

Supporting Information

Two novel pillared-layer lanthanide borates built by Ln@B₁₂O_{28/29} ring clusters and dicarboxylate linkers (Ln = Pr, Nd)

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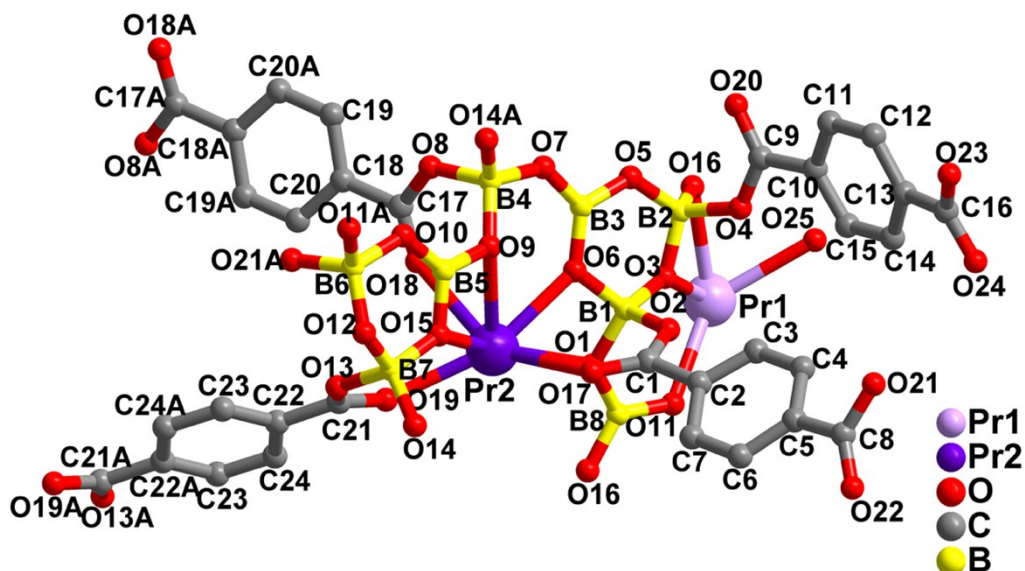
Experimental Section

Materials and Methods. All chemicals were purchased commercially and used without further purification. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). C, H and N elemental analyses were performed on a Euro EA 3000 CHNS/O analyzer. IR spectra were obtained on a Smart Omin-Transmission spectro- photometer with KBr pellets in the range of 4000–500 cm⁻¹. Thermogravimetric (TG) analyses were carried out on a Mettler TGA/SDTA 851 thermal analyzer in the temperature range of 30–1000 °C in air atmosphere with a heating rate of 10 °C min⁻¹. The diffuse-reflectance spectra were recorded at room temperature on a computer-controlled PE Lambda 900 UV-vis spectrometer equipped with an integrating sphere in the wavelength range of 200–800 nm. Luminescence measurements were performed in the solid state at room temperature with an Edinburgh FLS920 fluorescence spectrometer.

Synthesis of 1-2. A mixture of Pr₆O₁₁ (0.085 g, 0.083 mmol) for **1** and Nd₂O₃ (0.084 g, 0.25 mmol) for **2**, H₃BO₃ (0.618 g, 10 mmol), 1,4-benzene dicarboxylic acid (0.041 g, 0.25 mmol), LiNO₃ (0.017 g, 0.25 mmol) and H₂O (0.50 g, 27.80 mmol) was sealed in a 25 mL Teflon-lined bomb at 220 °C for 7 days and cooled to room temperature. Green for **1** and pink for **2** prismatic crystals were isolated by filtration, washed with distilled water, and dried in air. Yield: *ca.* 55% for **1** and 47% for **2**. Elemental analyses (%) calcd. for **1**: C 7.94, H 1.48. Found: C 7.90, H 1.45. calcd. for **2**: C 7.90, H 1.47. Found: C 7.87, H 1.45.

Table S1. Crystal and structure refinement data for **1** and **2**.

	1	2
formula	C ₂₄ H ₁₆ B ₈ O ₂₆ Pr ₂	C ₂₄ H ₁₆ B ₈ O ₂₆ Nd ₂
fw	1088.67	1095.33
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	12.7199(5)	12.6812(6)
<i>b</i> , Å	22.5919(6)	22.5579(7)
<i>c</i> , Å	12.8072(5)	12.7742(5)
α , deg	90	90
β , deg	119.035(5)	119.103(6)
γ , deg	90	90
<i>V</i> , Å ³	3217.81(19)	3192.8(2)
<i>Z</i>	4	4
<i>D_c</i> , g cm ⁻³	2.247	2.279
<i>T</i> , K	293(2)	293(2)
<i>F</i> (000)	2104	2112
μ , mm ⁻¹	3.106	3.330
Reflections collected/unique	33816/5652	15803/5617
<i>R</i> _{int}	0.0352	0.0323
<i>GOF</i> on <i>F</i> ²	1.048	1.003
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0298, 0.1099	0.0257, 0.0651
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0336, 0.1132	0.0335, 0.0679

**Figure S1.** View of the asymmetric unit of **1**.

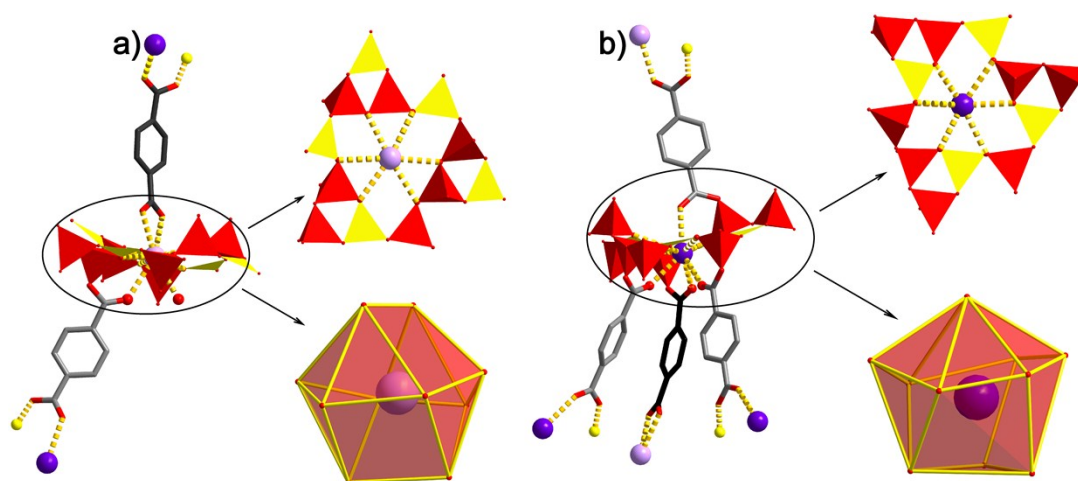


Figure S2. (a) View of the coordination environment and geometry of Pr1 in **1**. (b) View of the coordination environment and geometry of Pr2 in **1**. Color code: BO₃ triangle, yellow; BO₄ tetrahedra, red.

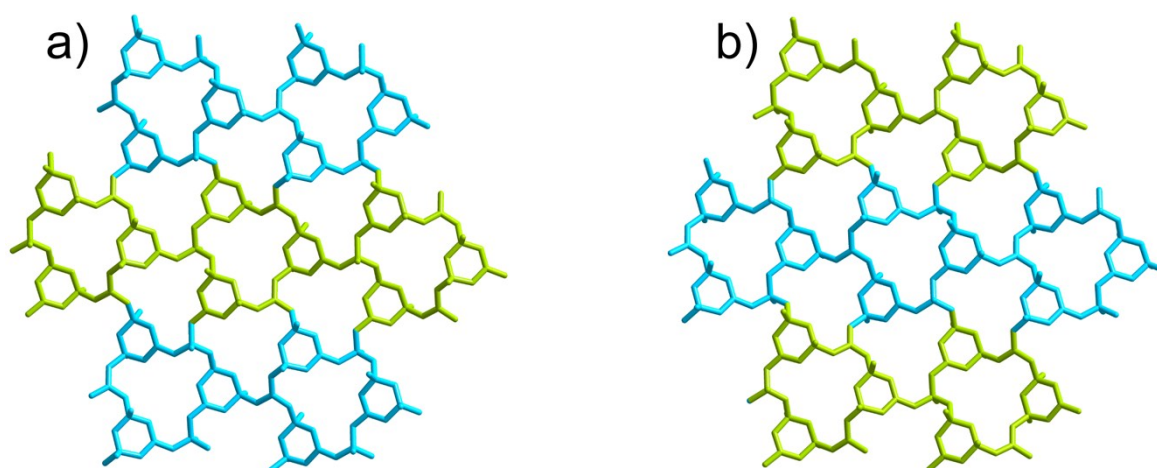


Figure S3. (a) Each B₁₂O₂₈ ring cluster links two B₁₂O₂₈ and four B₁₂O₂₉ clusters via oxygen atoms in the same B-O layer. (b) Each B₁₂O₂₉ ring cluster links two B₁₂O₂₉ and four B₁₂O₂₈ clusters via oxygen atoms in the same B-O layer. Color code: B₁₂O₂₈, yellow green; B₁₂O₂₉, cyan.

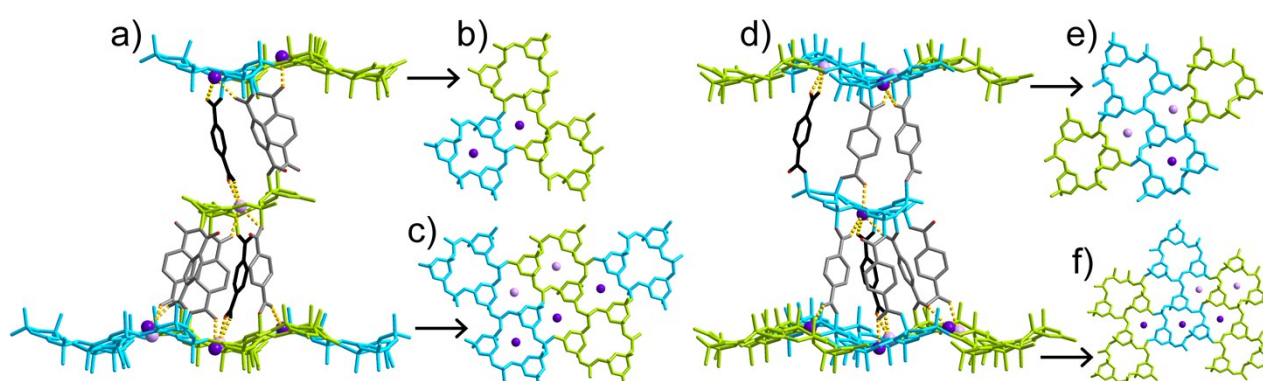


Figure S4. (a) Each B₁₂O₂₈ ring cluster links two B₁₂O₂₈, one B₁₂O₂₉ clusters in the upper B-O layer (b) and two B₁₂O₂₈, three B₁₂O₂₉ clusters in the lower B-O layer (c) via C-O-B and C-O-Pr linkages. (d) Each B₁₂O₂₉ ring cluster links two B₁₂O₂₈, two B₁₂O₂₉ clusters in the upper B-O layer (e) and four B₁₂O₂₈, two B₁₂O₂₉ clusters in the lower B-O layer (f) via C-O-B and C-O-Pr linkages.

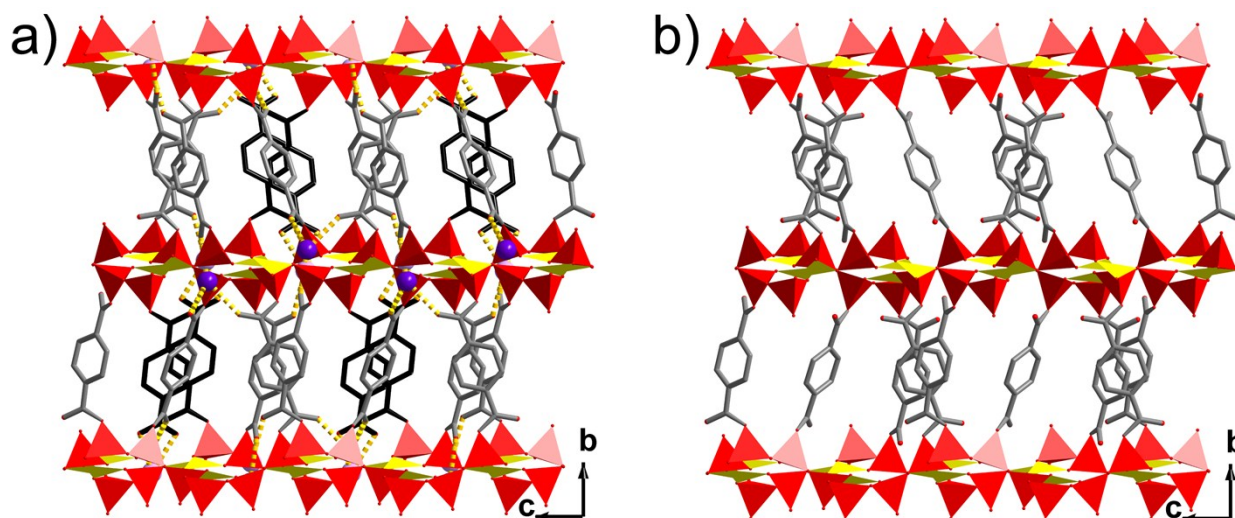


Figure S5. (a) View of the 3D pillared-layer framework of **1** linked via C-O-B and C-O-Pr linkages along the [100] direction. (b) View of the 3D pillared-layer framework of **1** linked via C-O-B linkage along the [100] direction.

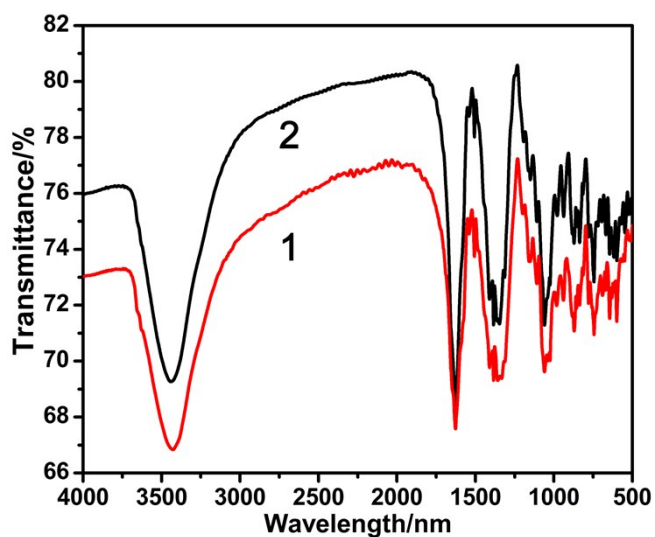


Figure S6. The IR spectra of **1-2**.

In order to further verify the existence of bdc and the borate groups in the structures, the infrared spectroscopy was measured (Figure S6). The broad bands in the range of $3713\text{--}3046\text{ cm}^{-1}$ correspond to the stretching bands of the C–H, and O–H and the sharp peak at 1628 cm^{-1} is characteristic of $\text{--CO}_2\text{--}$ stretching vibrational bands, which convincingly shows the existence of bdc. The bands at about 1425 cm^{-1} are due to the asymmetric stretching of BO_3 units, while the band at 1062 cm^{-1} should be associated with BO_4 units.

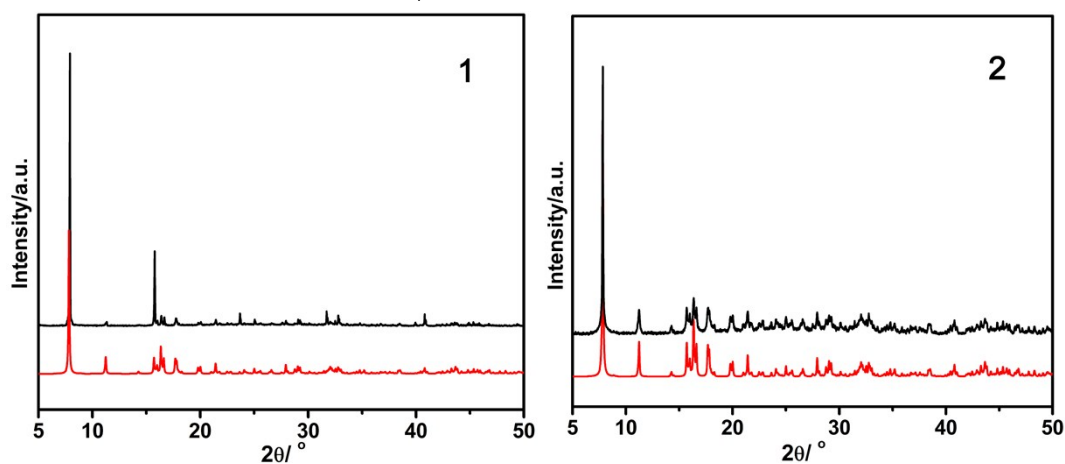


Figure S7. Experimental and simulated PXRD patterns for **1** (left) and **2** (right).

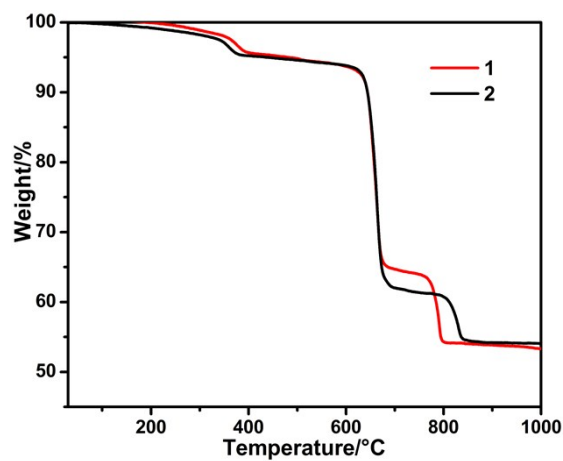


Figure S8. TG curves of 1-2.

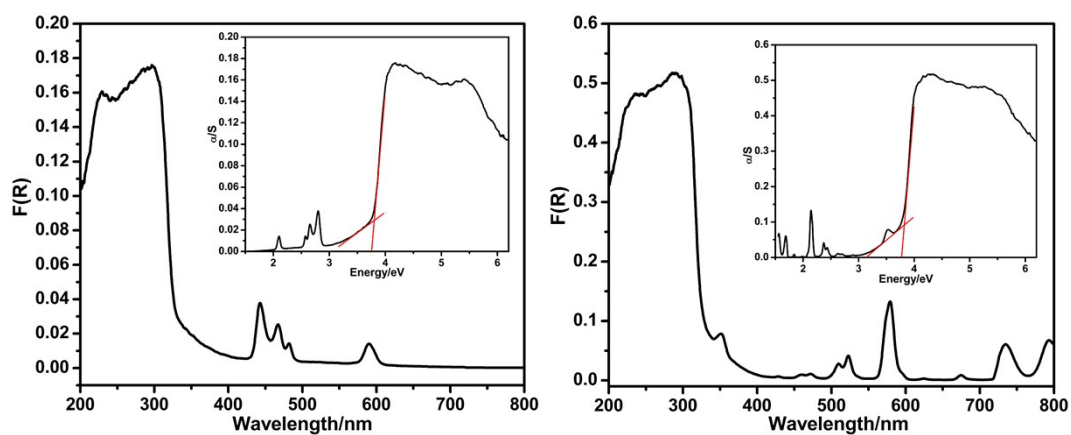


Figure S9. The solid-state UV/Vis spectra of 1 (left) and 2 (right) in the 200-800 nm range at room temperature.