Supporting Information

A novel aluminoborate open-framework $[In(dien)_2][Al_2B_7O_{16}H_2]$ with large chiral cavities templated by main group metal complexes

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Table S1. Hydrogen bonds data for **1**.[a]

D-H...A	*d*(D-H)	*d*(H...A)	*d*(D...A)	<(DHA)
N(2)-H(2A)...O(1)#1	0.90	2.12	2.84(2)	135.8
N(2)-H(2A)...O(3)#1	0.90	2.64	3.45(2)	150.9
N(2)-H(2B)...O(1)#2	0.90	2.62	3.20(2)	122.8
N(1)-H(1A)...O(1)#3	0.90	2.11	2.98(1)	163.0
N(3)-H(3C)...O(3)#2	0.90	2.09	2.98(2)	172.7
N(3)-H(3D)...O(3)#4	0.90	2.35	3.22(2)	160.4

[a]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 spectro-meter. Thermal analyses were performed in a dynamic oxygen atmosphere with a heating rate of 10 ºC/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 F^2 by full-matrix, last-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 $BaSO_4$ as a standard (100% reflectance) on a PerkinElmer Lamda-950 UV spectrophotometer and scanned at 200-800 nm.

Synthesis:

A mixture of H_3BO_3 (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 H_2O, 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**·2H_2O, 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**·2H_2O: 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.

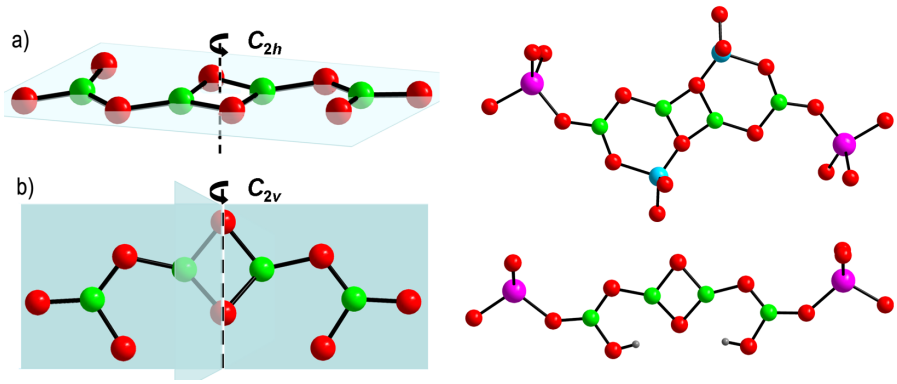

Fig. S1 Comparison of the B_4O_8 units in a) $[In(dien)_2][Al_2B_7O_{16}H_2]$ (**1**) and b) $[M(en)_3][AlB_7O_{12}(OH)_2]\cdot(H_2O)_{0.25}$ (**2**, M = Co/Ni), showing different coordination modes for the B_4O_8 units.

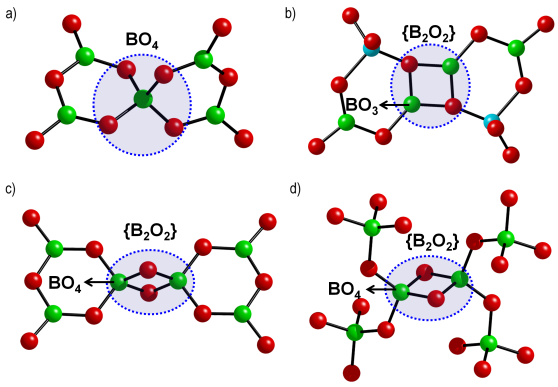

Fig. S2 Comparison of a) the B_5O_{10} cluster, b) AlB_5O_{12} cluster in **1**, c) B_6O_{12} cluster in $Ba_4Na_2Zn_4(B_3O_6)_2(B_{12}O_{24})$, and d) B_6O_{18} unit in $Dy_4B_6O_{15}$, respectively.

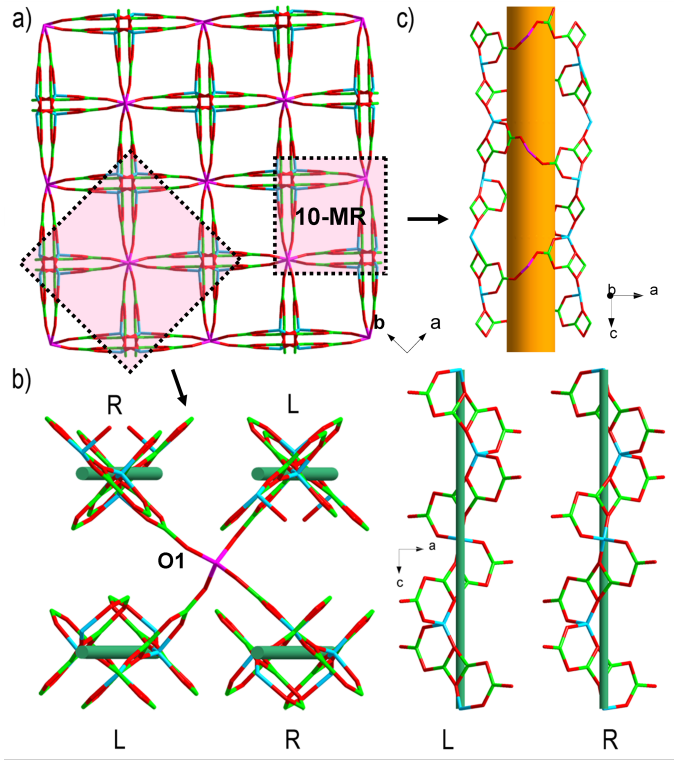

Fig. S3 a) View of the framework with 12-MR chennels along the *c*-axis. b) One Al atom links four helical chains with the left- and right-handedness through O(1) atoms. c) View of the 10-MR chennels.

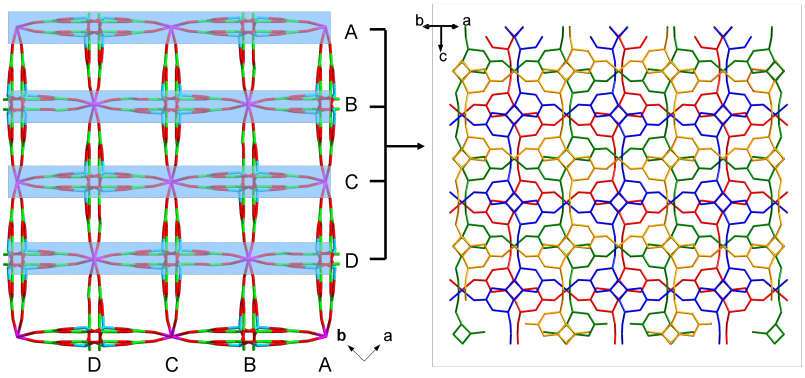

Fig. S4 Stacking view of the ABCDA sequence of the ABO layers along [110] and [1-10] directions. The different colors represent different layers.

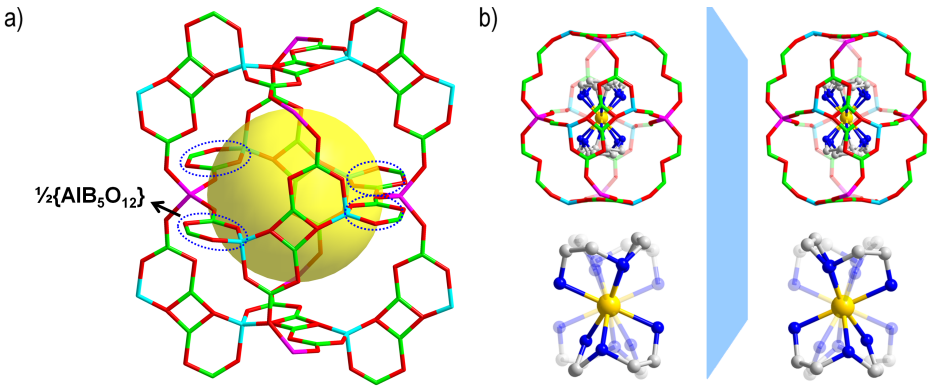

Fig. S5 a) View of the cages constructed from six AlO_4 and ten $\{AlB_5O_{12}\}$ units. b) A pair of enantiomers of cavities of C_2 symmetry, each of which contains a $[In(dien)_2]^{3+}$ cations of Λ and Δ configuration. All of the $[In(dien)_2]^{3+}$ cations are in *u-fac*-configuration.

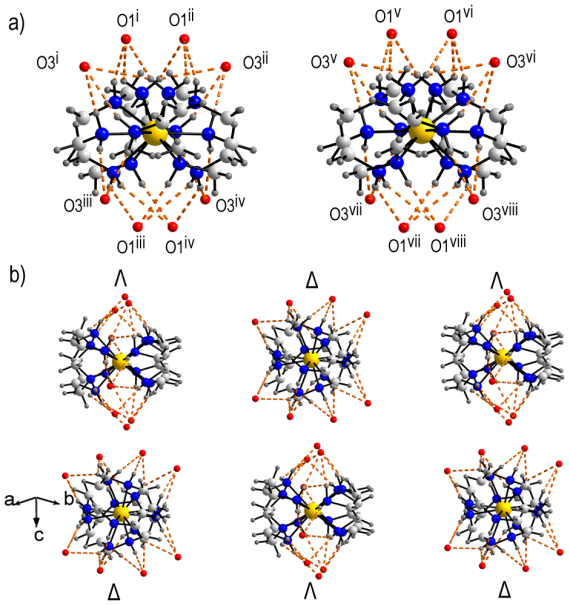

Fig. S6 a) Chiral $[In(dien)_2]^{3+}$ complexes with *Λ* and *Δ* configurations interacted with framework O atoms via H-bonds, respectively. (Each In atoms is coordinated by four dien because each dien has the occupancy of 50%). b) View of the arrangement of the complexes with *Λ* and *Δ* configurations 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*.

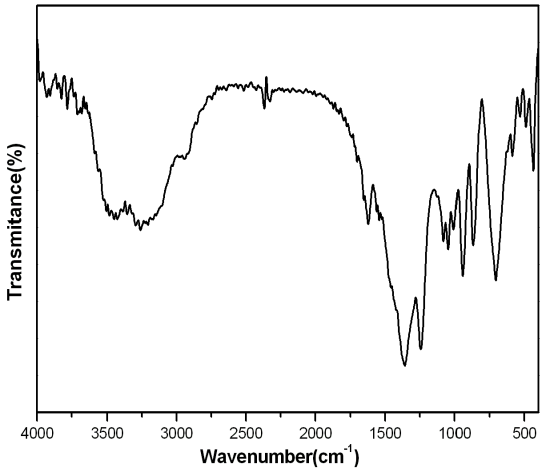

Fig. S7 IR spectrum of **1**.

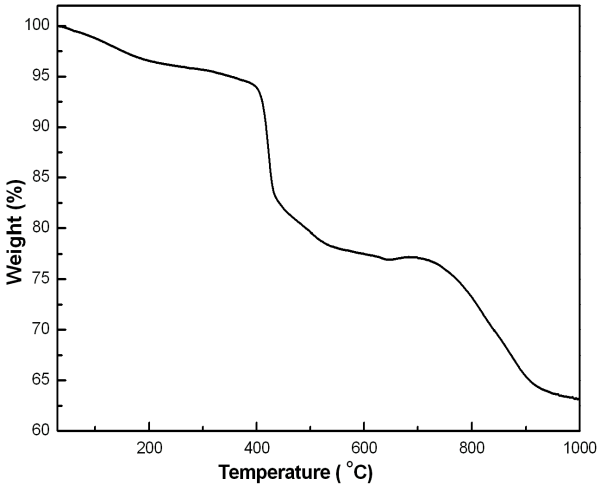

Fig. S8 TGA curve of **1** under air atmosphere (10ºC/min)

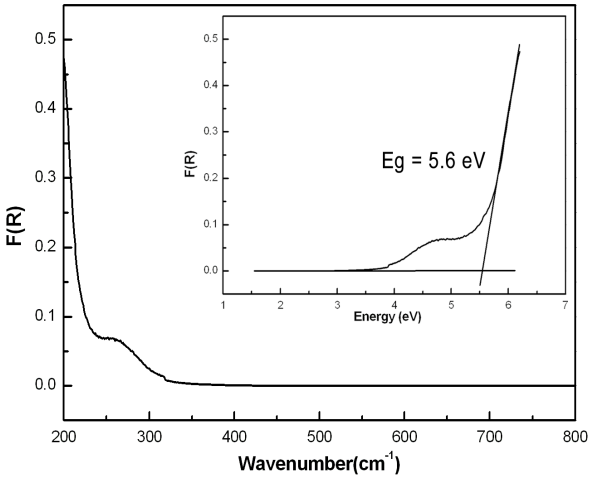

Fig. S9 UV-vis optical diffuse reflectance spectra for **1**.

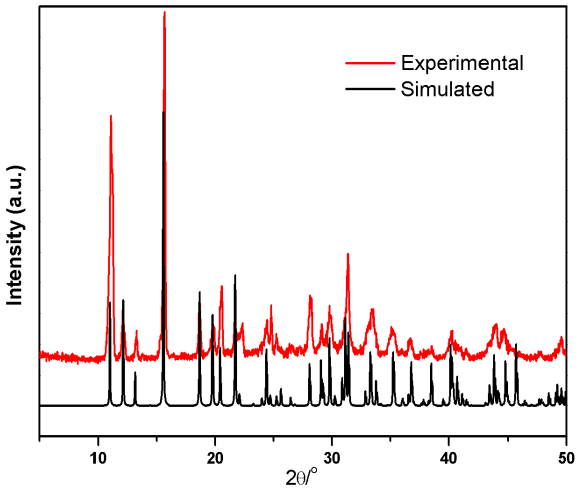

Fig. S10 The experimental and simulated PXRD patterns of **1.**