

## Electronic Supporting Information

# The first lanthanide organophosphonate nanosheet by exfoliation of layered compound

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## 1. Experimental details

**Materials:**  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  of 99.0 % purity,  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  of >99.95 % purity and dimethylformamide were purchased from Kanto Chemical Co. and used as received.  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  of 99.9 % purity was purchased from Soekawa Chemical Co.. 1,3,5-benzenetriphosphonic acid (BTP) was prepared in a two-step reaction from 1,3,5-tribromobenzene according to the literatures.<sup>1,2</sup> Milli-Q filtered water with resistivity >18  $\text{M}\Omega \cdot \text{cm}$  was used throughout the experiments.

**Preparation of LBP-II:** In a typical preparation procedure of LBP-II, a starting mixture ( $1\text{BTP} \cdot 1\text{La}(\text{NO}_3)_3 \cdot 830\text{H}_2\text{O}$ ) was stirred at an ambient temperature for 30 min. and the resulting hydrous gel solution was hydrothermally treated in a 23 mL Teflon-lined stainless steel autoclave at 120 °C for 72 h. LBP-II was obtained as white powder. Elemental analysis (%) LBP-II: calcd. for  $\text{C}_6\text{H}_{10}\text{La}_1\text{O}_{11}\text{P}_3$ : C 14.71 H 2.05 found C 14.74 H 1.89.

**Preparation of LBP-II /Tb and LBP-II /Eu:** In a typical preparation procedure of LBP-II / Tb and LBP-II /Eu, a starting mixture ( $1\text{BTP} \cdot 0.95\text{La}(\text{NO}_3)_3 \cdot 0.05\text{Ln}(\text{NO}_3)_3 \cdot 830\text{H}_2\text{O}$  ( $\text{Ln} = \text{Tb}$  or  $\text{Eu}$ )) was stirred at an ambient temperature for 30 min. and the resulting hydrous gel solution was hydrothermally treated in a 23 mL Teflon-lined stainless steel autoclave at 120 °C for 72 h. LBP-II was obtained in white powder. Elemental analysis (%) LBP-II/Eu: calcd. for  $\text{C}_6\text{Eu}_{0.05}\text{H}_{10}\text{La}_{0.95}\text{O}_{11}\text{P}_3$ : C 14.69 H 2.05 found C 14.73 H 2.06; LBP-II/Eu: calcd. for  $\text{C}_6\text{H}_{10}\text{La}_{0.95}\text{O}_{11}\text{P}_3\text{Tb}_{0.05}$ : C 14.69 H 2.05 found C 14.73 H 1.75.

**Exfoliation of LBP-II:** LBP-II (1 mg) was dispersed in dimethylformamide (5 mL). The dispersion solution was shaken for 3 h at 40 °C. After placing the solution for 5 min at ambient temperature, preliminarily cleaned Si substrates were dipped in the supernatant of the dispersion solution for 30 min.

**Characterization:** CHN elemental analysis was performed on a Perkin-Elmer Series II CHNS/O analyzer 2400. Energy-dispersive X-ray spectrometry was measured on a PHILIPS EDAX-DX-4. TG-DTA was measured on a Rigaku Thermo Plus 2 at a heating rate of 10  $\text{K min}^{-1}$  under an air flow at 100  $\text{ml min}^{-1}$ . Powder X-ray diffraction (XRD) patterns except the high resolution data used for structure solution and indexing were measured on a Rigaku RINT-2100S using monochromated  $\text{Cu-K}\alpha$  radiation. SEM images were obtained on a JEOL JSM-6510 scanning electron microscope. The infrared data were collected at room temperature (RT) using a FT-IR JASCO FT / IR - 4200 Spectrometer. The spectra were collected over the range 4000-400  $\text{cm}^{-1}$  by averaging 256 scans at a maximum resolution of 4  $\text{cm}^{-1}$  (KBr pellets). The thickness of the exfoliated nanosheets was confirmed by atomic force microscopy an AFM, Veeco Nanoscope Multimode Atomic Force Microscope. Fluorescence spectra were recorded using a JASCO FP-6500 spectrofluorometer at room temperature (bulk LBP-II/Eu:  $\lambda_{\text{exc.}} = 272 \text{ nm}$ ,  $\lambda_{\text{em.}} = 611 \text{ nm}$ ; bulk LBP-II/Tb:  $\lambda_{\text{exc.}} = 272 \text{ nm}$ ,  $\lambda_{\text{em.}} = 549 \text{ nm}$ ; dispersion LBP-II/Eu:  $\lambda_{\text{exc.}} = 274 \text{ nm}$ ,  $\lambda_{\text{em.}} = 610 \text{ nm}$ ; dispersion LBP-II/Tb:  $\lambda_{\text{exc.}} = 274 \text{ nm}$ ,  $\lambda_{\text{em.}} = 549 \text{ nm}$ ). UV-Vis spectrum was recorded using a JASCO V-670 at a room temperature.

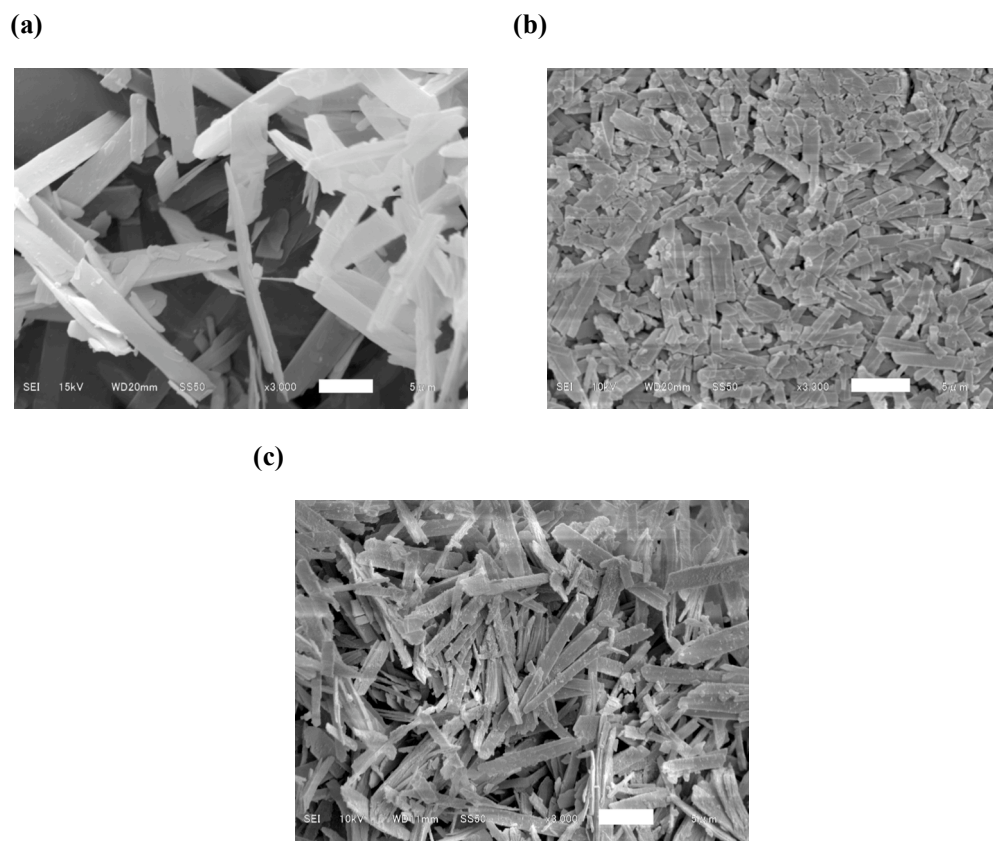
**Crystal Structure Determination:** The high resolution synchrotron diffraction data of LBP-II was collected on the diffractometer of the BL02B2 ( $\lambda = 0.79788 \text{ \AA}$ ) at SPring-8 (Hyogo, Japan) using a powder sample loaded in a 0.5 mm glass capillary. The diffraction data was successfully indexed

with monoclinic unit cell using NTREOR in EXPO2009.<sup>3</sup> The extinction rule suggested the space group  $P2_1/c$ . An almost complete layered structural model of LBP-II was obtained in the direct method using EXPO2009 from the extracted intensities in the Le Bail method, and the missing one oxygen, one carbon and hydrogen atoms were modelled. Water molecules and hydroxyl groups were treated as virtual atoms Ow (1O + 2H) and Op (1O + 1H). The complete model was refined in the Rietveld method using RIETAN-FP<sup>4</sup> with soft geometrical restrains [prescribed distances/Å: La-O 2.5(8), P-O 1.53(1), P-C 1.79(1), C-C (aromatic) 1.400(2), C-H 0.9300(1); prescribed angles/°: C-C-C(H) 120.0(9), O-P-O 109(3)] to the convergence ( $R_{wp} = 0.0436$ ). To reduce the number of parameters and stabilize the refinement, the displacement parameters for similar atoms (C/O/H, La, and P, respectively) were constrained to be same. The structure model is drawn using VESTA.<sup>5</sup>

## References

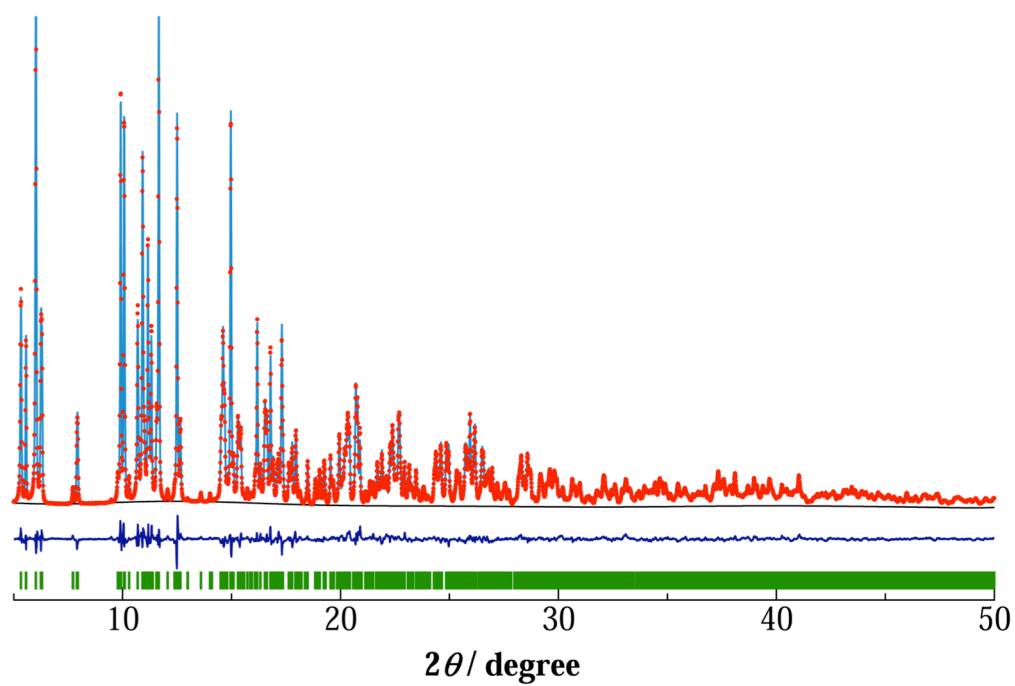
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- 2) M. Henn, K. Jurkschat, D. Mansfeld, M. Mehring and M. Schümann, *J. Mol. Struct.*, 2004, **697**, 213.
- 3) A. Altomare, M. Camalli, C. Cuocci, C. Giacovazzo, A. Moliterni and R. Rizzi, *J. Appl. Cryst.*, 2009, **42**, 1197.
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## 2. SEM images



**Fig. S1** SEM images (a) LBP-II, (b) LBP-II/Tb, and (c) LBP-II/Eu (Scale bars indicate 5  $\mu\text{m}$ ).

### 3. Rietveld refinement



**Fig. S2** Observed (red points), calculated (light blue line), and residual (blue line) profile for the Rietveld refinement of LBP-II.

**Table S1** Crystallographic data for LBP-II

Parameter	
Formula	C <sub>6</sub> H <sub>10</sub> LaO <sub>11</sub> P <sub>3</sub>
Formula Weight / g·mol <sup>-1</sup>	489.97
Crystal System	monoclinic
Space Group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> / Å	9.6708 (2)
<i>b</i> / Å	16.3872 (3)
<i>c</i> / Å	9.2210 (2)
<i>β</i> / °	117.8512 (6)
<i>V</i> / Å <sup>3</sup>	1291.03 (4)
<i>Z</i>	4
Pattern Range (2θ) / °	5.00 – 50.00
<i>λ</i> / Å	0.79788
<i>R</i> <sub>wp</sub>	0.0436
<i>R</i> <sub>F</sub>	0.0092
<i>R</i> <sub>exp</sub>	0.0281
<i>S</i>	1.553

#### 4. TG-DTA

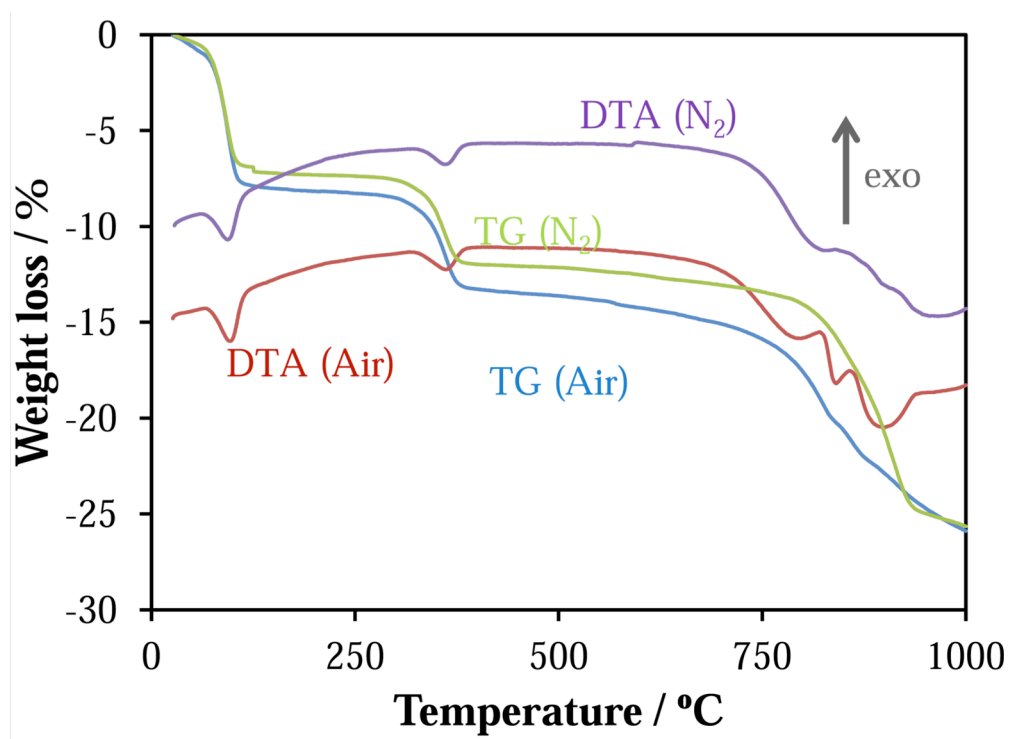
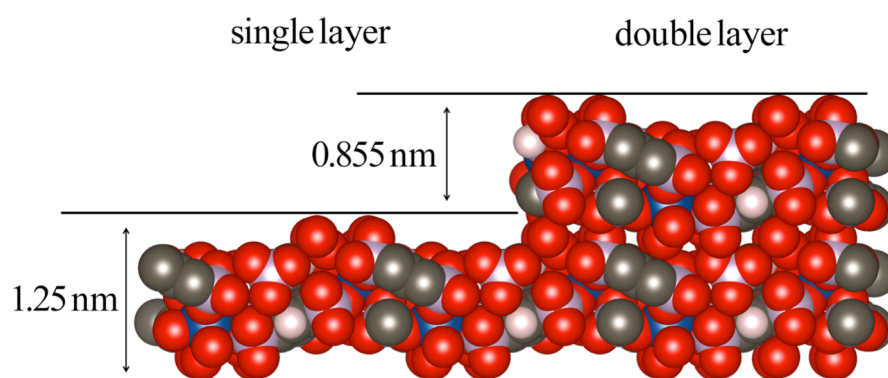


Fig. S3 TG-DTA of LBP-II.

## 5. Nanosheets and AFM images

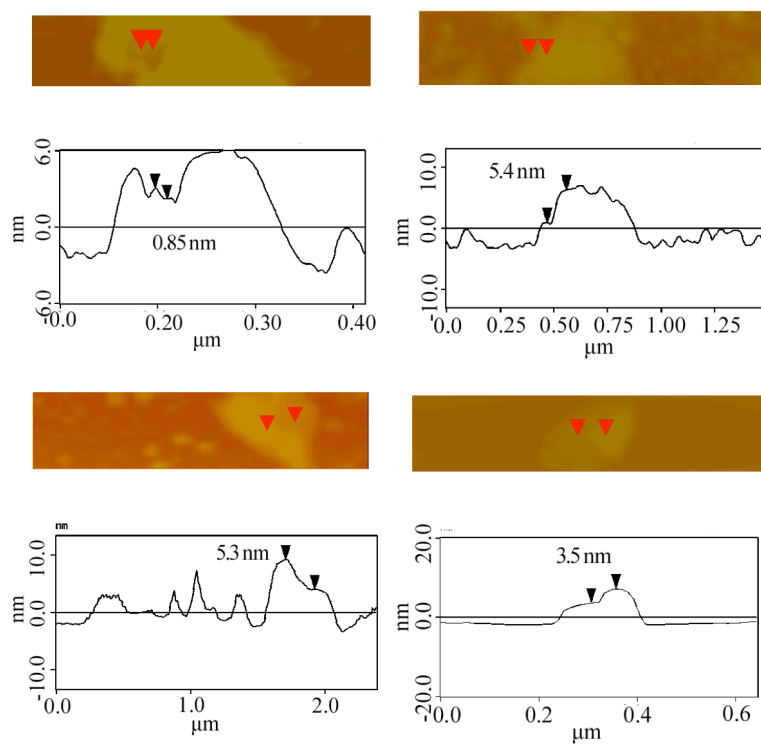


**Fig. S4** Tyndall effect observed in dispersion solution of LBP-II.



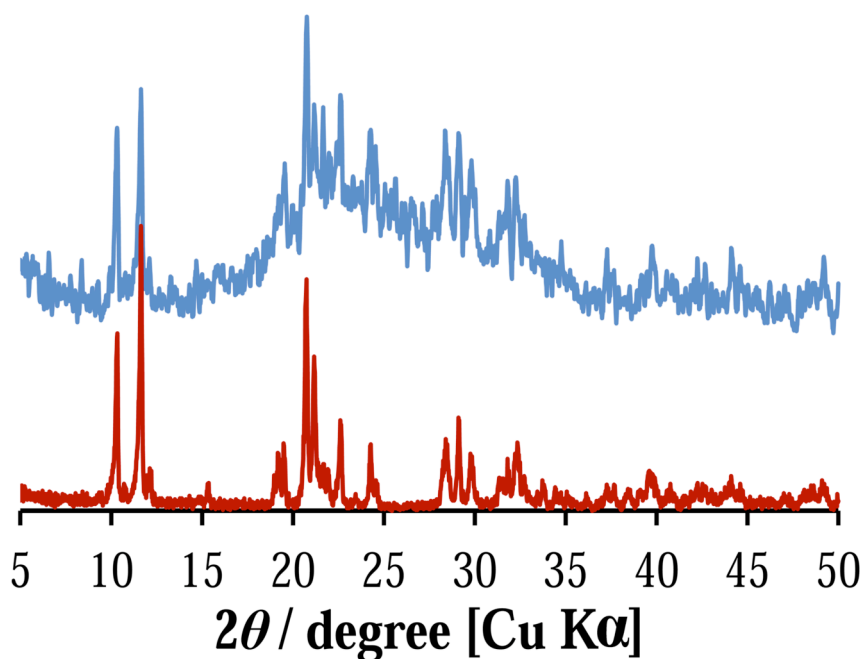
**Fig. S5** Van der Waals model of LBP-II layers. Lanthanum: blue; phosphorus: purple; carbon: black; hydrogen: pink; oxygen (including water): red.





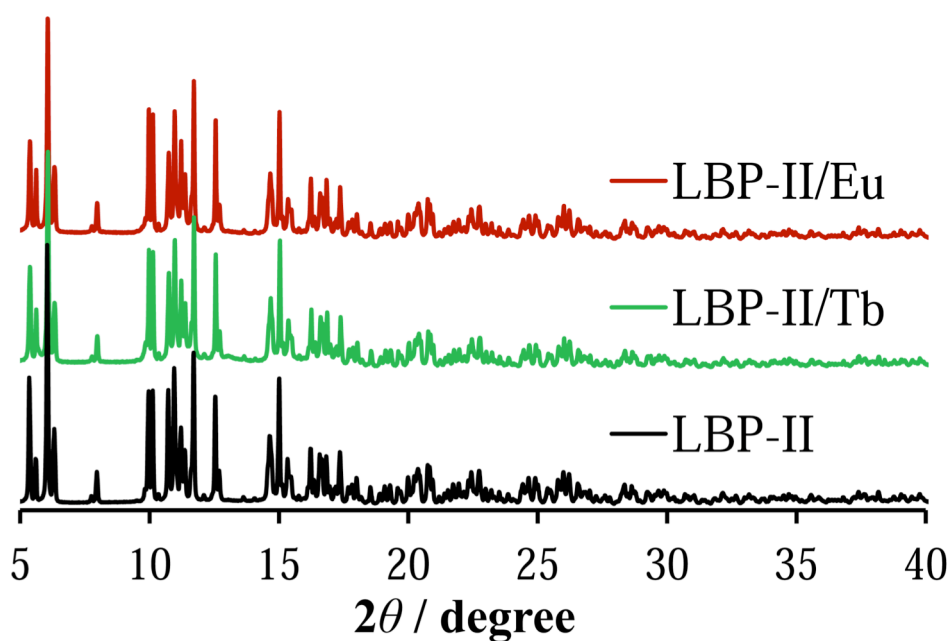
**Fig. S6** AFM images of several nanosheets.

## 6. Powder X-ray diffraction patterns



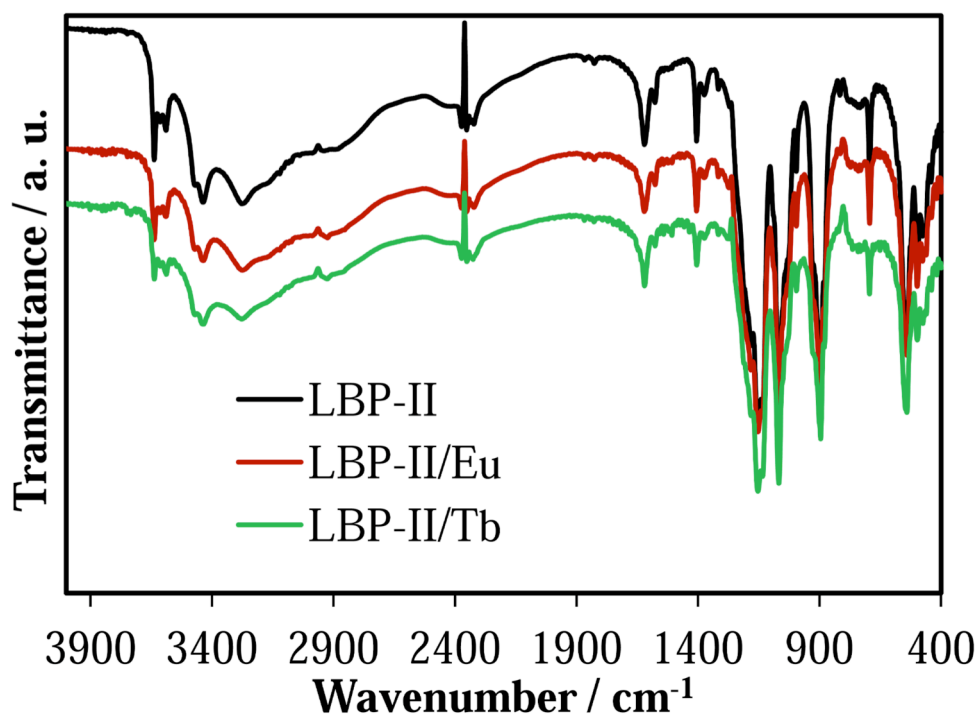
**Fig. S7** PXRD patterns (wavelength: 1.5418 Å) of precipitates obtained after the dispersion treatment of LBP-II (blue line) and as-synthesized LBP-II (red line).

\*The high background of LBP-II after exfoliation treatment is not derived from the sample but the sample holder because of small amount of the sample.



**Fig. S8** PXRD patterns (wavelength: 0.7986 Å) of LBP-II (black line), LBP-II/Tb (green line), and LBP-II/Eu (red line).

## 7. IR spectra



**Fig. S9** IR spectra of LBP-II (black line), LBP-II/Eu (red line), and LBP-II/Tb (green line).