Electronic Supplementary Information (ESI)

Controllable luminescence of layered rare-earth hydroxide composites with fluorescent molecule: blue emission by delamination in formamide

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Experimental Section.

Preparation of NO_3–LEuH precursor. An aqueous solution containing $Eu(NO_3)_3\cdot6H_2O$ (1 mmol), hexamethylenetetramine (HMT, 1 mmol), $NaNO_3$ (13 mmol), in deionized water (80 mL) was heated at 90 °C for 12 h in a Teflon-autoclave. After the reaction, the product was filtered, washed, and vacuum-dried (40 °C for 24 h), obtaining the NO_3–LEuH precipitate.

Intercalation of HPTS/OS into LEuH by ion-exchange method. The ion-exchange reactions between NO_3^- and the organic anions were processed at 70 °C in a Teflon-autoclave. Firstly, 0.0315 g of HPTS (0.06 mmol) and 0.6358 g of OS (2.94 mmol) were pre-treated by the addition of NaOH or HNO_3 to obtain aqueous solutions with various pH values of 2.9, 4.0, 5.3, 7.3 and 10.3. The NO_3–LEuH powder (0.1 g) was afterwards dispersed upon the above solutions, and reacted at 70 °C for 24 h in a Teflon-autoclave. The resulting precipitates were collected by filtration, washed with deionized water, and vacuum-dried at 40 °C for 24 h. After the reactions, the pH values of the filtrates were tested to be 6.2, 6.4, 6.9, 7.5, and 8.2, respectively. The composites discussed below were labelled with an initial pH used.

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Intercalation of HPTS/OS into LEuH *via* co-precipitation method. A mixed solution prepared by dissolving $Eu(NO_3)_3 \cdot 6H_2O$ (0.4461 g, 1 mmol), HMT (0.1402 g, 1 mmol), HPTS (0.0315 g, 0.06 mmol, with 2 % molar percentage in HPTS+OS mixture), and OS (0.6358 g, 2.94 mmol, with 98 % molar percentage in HPTS+OS mixture) in 80 mL deionized water was reacted at 90 °C for 12 h in a Teflon–autoclave. The obtained product was filtered, washed with deionized water to remove impurities, and then vacuum–dried at 40 °C for 24 h. The pH of the filtrate after the reaction was tested to be 6.5.

Preparation of NO_3–LGdH precursor. An aqueous solution containing $Gd(NO_3)_3 \cdot 6H_2O$ (1 mmol), hexamethylenetetramine (HMT, 1 mmol), $NaNO_3$ (13 mmol), in deionized water (80 mL) was heated at 90 °C for 12 h in a Teflon-autoclave. After the reaction, the product was filtered, washed, and vacuum-dried (40 °C for 24 h), obtaining the NO_3–LGdH precipitate.

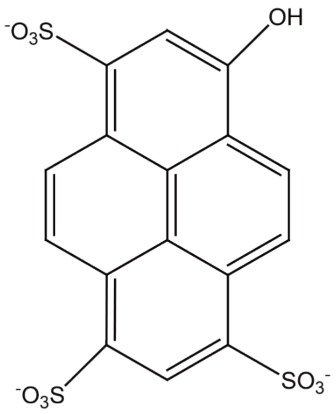
Intercalation of HPTS/OS into LGdH by ion-exchange method. The ion-exchange reactions between NO_3^- and the organic anions were processed at 70 °C in a Teflon-autoclave. Firstly, 0.0315 g of HPTS (0.06 mmol) and 0.6358 g of OS (2.94 mmol) were dissolved in water to obtain aqueous solutions. The NO_3–LGdH powder (0.1 g) was afterwards dispersed upon the above solutions, and reacted at 70 °C for 24 h in a Teflon-autoclave. The resulting precipitates were collected by filtration, washed with deionized water, and vacuum-dried at 40 °C for 24 h.

Characterization Techniques. The powder X-ray diffraction (XRD) patterns were collected by using a Phillips X'pert Pro MPD diffractometer with Cu-Kα 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) observations were carried out by using a Hitachi S-4800 microscope at 5.0 kV. Thermo-gravimetric and differential thermal analysis (TG-DTA) measurements were performed with a ZRY-2P thermal analyzer in air atmosphere. Luminescence spectra in the solutions were obtained on a Cary Eclipse spectrofluorimeter, while the solide state luminescence spectra was performed in the PerkinElmer-LS55 spectrofluorimeter.

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

Table S1. Chemical compositions for LEuH precursor and the composites.

Samples	Chemical formula	Wt %, Found(Calcd.)			
		Eu	C	H	N
NO_3–LEuH	$Eu(OH)_{2.41}(NO_3)_{0.49}(CO_3)_{0.05}\cdot 0.85H_2O$	62.00	0.27	1.63	2.81
		(62.50)	(0.25)	(1.73)	(2.88)
co-HPTS/OS-LEuH	$Eu(OH)_{2.41}(HPTS)_{0.094}(OS)_{0.42}(NO_3)_{0.005}\cdot 1.97H_2O$	44.61	18.63	4.40	0.02
		(43.01)	(16.52)	(4.24)	(0.02)
(pH=2.9) HPTS/OS-LEuH	$Eu(OH)_{2.41}(HPTS)_{0.094}(OS)_{0.42}(NO_3)_{0.01}\cdot 1.89H_2O$	44.92	18.85	4.39	0.05
		(43.12)	(16.56)	(4.21)	(0.05)
(pH=4.0) HPTS/OS-LEuH	$Eu(OH)_{2.41}(HPTS)_{0.06}(OS)_{0.31}(NO_3)_{0.07}\cdot 1.37H_2O$	48.98	13.42	3.72	0.30
		(48.99)	(13.42)	(3.72)	(0.30)
(pH=5.3) HPTS/OS-LEuH	$Eu(OH)_{2.41}(HPTS)_{0.068}(OS)_{0.31}(NO_3)_{0.04}\cdot 1.46H_2O$	48.47	13.79	3.76	0.18
		(48.41)	(13.77)	(3.75)	(0.18)
(pH=7.3) HPTS/OS-LEuH	$Eu(OH)_{2.41}(HPTS)_{0.080}(OS)_{0.39}(NO_3)_{0.007}\cdot 1.75H_2O$	44.76	15.61	4.10	0.03
		(45.01)	(15.70)	(4.12)	(0.03)
(pH=10.3) HPTS/OS-LEuH	$Eu(OH)_{2.41}(HPTS)_{0.075}(OS)_{0.31}(NO_3)_{0.03}\cdot 1.71H_2O$	46.79	13.56	3.77	0.14
		(47.47)	(13.76)	(3.82)	(0.14)



Scheme S1. The structure of HPTS anion.

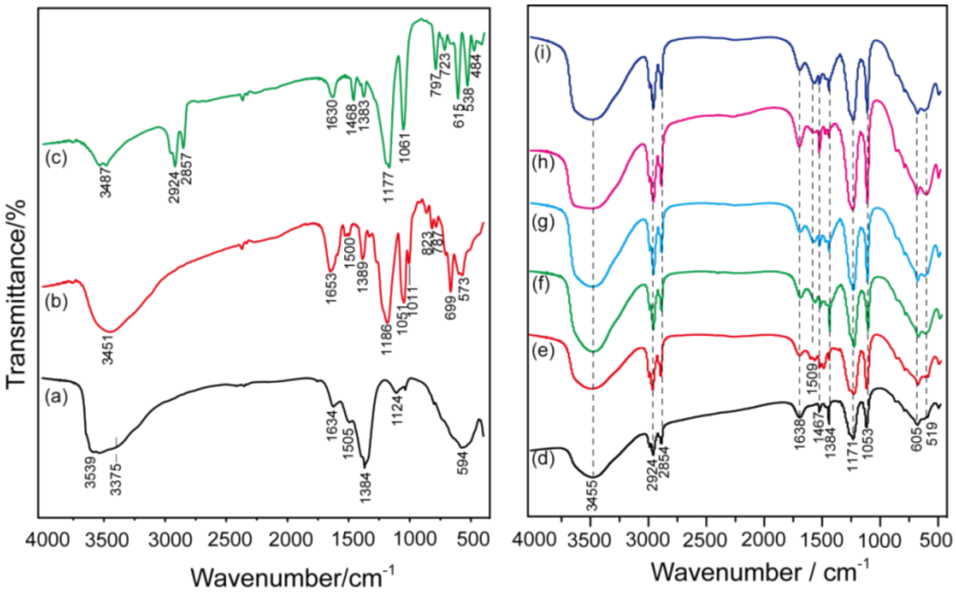


Fig. S1 FT-IR spectra of precursor NO_3-LEuH (a), HPTS (b), OS (c), composites obtained by co-precipitation (d), and ion exchange under different pH values of 2.9, 4.0, 5.3, 7.3, 10.3 (e-i).

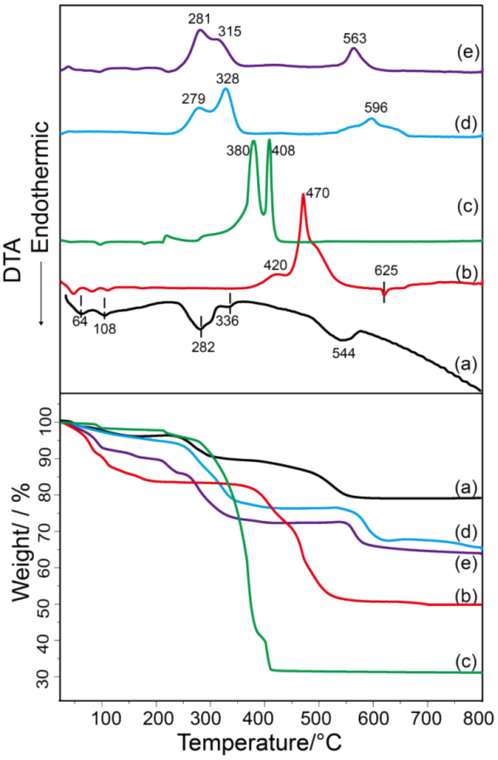


Fig. S2 TG-DTA spectra of precursor LEuH (a), HPTS (b), OS (c), and composites obtained by co-precipitation (d) and ion exchange at pH=7.3 (e).

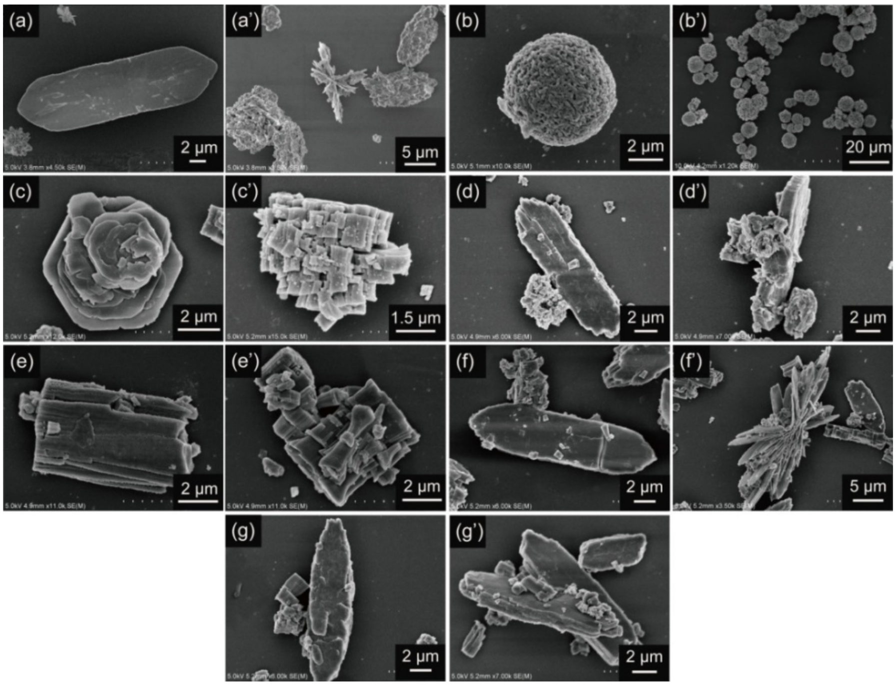


Fig. S3 SEM images of precursor NO_3-LEuH (a, a’), and composites obtained by co-precipitation (b, b’) and ion exchange at different initial pH: pH=2.9 (c, c’), pH=4.0 (d, d’), pH=5.3 (e, e’), pH=7.3 (f, f’), pH=10.3 (g, g’).

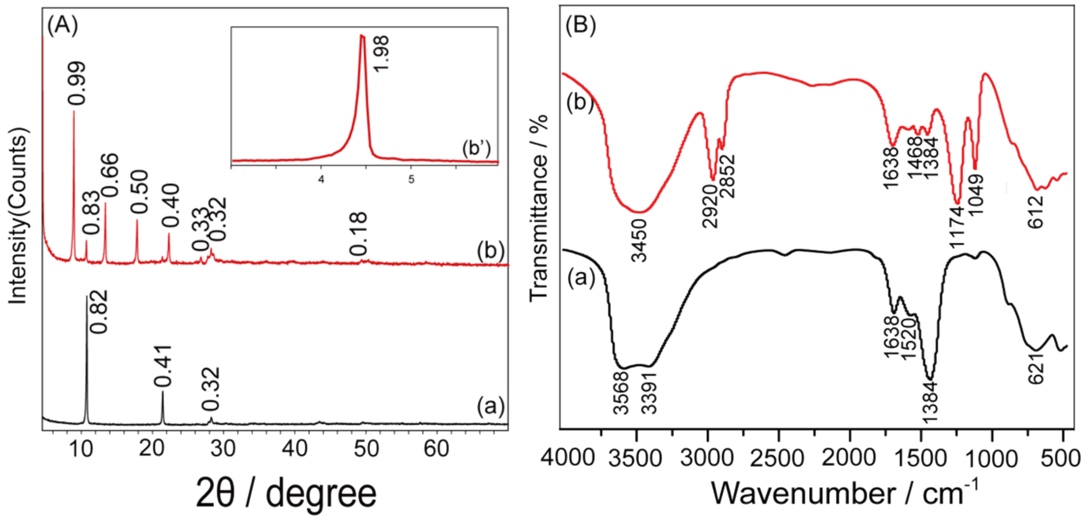


Fig. S4 (A) XRD patterns and (B) FT-IR spectra of NO$_3$-LGdH precursor (a) and composite obtained by ion exchange at pH=7.3 (b).

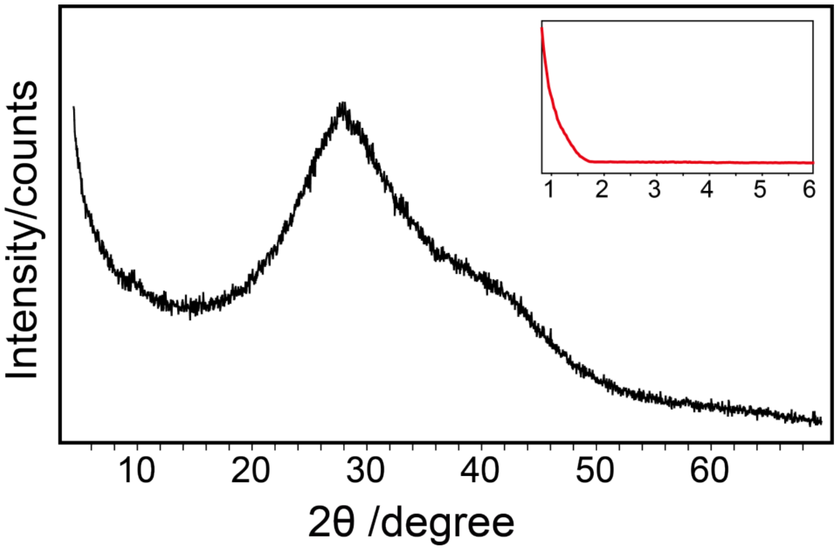


Fig. S5 XRD pattern of colloidal aggregate by centrifugation of LEuH composite (pH=2.9) in FM/water.

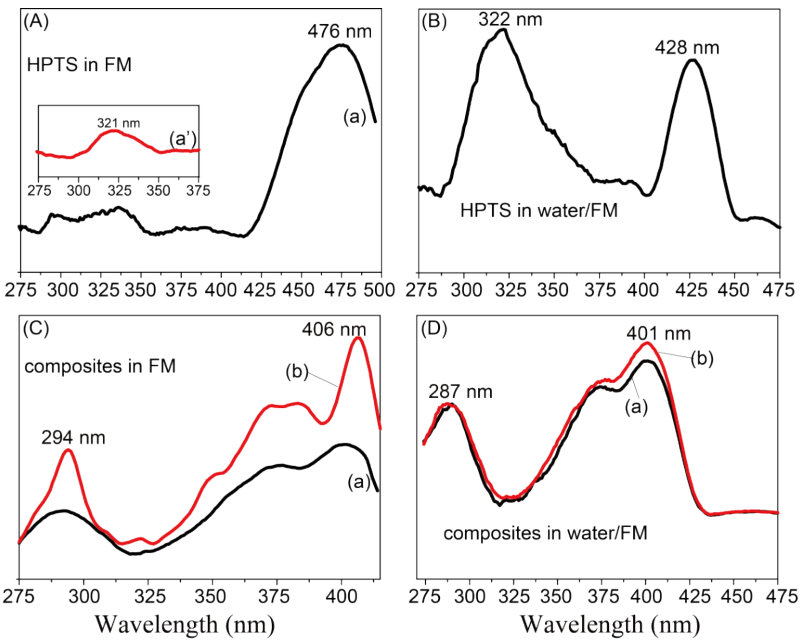


Fig. S6 Excitation spectra of HPTS and LEuH-HPTS composites in FM and water/FM. (A): HPTS in FM (a), the inset (a′) is the excitation spectra (275-375 nm) by increasing slit. (B): HPTS in water/FM. (C): LEuH-HPTS composites in FM: pH = 7.3 (a) and 10.3 (b). (D): LEuH-HPTS composites in water/FM: pH = 7.3 (a) and 10.3 (b).