

## Supporting Information

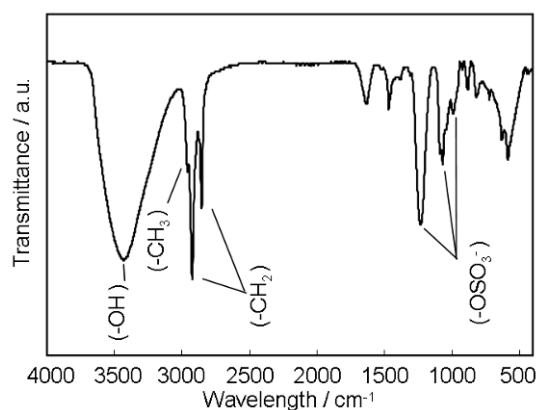
# Drastic Changes in Photoluminescence Properties of Multilayer Films Composed of Europium Hydroxide and Titanium Oxide Nanosheets

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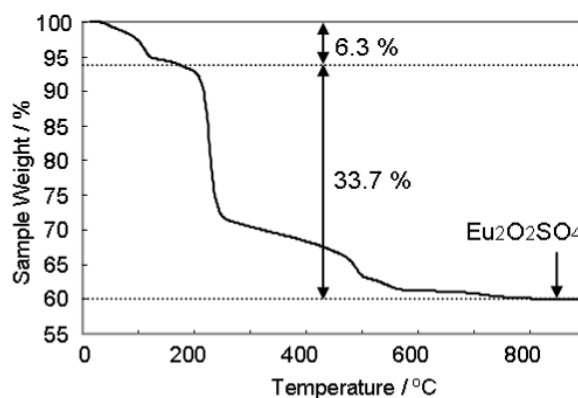
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**Figure S-1** FT-IR spectrum of the  $\text{Eu}(\text{OH})_{3-x}\text{DS}_x$ . The broad peak around  $3580\text{--}3400\text{ cm}^{-1}$  indicates the presence of hydroxyl groups and water molecules. The strong peaks at  $2923$  and  $2854\text{ cm}^{-1}$  were due to the asymmetric and symmetric  $\text{CH}_2$  stretching vibrations, respectively, and the relatively weak band at  $2958\text{ cm}^{-1}$  was assigned to the stretching vibration of the  $\text{CH}_3$  group of the alkyl chain of  $\text{DS}^-$  ions. The peak at  $1468\text{ cm}^{-1}$  was due to the  $\text{CH}_2$  bending (or scissor) mode. The peaks at  $1229$  and  $1067\text{ cm}^{-1}$  were attributed to the sulfate group of  $\text{DS}^-$  ion.

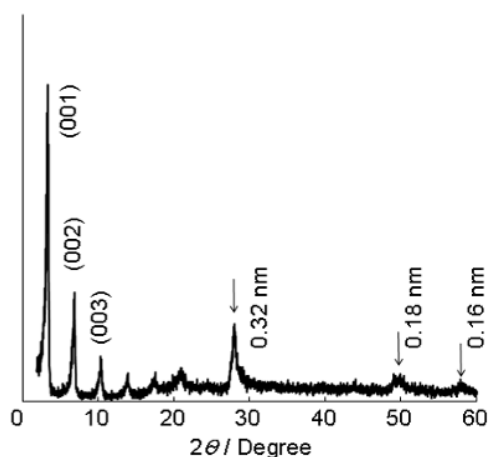


**Figure S-2** TGA trace for  $\text{Eu}(\text{OH})_{3-x}\text{DS}_x \cdot n\text{H}_2\text{O}$  showing mass losses of 6.3 % below  $150^\circ\text{C}$  and further mass losses of 40.0 % by  $900^\circ\text{C}$ . After heat treatment at  $900^\circ\text{C}$ ,  $\text{Eu}_2\text{O}_2\text{SO}_4$  was produced.

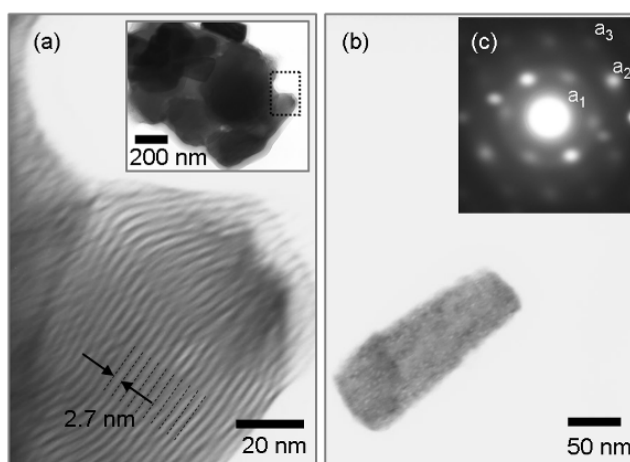
**Table S-1.** Characterizing data for  $\text{Eu}(\text{OH})_{3-x}\text{DS}_x \cdot n\text{H}_2\text{O}$ .

Composition	Elemental analysis	
	Observed (%) <sup>[a]</sup>	Calculated (%)
$\text{Eu}(\text{OH})_{2.46}\text{DS}_{0.54} \cdot 1.26\text{H}_2\text{O}$	C(21.40 %), H(4.90 %), Eu (43.02 %)	C(21.68 %), H(5.15%), Eu (42.20%)

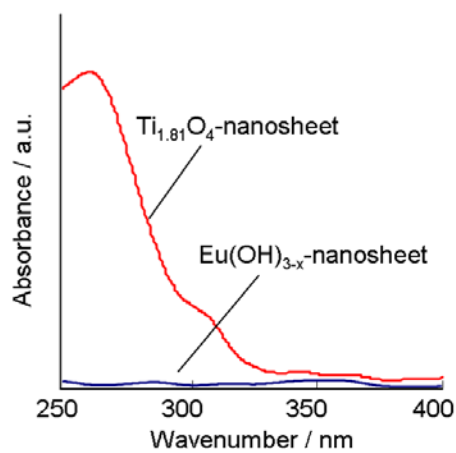
[a]: C and H % were measured by elementary analysis. Eu % was measured by ICP analysis.



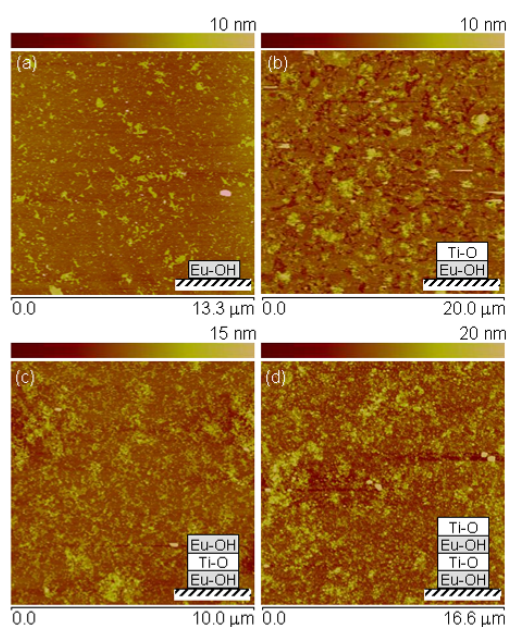
**Figure S-3.** XRD pattern for the  $\text{Eu}(\text{OH})_{3-x}\text{DS}_x$ . Several (00 $l$ ) reflections were observed. The basal spacing calculated from the diffraction angle was 2.69 nm. In addition, several non-(00 $l$ ) diffractions at 28.04° (0.318 nm), 49.36° (0.184 nm), and 58.00° (0.159 nm) were observed.



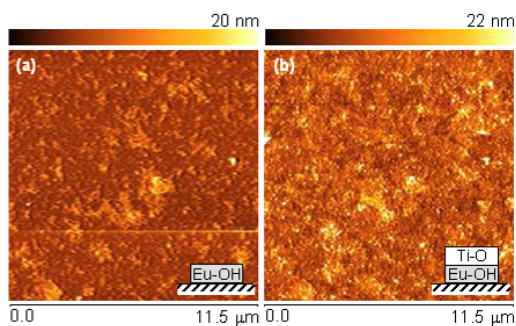
**Figure S-4.** (a, b) TEM images and (c) SAED pattern of the  $\text{Eu}(\text{OH})_{3-x}\text{DS}_x$  particles. The basal spacing estimated from the TEM image was around 2.7 nm, which is similar to that calculated from the (001) reflection in XRD data (Figure S-3). The SAED pattern displayed several spots, although they tended to change into arcs or rings during the observation. The spot positions correspond to lattice spacings between the atomic planes ( $d$ -spacings) of  $a_1 = 0.32$ ,  $a_2 = 0.18$ , and  $a_3 = 0.16$  nm. These  $d$ -spacings correspond to the diffractions at 28.04, 49.36, and 58.00° in the XRD data (Figure S-3), indicating that these peaks are due to diffraction from the direction of the plane of the host europium hydroxide layer. Unfortunately, we couldn't determine the crystal structure from the XRD and SAED patterns.



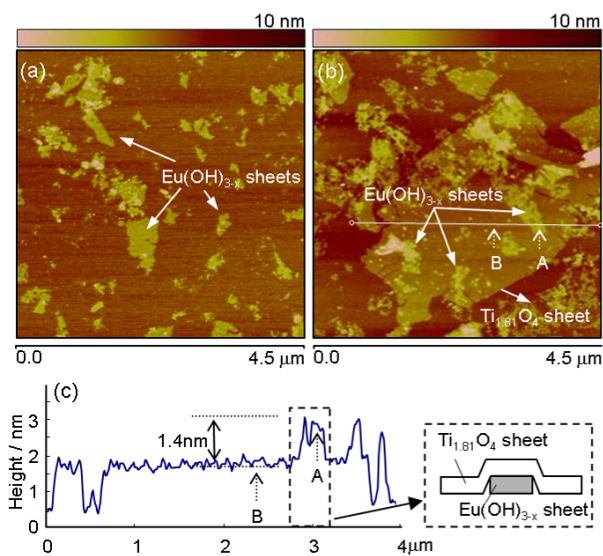
**Figure S-5.** UV-vis spectra of  $\text{Ti}_{1.81}\text{O}_4$ -nanosheet and  $\text{Eu}(\text{OH})_{3-x}$ -nanosheet.



**Figure S-6.** AFM images of the multilayer films (1-4 layers); (a) 1-layer, (b) 2-layer, (c) 3-layer, and (d) 4-layer films.



**Figure S-7.** AFM images of (a) the 1-layer film of  $\text{Eu}(\text{OH})_{3-x}$  nanosheets and (b) the 2-layer film composed of  $\text{Eu}(\text{OH})_{3-x} / \text{Ti}_{1.81}\text{O}_4$  nanosheets.



**Figure S-8.** AFM images of (a) the 1-layer film of  $\text{Eu(OH)}_{3-x}$  nanosheets and (b) the 2-layer film composed of  $\text{Eu(OH)}_{3-x} / \text{Ti}_{1.81}\text{O}_4$  nanosheets on a Si substrate, and (c) cross-sectional profile of the 2-layer film composed of  $\text{Eu(OH)}_{3-x} / \text{Ti}_{1.81}\text{O}_4$  nanosheets.

## Experimental details

### Materials.

Layered europium hydroxides intercalated with dodecyl sulfate ions ( $\text{Eu}(\text{OH})_{3-x}\text{DS}_x$ ) were prepared as follows. Three types of aqueous solutions (500 mM  $\text{Eu}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ , 100 mM sodium dodecyl sulfate (SDS), and 2 M hexamethylenetetramine (HMT) solutions) were prepared, and then the trivalent europium (8.0 mL), SDS (2.4 mL), and HMT (0.8 mL) solution were mixed in a 50 cm<sup>3</sup> vessel with deionized Milli-Q water (28.8 mL).  $\text{Eu}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  was 99.9 % purity purchased from Wako Chemicals Co., Ltd. and were used as received without further treatment. The mixed solutions were heated at 85°C for 1 h under air-tight conditions. In this reaction,  $\text{Eu}(\text{OH})_{3-x}\text{DS}_x$  is synthesized by precipitation of an aqueous solution of trivalent lanthanide and SDS through HMT hydrolysis. After the reaction, the precipitates obtained were centrifuged and washed with distilled water and ethanol, and dried at room temperature. As the starting material for the titanium oxide nanosheets,  $\text{Cs}_{0.76}\text{Ti}_{1.81}\text{O}_4$  (CTO) was prepared by the complex polymerization method.<sup>[S-1]</sup>

[S-1] Y. Matsumoto, U. Unal, Y. Kimura, S. Ohashi, K. Izawa, *J. Phys. Chem. B* **2005**, *109*, 12748–12754.

### Exfoliation.

The exfoliation of the  $\text{Eu}(\text{OH})_{3-x}\text{DS}_x$  was carried out as follows. The  $\text{Eu}(\text{OH})_{3-x}\text{DS}_x$  (100 mg) were mixed with formamide (50 mL) to exfoliate the host layers, and the resulting suspensions were heated for several days at 40°C without agitation. The suspensions were centrifuged (12000 rpm, 60 min) to remove nanosheets with small lateral size, and then the sediments were mixed with formamide (30 mL). Subsequently, the suspensions were centrifuged (2000 rpm, 20 min), and then the supernatants were used as the colloidal solutions of europium hydroxide ( $\text{Eu}(\text{OH})_{3-x}$ ) nanosheets. The exfoliation of the CTO was carried out as follows. The CTO (1g) was converted into a protonic form by immersion in 0.5 M HCl solution at room temperature. The protonated powder (0.5 g) was exfoliated in tetrabutylammonium (TBA) solution (300 mL) for 72 h. The subsequent centrifugation of the solution under 3000 rpm for 30 min yielded colloidal suspension of titanium oxide ( $\text{Ti}_{1.81}\text{O}_4$ ) nanosheets.

### Preparation of multilayer films of nanosheets.

The  $\text{Eu}(\text{OH})_{3-x}$  and  $\text{Ti}_{1.81}\text{O}_4$  nanosheet layers were prepared by soaking method and Langmuir-Blodgett (LB) method, respectively. Cleaned Si substrates were dipped into the colloidal solution having positively charged  $\text{Eu}(\text{OH})_{3-x}$  nanosheets for 20 min. The substrates were rinsed in formamide and pure water, and then dried under  $\text{N}_2$  stream. Next,  $\text{Ti}_{1.81}\text{O}_4$  nanosheet layers were prepared by Langmuir-Blodgett (LB) method according to literature procedure.<sup>S-2</sup> The substrates were rinsed in pure water, and then dried under  $\text{N}_2$  stream. The sequence was carried out *n* times.

[S-2] M. Muramatsu, K. Akatsuka, Y. Ebina, K. Wang, T. Sasaki, T. Ishida, K. Miyake, M. Haga, *Langmuir* **2005**, *21*, 6590.

### Characterization and Equipment.

The crystal structure was analyzed using X-ray powder diffraction (XRD) patterns (using Cu  $K\alpha$  radiation, Rigaku RINT-2500VHF). The concentration of the nanosheets in the solution was analyzed by an inductively coupled plasma (ICP) spectrometer (Seiko Instruments, SPS7800). The concentration of Eu in the  $\text{Eu}(\text{OH})_{3-x}$  nanosheet suspension was  $5.4 \times 10^{-3}$  M. FT-IR spectra were recorded on a Perkin-Elmer spectrometer using a KBr method. Thermogravimetric differential thermal analysis curves were obtained by thermal analysis (Seiko TG/DTA). UV-vis absorption spectra were obtained using a Jasco V-550 spectrometer. The microstructure and surface morphology were observed by TEM (JEOL 2000FX, 200 kV). The thickness of the exfoliated nanosheets was confirmed by atomic force microscopy (AFM, Veeco Nanoscope-V) measurements. The X-ray absorption fine structures (XAFS) measurement was performed at the BL14B2 beam line, SPring-8, Japan Synchrotron Radiation Research Institute (JASRI), Hyogo, Japan. The appropriate amount of well-grounded samples were mixed with boron nitride powder, pressed into a disk of 10 mm diameter, and used for XAFS measurements. The absorption edges used was Eu K-edge (48.52 keV). X-ray was monochromatized by a double crystal monochromator using Si(311) plane. The measurements were carried out using a transmission method. The EXAFS spectra were analyzed for the nearest shell. The structural parameters were determined by curve-fitting procedures using REX2000 data analysis software (Rigaku).  $\text{EuTiO}_3$  was used as a reference sample for the curve-fitting. Theoretical parameters of backscattering factors and phase shifts used in the curve-fitting analysis were calculated by FEFF7. Photoluminescence spectra were obtained using a Jasco FP-6500 spectrofluorometer with a 150-W Xe lamp at room temperature. The excitation and emission spectra were corrected for the spectral distribution of the Xe lamp intensity by the Rodamine B (5.5g/L, ethylene glycol solution) and a JASCO ESC-333 reference light source.