Supporting Information

A novel aluminoborate open-framework [In(dien)$_2$][Al$_2$B$_7$O$_{16}$H$_2$] with large chiral cavities templated by main group metal complexes

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Table S1. Hydrogen bonds data for 1.

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(2)-H(2A)...O(1)#1</td>
<td>0.90</td>
<td>2.12</td>
<td>2.84(2)</td>
<td>135.8</td>
</tr>
<tr>
<td>N(2)-H(2A)...O(3)#1</td>
<td>0.90</td>
<td>2.64</td>
<td>3.45(2)</td>
<td>150.9</td>
</tr>
<tr>
<td>N(2)-H(2B)...O(1)#2</td>
<td>0.90</td>
<td>2.62</td>
<td>3.20(2)</td>
<td>122.8</td>
</tr>
<tr>
<td>N(1)-H(1A)...O(1)#3</td>
<td>0.90</td>
<td>2.11</td>
<td>2.98(1)</td>
<td>163.0</td>
</tr>
<tr>
<td>N(3)-H(3C)...O(3)#2</td>
<td>0.90</td>
<td>2.09</td>
<td>2.98(2)</td>
<td>172.7</td>
</tr>
<tr>
<td>N(3)-H(3D)...O(3)#4</td>
<td>0.90</td>
<td>2.35</td>
<td>3.22(2)</td>
<td>160.4</td>
</tr>
</tbody>
</table>

*Symmetric codes: #1 -y+0.75, -x+0.25, z+0.25; #2 y-0.75,x+0.25, z+0.25; #3 x, y-0.5, -z; #4 -x, -y+1, -z.
Experimental Section

All chemicals employed in this study were analytical reagent. IR spectra (KBr pellets) were recorded on an ABB Bomen MB 102 spectrometer. Thermal analyses were performed in a dynamic oxygen atmosphere with a heating rate of 10 °C/min using a METTLER TGA/SDTA 851e thermal analyzer. The X-ray diffraction data were collected on a SuperNova, Atlas diffractometer equipped with mirror-monochromated CuKα radiation (λ = 1.5418 Å) at room temperature. The structure was solved by direct methods and refined on F² by full-matrix, least-squares methods using the SHELEL-97 program package. Powder XRD patterns of polycrystalline sample was collected on a Philips X'Pert-MPD diffractometer using CuKα radiation (λ = 1.540598 Å) at room temperature in the angular range of 2θ = 5–50° with a step size of 0.02°. The UV diffuse reflection data were recorded at room temperature using a powder sample with BaSO₄ as a standard (100% reflectance) on a PerkinElmer Lamda-950 UV spectrophotometer and scanned at 200-800 nm.

Synthesis:

A mixture of H₃BO₃ (0.372 g, 6 mmol), Al(i-PrO)₃ (0.204 g, 1 mmol) and In(i-PrO)₃ (0.147g, 0.25mmol) was added to the mixture of 0.5 mL H₂O, 3 mL pyridine and 0.5 mL dien, and stirred for about one hour, the final solution was sealed in a 30 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 7 days under autogenous pressure, and then cooled to room temperature. The pure, colorless, colorless quadrangular prism crystals of 1 were obtained (yield 32% based on In(i-PrO)₃). By calculation, when one formula absorbs two water molecules from the air to become 1·2H₂O, the calculated and observed values of the C, H, N, B, Al and In atoms are in good accordance with each other (elemental analysis calcd (%) for 1·2H₂O: C 12.90, N 11.28, H 4.33, B 10.16, Al 7.24, In 15.41; found: C 12.86, N 11.39, H 4.15, B 10.50, Al 6.79, In 15.19), which are accordant with TGA analysis.

Fig. S1 Comparison of the B₄O₈ units in a) [In(dien)₂][Al₂B₇O₁₆H₂] (I) and b) [M(en)₃][AlB₇O₁₂(OH)₂](H₂O)₀.₂₅ (2, M = Co/Ni), showing different coordination modes for the B₄O₈ units.

Fig. S2 Comparison of a) the B₄O₁₀ cluster, b) AlB₄O₁₂ cluster in 1, c) B₆O₁₂ cluster in Ba₄Na₂Zn₄(B₃O₆)₂(B₁₂O₂₄)₃, and d) B₆O₁₈ unit in Dy₄B₆O₁₅, respectively.
**Fig. S3**

a) View of the framework with 12-MR channels along the c-axis.  
b) One Al atom links four helical chains with the left- and right-handedness through O(1) atoms.  
c) View of the 10-MR channels.

**Fig. S4**

Stacking view of the ABCDA sequence of the ABO layers along [110] and [1-10] directions. The different colors represent different layers.

**Fig. S5**

a) View of the cages constructed from six AlO₄ and ten {AlB₅O₁₂} units.  
b) A pair of enantiomers of cavities of C₂ symmetry, each of which contains a [In(dien)₂]³⁺ cations of $\Lambda$ and $\Delta$ configuration. All of the [In(dien)₂]³⁺ cations are in u-fac-configuration.
**Fig. S6**  
a) Chiral [In(dien)]$_3$$^+$$^+$ complexes with $\Lambda$ and $\Delta$ configurations interacted with framework O atoms via H-bonds, respectively. (Each In atom is coordinated by four dien because each dien has the occupancy of 50%). b) View of the arrangement of the complexes with $\Lambda$ and $\Delta$ configurations interacted with framework O atoms via H-bonds. Symmetry codes: i, -x, -0.5+y, -0.5-z; ii, x, 1-y, -0.5-z; iii, -0.75+y, 0.25-x, -0.25+z; iv, 0.75-y, 0.25+x, -0.25+z; v, 0.5-x, 0.5-y, -0.5-z; vi, 0.5+x, -1+y, -0.5-z; vii, -0.25+y, -0.25+x, -0.5+z; viii, 1.25-y, -0.25-x, -0.25+z.

**Fig. S7** IR spectrum of 1.

**Fig. S8** TGA curve of 1 under air atmosphere (10°C/min)
**Fig. S9** UV-vis optical diffuse reflectance spectra for 1.

**Fig. S10** The experimental and simulated PXRD patterns of 1.