

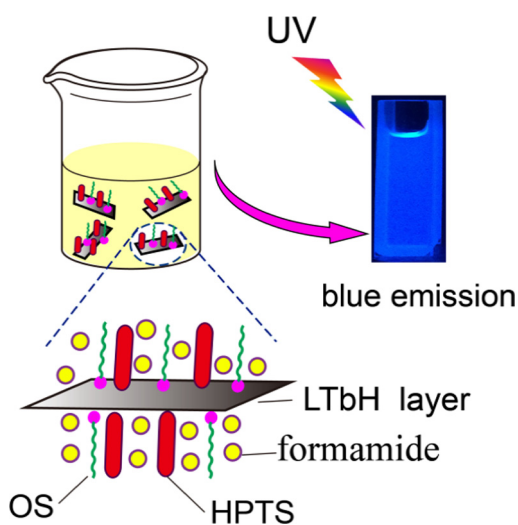
## Regular Article

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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## GRAPHICAL ABSTRACT

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

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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  $HPTS_xOS_{1-x}-LTb_yY_{1-y}H$  composites presented varied luminescence behavior depending on their physical state. In solid state, dual-color luminescence was observed: blue-dominant emissions (437 nm) for  $HPTS_xOS_{1-x}-LTb_yY_{1-y}H$  and blue- (437 nm) to green-dominant (516 nm) luminescence for  $HPTS_{0.02}OS_{0.98}-LTb_yY_{1-y}H$ . In delaminated state in formamide, purified luminescence was present: pure blue emission (440 nm) for  $HPTS_xOS_{1-x}-LTb_yY_{1-y}H$  and  $HPTS_{0.02}OS_{0.98}-LTb_yY_{1-y}H$  ( $y \geq 0.5$ ), while pure bluish-green emission (498 nm) for  $HPTS_{0.02}OS_{0.98}-LTb_yY_{1-y}H$  ( $y \leq 0.3$ ). 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.

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## 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  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Dy}^{3+}$  [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  $\text{Eu}^{3+}$ -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 L $\text{EuH}$  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 ( $\text{R} = \text{Eu}/\text{Gd}$ ,  $\text{Tb}/\text{Y}$ ) 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  $\text{Y}:\text{LTbH}$  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 $\text{NO}_3$ -LRH precursor

$\text{Tb}_4\text{O}_7$  (99.9%) and  $\text{Y}_2\text{O}_3$  (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  $\text{Tb}^{3+}$  and  $\text{Y}^{3+}$  was fixed to be 1.0 mmol, where the molar ratios of  $\text{Tb}^{3+}$  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  $\text{Tb}/\text{Y}$  ratios, HMT (1 mmol), and  $\text{NaNO}_3$  (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, $\text{HPTS}_x\text{OS}_{1-x}$ -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)  $\text{NO}_3$ -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  $\text{HPTS}_x\text{OS}_{1-x}$ -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  $\text{HPTS}_{0.05}\text{OS}_{0.95}$ -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  $\text{NO}_3$ -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  $\text{HPTS}_{0.02}\text{OS}_{0.98}$ - $\text{LTb}_y\text{Y}_{1-y}\text{H}$  ( $y = 1, 0.9, 0.7, 0.5, 0.3, 0.1$  and 0), taking the  $\text{HPTS}_{0.02}\text{OS}_{0.98}$ - $\text{LTb}_{0.1}\text{Y}_{0.9}\text{H}$  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  $\text{NO}_3$ - $\text{LTb}_{0.1}\text{Y}_{0.9}\text{H}$  powder was dispersed into the above solution. In the preparation of other composites, the moles of HPTS, OS and  $\text{NO}_3$ - $\text{LTb}_y\text{Y}_{1-y}\text{H}$  were kept constant but only changed the mass of the  $\text{NO}_3$ - $\text{LTb}_y\text{Y}_{1-y}\text{H}$  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)  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 3 mL  $\text{H}_2\text{O}$ , 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  $\text{Cu-K}\alpha$  radiation at room temperature, with a step size of 0.0167°, scan time of 15 s per step, and  $2\theta$  ranging from 4.5 to 70°. The generator

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