nm were observed. The $\text{HPTS}_x\text{OS}_{1-x}\text{-LTbH}$ ($x = 0.02$) with high OS contents (Fig. 1A-c) had a d_{basal} of 2.0 nm close to that of the OS-LTbH (Fig. 1A-b). Other composites with more HPTS (high x values) exhibited slightly increased d_{basal} values, indicating the gallery was supported by both HPTS and OS. As seen in Fig. 1A-d,d' ($x = 0.05$), a series of diffraction peaks at 2.03, 1.02, 0.69, 0.51 and 0.41 nm were observed, corresponding to a d_{basal} of 2.03 nm, while the diffraction peaks splitting at 1.02, 0.69, 0.51 and 0.41 nm revealed double phases, in which the ones with weak diffractions (also with smaller d_{basal}) may be attributed to the OS intercalated LTbH. On the basis of the layer thickness of LRH (0.65 nm) [27] and the size of HPTS ($\sim 1.01 \times 0.76 \times 0.24$ nm) and OS ($\sim 1.04 \times 0.37 \times 0.26$ nm) [32], the gallery spacing of ~ 1.35 nm ($= 2.00 - 0.65$) correspond to an alternating monolayered antiparallel arrangement for HPTS accompanying adjacent OS, as shown in Scheme 1b. Herein the HPTS anions preferred to a monolayered alternating antiparallel arrangement resulting from the three $-\text{SO}_3^-$ groups of HPTS. The negatively-charged $-\text{SO}_3^-$ combined with the positively-charged LRH layers *via* electrostatic

interactions, and also, the π - π stacking interactions between benzene rings further assures the stable structure. In addition, all of the samples had a nearly coincident peak at ~ 0.31 nm assigned to the non-basal (220) reflection coming from the LRH host layers [20, 29].

At the fixed HPTS/OS ratio of 0.02:0.98, Tb/Y ratio of the layer, the as-formed composites of HPTS_{0.02}OS_{0.98}-LTb_yY_{1-y}H demonstrated similar XRD patterns (Fig. 1B) to those above discussed, and also had d_{basal} values close to the HPTS_{0.02}OS_{0.98}-LEuH composites we previously reported [32]. Moreover, all of these composites were formed with single phases, suggesting low HPTS contents (here HPTS is 0.02) preferred a pure phase, and that the rare-earth ions of Y³⁺ and Tb³⁺ were successfully incorporated into the host lattice to form layered hydroxide solid solutions [19, 35].

Based on ICP, CHN analyses and charge balance considerations, the estimated compositions of the LRH precursor and some of as-prepared composites were shown in Table 1. The molar ratios of HPTS/OS and Tb/Y found in the as-prepared composites agreed well with those added in the starting materials, and the calculated elemental contents were coincident with the experimental ones in estimated chemical formulas, meaning small errors.

Fig. 2 showed the FT-IR spectra of the precursors and some composites. For HPTS (Fig. 2a), the bands at 1196 and 1047 cm⁻¹ were ascribed to characteristic vibrations of the SO₃⁻ group [36, 37]. For the OS anion (Fig. 2b), the SO₃⁻ absorptions appeared at 1200 and 1065 cm⁻¹, and the bands at 2920 and 2851 cm⁻¹ corresponded to the stretching vibrations of -CH₂ and -CH₃ groups, respectively. For NO₃-LTbH (Fig. 2c), the sharp and strong absorption peak at 1384 cm⁻¹ was characteristic of the ν_3 vibration mode of uncoordinated NO₃⁻. After intercalation, the NO₃⁻ band in all of the composites (Fig. 2d-g showed some of them) became

unobvious, suggesting a nearly complete ion-exchange. The presence of the bands at 2922 and 2853 cm^{-1} ascribed to aliphatic C-H stretching vibrations signified the introduction of OS into the interlayer. In addition, the characteristic vibrations of the SO_3^- group in all of the composites appeared at 1171 and 1049 cm^{-1} , where the shifts indicate the interactions of the introduced guests with the layer hydroxides.

To further investigate the structure and morphology of the as-prepared samples, SEM observations were employed (Fig. 3). It can be seen that the samples were composed of microcrystalline particles showing plate-like morphology with rough surface. The $\text{NO}_3\text{-LTbH}$ crystals (Fig. 3a,a') were mainly crystallized into elongated hexahedron platelets and some of them grew into columnar or flower-like aggregates. In compare with extremely elongated hexagons for NO_3^- type LGdH [38] and LLeuH [32], the present $\text{NO}_3\text{-LTbH}$ sample was crystallized with relatively short broadsides. In contrast to $\text{NO}_3\text{-LTbH}$, the $\text{NO}_3\text{-LYH}$ (Fig. 3c,c') exhibited nearly regular hexagon shape. The slightly elongated hexagon morphology (Fig. 3b,b') for $\text{NO}_3\text{-LTb}_{0.5}\text{Y}_{0.5}\text{H}$ would originate from the doping of Tb^{3+} and Y^{3+} . The composites of $\text{HPTS}_{0.02}\text{OS}_{0.98}\text{-LTb}_y\text{Y}_{1-y}\text{H}$ (Fig. 3d-j) displayed morphologies from elongated to regular hexahedron platelets with increasing Y^{3+} amount, for which the morphology coincidence of the composites with their precursors implies a topotactic intercalation of the interlayer species.

Fig. 4 displayed the EDS and elemental mappings of Tb, Y and S in the three composites of $\text{HPTS}_{0.02}\text{OS}_{0.98}\text{-LTb}_y\text{Y}_{1-y}\text{H}$ ($y = 1, 0.7$ and 0.1 , corresponding to the samples of a, b and c). The relative molar ratios of these samples obtained by EDS were consistent with those in the starting materials as expected, which indicates nearly complete reactions of the metal ions in

the LTbH:Y layers. The relative brightness of each element represented the contents corresponding to the compositions. The three elements presented unanimous distribution of density following the thickness of the LRH plates.

3.2. Luminescence property of composites in solid state.

The powder emission spectra of HPTS and the composites of $\text{HPTS}_x\text{OS}_{1-x}\text{-LTbH}$ (with changed HPTS/OS ratios) and $\text{HPTS}_{0.02}\text{OS}_{0.98}\text{-LTb}_y\text{Y}_{1-y}\text{H}$ (with varied Tb/Y ratios) were detected and the emission spectra were shown in Fig. 5. For HPTS, no emission was observed (Fig. 5A-a), no matter what excitation wavelengths were used. This may originate from the aggregation of the HPTS molecules [3], as found in our previous work [32]. The powdered $\text{NO}_3\text{-LTbH}$, measured with the 368 nm excitation wavelength of Tb^{3+} , depicted characteristic Tb^{3+} emissions at 488, 545, 587 and 620 nm (Fig. 6), respectively assigned to $^5\text{D}_4\text{-}^7\text{F}_J$ ($J = 6, 5, 4, 3$) radiative-relaxational transitions of Tb^{3+} . For the composites of $\text{HPTS}_x\text{OS}_{1-x}\text{-LTbH}$ (with pure Tb^{3+} layers but changed interlayer HPTS/OS ratios), the characteristic emissions of Tb^{3+} above-mentioned were found to be fully quenched, while a strong blue emission at 437 nm accompanying a weaker green emission (~ 516 nm) appeared. The CIE 1931 chromaticity diagram revealed the photoluminescence color located in the blue color region (Fig. 5A'). Here the marked quenching of the emission of the layer Tb^{3+} may originate from the significant nonradiative relaxation channels provided by the high-energy vibration of -OH of HPTS, as we previously reported [32]. The two emissions centred at 437 and 516 nm are attributed to the HPTS. As known, the emission spectrum of HPTS normally consists of two well-separated bands centered at 440-453 and 515-520 nm, corresponding to the protonated (ROH) and deprotonated (RO^-) emissions, respectively [39, 40]. The visibility of the HPTS

emissions indicates the LRH layers play a key role in preventing the aggregation effect of the HPTS molecules within the host layers, as the LDH layers acted [3]. The rigid and enclosed environment provided by the LRH layers confines the internal mobility and flexibility of the interlayer guests, especially the HPTS with a planar configuration, thus promoting the occurrence of HPTS emissions. In addition, the long-chain surfactant (here is OS) can also dilute and isolate the HPTS anions, thus enlarging the distance of HPTS enough to restrict their aggregation which quenched the luminescence [3]. It was previously reported that the surfactant 1-heptanesulfonate can hold back the aggregation of the fluorescent molecule of 1-pyrenesulfonate in Zn/Al LDH thus regulating its microenvironment within the LDH galleries [41]. More interestingly and importantly, the present LTbH composites demonstrate markedly different luminescence behavior from our previous HPTS/OS-LEuH composites showing quenching of the emissions for both of the layer Eu^{3+} and HPTS guest [32], for which the reason of the difference will be discussed below.

In addition, following the increase of HPTS content relative to OS, the emission intensity of the composites became weaker, and the 0.02:0.98 ratio of HPTS:OS gave the strongest intensity (Fig. 5A-b). Thus the 0.02:0.98 ratio of HPTS:OS was selected to check the luminescence behaviors of the composites with Tb/Y doped layers. As seen in Fig. 7A, the $\text{HPTS}_{0.02}\text{OS}_{0.98}\text{-LTb}_y\text{Y}_{1-y}\text{H}$ also presented two peaks at 437 nm (blue color) and 516 nm (green color) as observed above, while following the decreased Tb^{3+} content (decreased y), the intensity of blue emission became weaker while the green emission became stronger. The CIE 1931 chromaticity diagrams (Fig. 7A') displayed the gradual change of the luminescence color following the varied Tb/Y proportions. Herein the different functions of the layer ions

(Y³⁺ and Tb³⁺) on the luminescence imply their varied energy levels contribute to various energy transition processes. Therefore, a meticulous selection of the layer lanthanide ions and a careful dosing for them can effectively tune luminescence thus achieving pure emissions.

3.3. Luminescence of composites under delaminated state in FM.

The luminescence property of the HPTS solution in FM and the colloidal suspensions of the composites in FM was investigated systematically. When the composites were dispersed in FM followed by mechanical shaking for 2 h, transparent colloidal suspensions were formed. The delaminated HPTS_xOS_{1-x}-LTbH composites displayed nearly pure blue emissions (~440 nm) (Fig. 5B), forming sharp contrast to the dual fluorescence (blue and green color) in solid state (Fig. 5A). This is also obviously different from the luminescence of HPTS solution in FM which presented mainly a green emission at 522 nm (with a concomitant blue emission at ~433/454 nm), as seen in Fig. 5B-a. This means that the LTbH layer contributes to the blue emission for the composites. Moreover, the purest blue emission was found at the smallest HPTS content of 0.02, and upon the increase of HPTS content, the ~440 nm blue emission band became widened, companying a right-hand shoulder belonging to green emission (Fig. 5B-d-f). This suggests low HPTS content is in favor of the purification of the blue emission.

For HPTS_{0.02}OS_{0.98}-LTb_yY_{1-y}H composites, the emission spectra of their colloidal suspensions in FM were displayed in Fig. 7B. The LTb_yY_{1-y}H composites with $y \geq 0.5$ (Fig. 7B-b-e) exhibited one pure blue emission at 440 nm, while those with $y \leq 0.3$ (Fig. 7B-f-h) presented a nearly pure blue-green emission at 498 nm. In comparison to the green emission (522 nm) of free HPTS, the blue shift (24 nm) for the composites with more Y³⁺ verifies the function of the LYH layer, as well as the purified blue emission for composites with more

Tb³⁺ proves the action of the LTbH layer. From the CIE 1931 chromaticity diagrams (Fig. 7B'), there appeared an abrupt transformation of the photoluminescence color, contrasting with the gradual color change in solid state (Fig. 7A'), indicating the purification function *via* delamination of the LRH sheets in FM.

3.4. Fluorescence lifetimes of HPTS and composites.

The fluorescence decay times were obtained for samples in FM at $\lambda_{\text{ex}} = 312$ nm for free HPTS and $\lambda_{\text{ex}} = 375$ nm for the HPTS_{0.02}OS_{0.98}-LTbH composite and $\lambda_{\text{em}} = 440$ nm. The logarithmic decay graphs (Fig. 8) were fitted by a single exponential equation [42]:

$$I(t) = I_0 \cdot \exp(-t/\tau)$$

where $I(t)$ is the fluorescence intensity dependence with time, I_0 is the fluorescence intensity at time zero, τ is the decay lifetime for each component. The τ values for HPTS and HPTS_{0.02}OS_{0.98}-LTbH were 3.68 and 4.13 ns, respectively. The composites showed longer lifetimes than the free HPTS, indicating certain energy transfer from Tb³⁺ to HPTS existed which contributed to the longer decay time.

3.5. Analysis of luminescence mechanism and physical state.

From the results stated above, we can conclude that different states of the composites contribute to different luminescence behaviors. Taking the HPTS_{0.02}OS_{0.98}-LTbH as an example, in FM at an exfoliated state, it prefers pure blue emission (Scheme 2C), and thus is different from the dual-luminescence in solid state (Scheme 2B). The purification function on the luminescence by the LYH layers in delaminated state was shown in Scheme 2C'.

As is known, FM is a highly polar solvent normally used in LDH exfoliation [43]. According to the delamination of LDHs [44], the carbonyl group (-C=O) of FM has a strong interaction with the hydroxyl slabs of LDH layers to form a large number of hydrogen bonds, thus massive FM molecules go into the interlayer to form a swelling phase [44]. With mechanical shaking or ultrasonic treatment imposing a transverse sliding force on the swollen phase, the exfoliation initiates and the layers come apart. The delamination process of LRHs is similar to that of LDHs. A high degree of interlayer expansion for LLeuH was found due to the presence of a large quantity of FM [45]. As shown in Scheme 2C, at delaminated state, the positively-charged LTbH sheets provide an unique microenvironment for the anionic HPTS adhering to the sheets, and strong electrostatic interaction between them makes the deprotonation of HPTS (*via* ESPT process) difficult. Previous work reported slow ESPT from HPTS to acetate within cetyltrimethyl ammonium bromide micellar medium due to a strong electrostatic interaction [46]. At this moment, the ESPT process becomes strongly retarded, consequently, the emission contribution of the protonated form ($\sim 440\text{ nm}$) increases with the concomitant decrease of the deprotonated emission. Thus we propose the LTbH layers play a key role for the favorite blue emission *via* inhibition of the ESPT process of the HPTS.

From the above mentioned results, we can conclude that beside the contribution of the delamination, the energy transfer from LTbH layers to HPTS provides important function in the blue luminescence of the composites, whatever in solid and delaminated state. Compare to our previous HPTS/OS-LLeuH composites showing quenching of the emissions for both of layer Eu^{3+} and the HPTS guest in solid state [32], the present HPTS/OS-LTbH composites displayed blue-dominant luminescence, thanks to the energy transfer from layer Tb^{3+} to HPTS.

When the composites were at a delaminated state, the energy transfer dominated the emission behavior, so the nearly pure blue luminescence was present.

With regard to the energy transfer, the overlap between the excitations and emissions of the interacted components may account for the mechanism. For $\text{NO}_3\text{-LTbH}$, the excitation wavelengths were observed ranged in 350-380 nm (Fig. 6A), and the emissions occurred around 475-625 nm (Fig. 6B), while for free HPTS, neither excitation peak (Fig. 9A-a) nor emission (Fig. 5A-a) was observed. Whereas, all of the $\text{HPTS}_x\text{OS}_{1-x}\text{-LTbH}$ composites demonstrated a distinct excitation peak at 411 nm, accompanying an excitation peak at 475 nm in the composites with less HPTS (Fig. 9A), and the blue-dominant emissions (Fig. 5A) for the composites originated from the HPTS rather than the layer Tb^{3+} . Here we see the excitation range for the composites (375-500 nm, Fig. 9A) and the emission range for Tb^{3+} (475-625 nm, Fig. 6B) had some overlaps, indicating that certain emissive energy was transmitted from the layer Tb^{3+} to the HPTS.

For the delaminated $\text{HPTS}_x\text{OS}_{1-x}\text{-LTbH}$ composites in FM, the excitation spectra revealed four excitation peaks at 298, 370, 402 and 475 nm (Fig. 9B). By contrast, in FM the free HPTS exhibited two excitation peaks at 312 (weak) and 478 nm (strong). So the two excitation peaks at 298 and 475 nm should be assigned to the adsorptions of HPTS, and the other two peaks at 370 and 402 nm would correspond to the adsorptions of the layer Tb^{3+} . The integration of all of the absorbed energy may facilitate the final blue emission of the composites in FM.

It is known when more than one kind of phosphors are present in proximity to each other, only the emission from that with the lower excited state energy would be observed [47]. The

triplet energy level of HPTS was determined by using the low-temperature phosphorescence spectra of its Gd(III) complex [48]. Under excitation at 245 nm at 77 K in a methanol solution, the HPTS-Gd complex displayed the HPTS phosphorescence with a band centered at 640 nm (Fig. 10). Referring to the shortest wavelength emission edge of 600 nm in the spectrum (Fig. 10), the triplet energy level (T1) of HPTS was estimated to $\sim 16667 \text{ cm}^{-1}$, which is lower than that of the $^5\text{D}_4$ levels of Tb^{3+} (20545 cm^{-1}) [49], having the energy difference of 3878 cm^{-1} for an efficient energy transfer. This demonstrates that the layer Tb^{3+} preferentially transferred the absorbed energy to the HPTS, as a result, the emissions of HPTS would be present rather than those of the Tb^{3+} .

On the basis of all of the above results, the energy transfer pathways involve the following steps (Scheme 3): (i) for HPTS/OS-LYH system, in virtue of the Y^{3+} -induced increased absorption cross-section as Gd^{3+} ions do [16], the LYH hosts help absorb the energy followed by an energy transfer to HPTS, thus generating the blue-green emission (498 nm) in delaminated state; (ii) for HPTS/OS-LTb_yY_{1-y}H, the UV absorption is performed initially by the LRH host layers, followed by the layer Tb^{3+} ions acting as energy-transfer bridges that connect host layers and HPTS, to achieve the blue-dominant emission; (iii) for HPTS/OS-LTbH, host layer Tb^{3+} ions preferentially absorb the energy and then transfer the energy to HPTS, in which the energy transfer or intersystem crossing probably contributes to the purified blue emission (440 nm).

4. Conclusions

In conclusion, this work demonstrates a novel example of purified luminescence behavior *via* delamination of the HPTS_xOS_{1-x}-LTb_yY_{1-y}H composites ($x = 0.02, 0.05, 0.10, 0.15$ and 0.20 , y

= 1, 0.9, 0.7, 0.5, 0.3, 0.1 and 0) and energy transfer from the layer rare-earth ions to the HPTS guest. In solid state, because of the confinement effect of the LRH layers, the composites with doped $\text{LTb}_y\text{Y}_{1-y}\text{H}$ layers present dual-color fluorescence between blue and green regions, in contrast to the scarce emission of free HPTS. The composites with pure LTbH layers, however, exhibit blue-dominant fluorescence, thanks for the energy transfer from layer Tb^{3+} to HPTS. At delaminated state in FM, the composites show purified luminescence behaviour: those with pure Tb^{3+} layers or Tb/Y doped layers (more Tb^{3+} than Y^{3+}) reveal single blue emission (440 nm), while those with Tb/Y doped layers (less Tb^{3+} than Y^{3+}) display pure bluish green emission (498 nm). We propose that the delamination of the LTbH layers and energy transfer from layered Tb^{3+} to HPTS both contribute to the favorite blue luminescence. The LTbH layers play a key role in the inhibition of the ESPT process of the HPTS, thus improving the purification effect for the blue luminescence compared to previously reported LEuH-HPTS composite [32]. This work highlights the utility of one-step delamination method and energy transfer effect for tuning luminescence color. The facile delamination of the LRH composites provides a beneficial pathway for assembly of tunable films especially blue luminous materials. The study is expected to open a new field for fabrication of promising LRH composite materials.

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Table 1. Chemical compositions for NO₃-LRH precursor and composites.

	Chemical formula	Wt %, Found (Cal.)				
		Tb	Y	C	H	N
NO ₃ -LTbH	Tb(OH) _{2.4} (NO ₃) _{0.46} (CO ₃) _{0.09} ·	62.40	-	0.44	1.78	2.53
	1.1H ₂ O	(62.83)	-	(0.52)	(1.79)	(2.55)
HPTS/OS-LTbH	Tb(OH) _{2.4} (C ₈ H ₁₇ O ₃ S) _{0.41}	46.34	-	15.00	4.13	-
	(C ₁₆ H ₇ O ₁₀ S ₃) _{0.06} ·2.2H ₂ O	(45.89)	-	(14.86)	(4.08)	-
HPTS/OS-LTb _{0.9} Y _{0.1} H	Tb _{0.90} Y _{0.10} (OH) _{2.4} (C ₈ H ₁₇ O ₃ S) _{0.46}	42.66	2.64	15.87	4.17	-
	(C ₁₆ H ₇ O ₁₀ S ₃) _{0.05} ·1.7H ₂ O	(42.98)	(2.66)	(15.99)	(4.20)	-
HPTS/OS-LTb _{0.7} Y _{0.3} H	Tb _{0.69} Y _{0.31} (OH) _{2.4} (C ₈ H ₁₇ O ₃ S) _{0.45}	34.50	8.79	16.69	4.46	-
	(C ₁₆ H ₇ O ₁₀ S ₃) _{0.05} ·1.9H ₂ O	(34.09)	(8.69)	(16.50)	(4.41)	-
HPTS/OS-LTb _{0.5} Y _{0.5} H	Tb _{0.50} Y _{0.50} (OH) _{2.4} (C ₈ H ₁₇ O ₃ S) _{0.42}	27.12	15.02	17.57	4.34	-
	(C ₁₆ H ₇ O ₁₀ S ₃) _{0.06} ·1.4H ₂ O	(26.77)	(14.83)	(17.35)	(4.28)	-
HPTS/OS-LTb _{0.3} Y _{0.7} H	Tb _{0.29} Y _{0.71} (OH) _{2.4} (C ₈ H ₁₇ O ₃ S) _{0.48}	15.73	21.33	18.22	5.00	-
	(C ₁₆ H ₇ O ₁₀ S ₃) _{0.04} ·2.0H ₂ O	(15.68)	(21.27)	(18.17)	(5.00)	-
HPTS/OS-LTb _{0.1} Y _{0.9} H	Tb _{0.10} Y _{0.90} (OH) _{2.4} (C ₈ H ₁₇ O ₃ S) _{0.50}	6.08	27.95	19.17	4.80	-
	(C ₁₆ H ₇ O ₁₀ S ₃) _{0.03} ·1.2H ₂ O	(6.36)	(29.26)	(20.07)	(5.02)	-
HPTS/OS-LYH	Y(OH) _{2.4} (C ₈ H ₁₇ O ₃ S) _{0.48}	-	31.83	19.29	5.16	-
	(C ₁₆ H ₇ O ₁₀ S ₃) _{0.04} ·1.8H ₂ O	-	(32.07)	(19.82)	(5.30)	-

Fig. 1. (A) Powder XRD patterns of precursor $\text{NO}_3\text{-LTbH}$ (a), composites of OS-LTbH (b, b') and $\text{HPTS}_x/\text{OS}_{1-x}\text{-LTbH}$: $x = 0.02$ (c, c'), 0.05 (d, d'), 0.1 (e, e'), 0.15 (f, f'), 0.20 (g, g'). (B) Powder XRD patterns of composites of $\text{HPTS}_{0.02}\text{OS}_{0.98}\text{-LTb}_y\text{Y}_{1-y}\text{H}$: $y = 1$ (a, a'), 0.9 (b, b'), 0.7 (c, c'), 0.5 (d, d'), 0.3 (e, e'), 0.1 (f, f'), and 0 (g, g'). The d -values are given in nanometers.

Fig. 2. FT-IR spectra of precursors HPTS (a), OS (b) and $\text{NO}_3\text{-LTbH}$ (c), composites of $\text{HPTS}_x\text{OS}_{1-x}\text{-LTbH}$ in which $x = 0.02$ (d) and 0.2 (e), and composites of $\text{HPTS}_{0.02}\text{OS}_{0.98}\text{-LTb}_y\text{Y}_{1-y}\text{H}$ with $y = 0.9$ (f) and 0 (g).

Fig. 3. SEM images of precursors $\text{NO}_3\text{-LTbH}$ (a, a'), $\text{NO}_3\text{-LTb}_{0.5}\text{Y}_{0.5}\text{H}$ (b, b') and $\text{NO}_3\text{-LYH}$ (c, c'), and composites of $\text{HPTS}_{0.02}\text{OS}_{0.98}\text{-LTb}_y\text{Y}_{1-y}\text{H}$: $y = 1$ (d, d'), 0.9 (e, e'), 0.7 (f, f'), 0.5 (g, g'), 0.3 (h, h'), 0.1 (i, i'), and 0 (j, j').

Fig. 4. SEM images of HPTS_{0.02}OS_{0.98}-LTb_yY_{1-y}H: (a) $y = 1$, (b) 0.7, (c) 0.1; (a-1) to (a-3), (b-1) to (b-3) and (c-1) to (c-3) show corresponding elemental distribution maps of Tb, Y and S; a', b' and c' are the related EDS and average compositions of a, b and c.

Fig. 5. Emission spectra of samples (A) in solid state ($\lambda_{\text{ex}} = 411$ nm) or (B) in delaminated state in FM: (a) free HPTS ($\lambda_{\text{ex}} = 370$ nm) and composites of HPTS _{x} OS _{$1-x$} -LTbH ($\lambda_{\text{ex}} = 370$ nm) in which $x = 0.02$ (b), 0.05 (c), 0.10 (d), 0.15 (e) and 0.20 (f); insets in (B) are corresponding photographs under 365 nm UV irradiation; (A') and (B') are CIE 1931 chromaticity diagrams of corresponding samples showing the photoluminescence colour.

Fig. 6. Photoluminescence (A) excitation ($\lambda_{\text{em}} = 545 \text{ nm}$) and (B) emission ($\lambda_{\text{ex}} = 368 \text{ nm}$) spectra of $\text{NO}_3\text{-LTbH}$ precursor.

Fig. 7. Emission spectra of samples (A) in solid state and (B) delaminated state in FM: (a) is for free HPTS ($\lambda_{\text{ex}} = 370$ nm) and (b)-(h) correspond to composites of HPTS_{0.02}OS_{0.98}-LTb_yY_{1-y}H ($\lambda_{\text{ex}} = 370$ nm) with y values of 1.0, 0.9, 0.7, 0.5, 0.3, 0.1 and 0, respectively; the insets in (B) are corresponding photographs under 365 nm UV irradiation of samples; (A') and (B') are CIE 1931 chromaticity diagrams of corresponding samples showing photoluminescence colour.

Fig. 8. Photoluminescence decay curves of free HPTS (a) and composite of HPTS_{0.02}OS_{0.98}-LTbH (b), respectively.

Fig. 9. Photoluminescence excitation spectra of HPTS ($\lambda_{em} = 516$ nm in solid state and $\lambda_{em} = 522$ nm in FM) and composites HPTS_xOS_{1-x}-LTbH in (A) solid state ($\lambda_{em} = 516$ nm) and (B) colloidal suspensions in FM ($\lambda_{em} = 440$ nm): (a) is pure HPTS, (b)-(f) are the composites of HPTS_xOS_{1-x}-LTbH with x values of 0.02, 0.05, 0.10, 0.15 and 0.20, respectively.

Fig. 10. Phosphorescence spectrum of Gd(III) complex of HPTS (Gd-HPTS) in a methanol solution (77 K).

Scheme 1. Arrangements of gallery species in (a) $\text{NO}_3\text{-LTbH}$ precursor and (b) HPTS/OS-LTbH composite.

Scheme 2. Sketch presentation of the formation process and luminescence behaviours of $\text{NO}_3\text{-LRH}$ and HPTS/OS-LRH ($R = \text{Tb}, \text{Y}$) composites under different state: (A, A') $\text{NO}_3\text{-LRH}$ in solid state, (B, B') HPTS/OS-LRH composites in solid state, (C) delaminated composites in FM.

Scheme 3. Schematic representation of the energy transfer process for composites of HPTS/OS-LRH.

Graphical Abstract

Energy transfer from layer Tb^{3+} to HPTS guest in delaminated HPTS/OS-LRH composites contributes to purified blue luminescence.