Supporting Information

Two Zeolitic Open-Framework Aluminoborates Directed by Similar Zn-complexes

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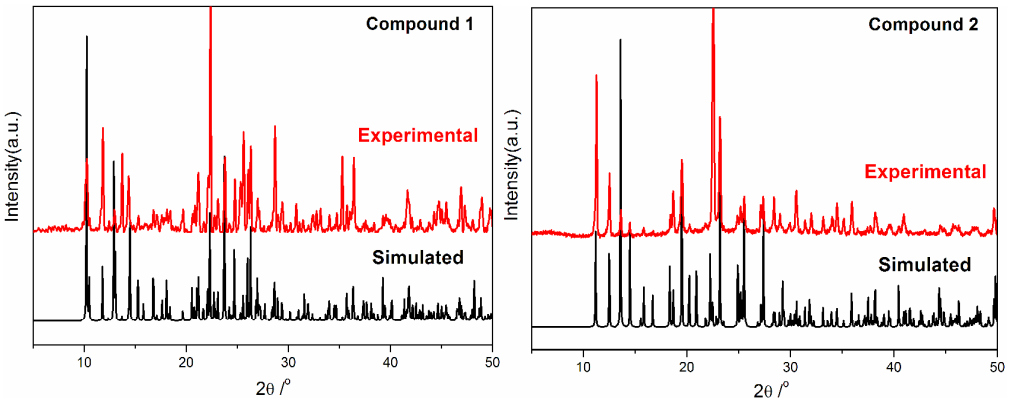
Table S1. Ranges of Selected bond distances (Å) of compounds **1** and **2**.

	Compound 1	**Compound 2**
Zn-N	2.034(3) - 2.225(3)	2.067(7) - 2.220(7)
Al-O	1.718(2) - 1.740(2)	1.723(5) - 1.750(6)
B_{Δ}-O	1.326(4) - 1.401(4)	1.299(10) - 1.412(10)
B_{T}-O	1.455(4) - 1.485(4)	1.431(9) - 1.506(9)
N-C	1.437(5) - 1.494(5)	1.442(11) - 1.478(12)
C-C	1.384(10) - 1.505(6)	1.468(14) - 1.558(14)

Table S2. Hydrogen bond lengths (Å) and angles (^{o}) compounds **1** and **2**.

Interaction	**H…A**	**D…A**	**Angle**	**Symmetry codes**
		Compound 1		
N1-H1D...O4	2.06	2.947(3)	168.0	[x+1/2, -y+1/2, -z+1]
N1-H1E...O2	2.31	3.147(3)	155.1	[-x, -y, -z+1]
N1-H1E...O5	2.32	3.089(3)	143.8	[-x, -y, -z+1]
N2-H2C...O8	2.37	3.103(4)	139.0	[x, -y+1/2, z-1/2]
N2-H2D...O1	2.63	3.304(4)	131.9	[x+1/2, y, -z+1/2]
N3-H3C...O6	2.40	3.195(4)	146.6	[-x, -y, -z+1]
N3-H3C...O5	2.45	3.286(4)	154.5	[-x, -y, -z+1]
N3-H3D...O4	2.50	3.374(4)	163.9	
N3-H3D...O6	2.51	3.211(4)	134.8	
N4-H4C...O6	2.30	3.056(4)	141.7	
N4-H4C...O4	2.43	3.268(4)	155.7	
N4-H4D...O1	2.44	3.321(4)	167.8	[x+1/2, -y+1/2, -z+1]
N5-H5C...O8	2.44	3.188(4)	141.2	[x, -y+1/2, z-1/2]
N5-H5C...O10	2.63	3.217(4)	123.4	[x+1/2, -y+1/2, -z+1]
		Compound 2		
O2-H2E...O8	2.08	2.743(8)	145.5	
N1-H1C...O10	2.56	3.439(10)	165.4	[x+1, y, z]
N1-H1D...O3	2.42	3.316(9)	170.4	[-x+1, y-1/2, -z+1]
N1-H1D...O2	2.56	3.191(9)	127.3	[-x+1, y-1/2, -z+1]
N2-H2C...O5	2.28	3.169(11)	172.6	[x, y, z-1]
N2-H2D...O1	2.30	3.109(8)	146.5	[-x+1, y+1/2, -z+1]
N2-H2D...O7	2.66	3.411(9)	142.2	[-x+1, y+1/2, -z+1]
N3-H3C...O2	2.40	3.253(10)	157.1	[-x+1, y-1/2, -z+1]
N3-H3C...O9	2.63	3.107(9)	113.8	[x+1, y, z]
N3-H3D...O4	2.32	3.157(8)	153.8	
N4-H4C...O10	2.49	3.077(8)	123.1	
N4-H4C...O11	2.57	3.323(8)	147.9	
N4-H4D...O6	2.12	3.009(9)	168.2	[x, y, z-1]
N5-H5A...O4	2.28	3.135(8)	158.0	
N5-H5B...O12	2.07	2.945(8)	162.7	[x+1, y, z]



(a) (b)

Figure S1. Experimental and simulated PXRD patterns of compounds **1** (a) and **2** (b).

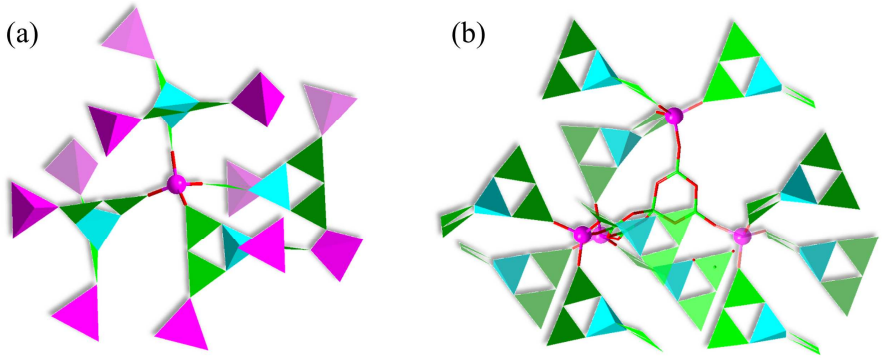


Figure S2. Views of the linkage of AlO_4 (a) and B_5 groups (b) in **1**. Each AlO_4/B_5 unit is bridged by four B_5/AlO_4 groups to 11 other AlO_4/B_5 units.

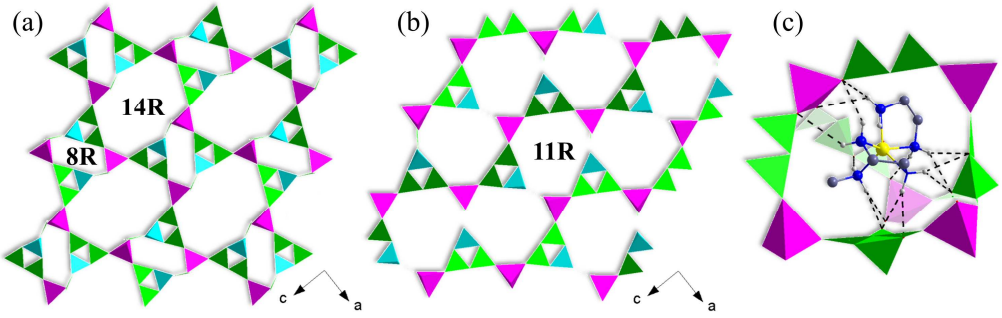


Figure S3. (a) View of the layer with 8-/14-MR along the [010] direction. (b) View of the layer with 11-MR along the [010] direction. (c) View of the $[Zn(ma)(en)_2]^{2+}$ cations, interacting with the inorganic framework through H-bonds.

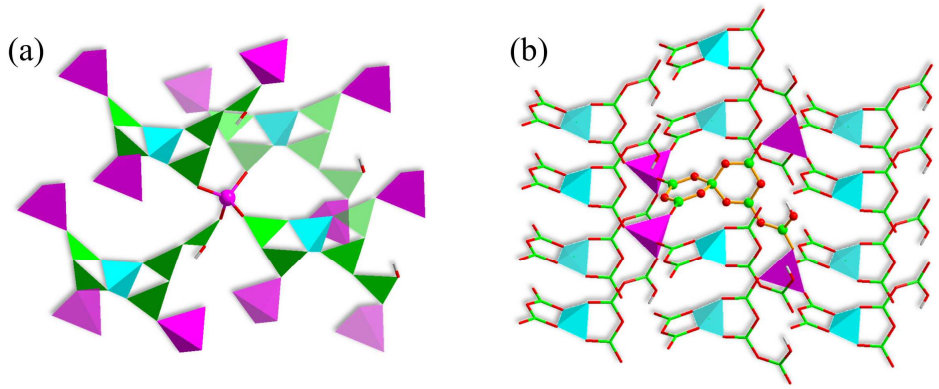


Figure S4. Views of the linkage of AlO_4 (a) and B_6 groups (b) in **2**. Each AlO_4/B_6 unit is bridged by four B_6/AlO_4 groups to 12 others.

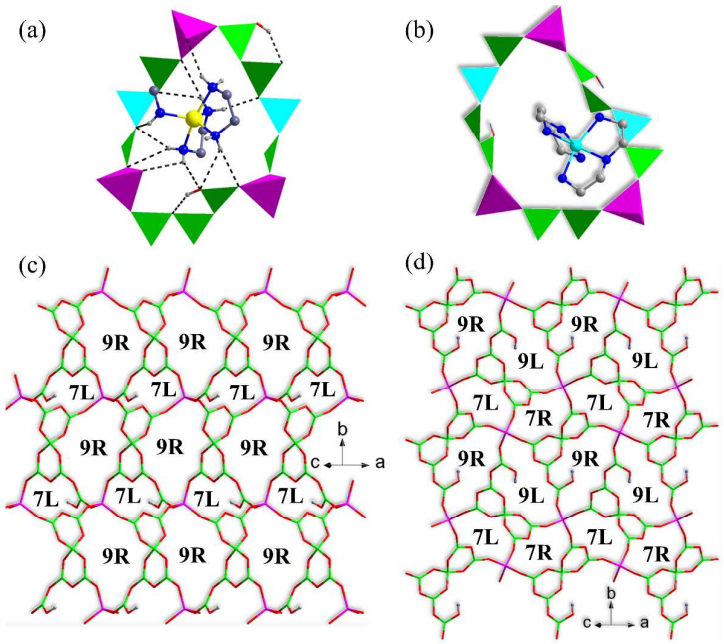


Figure S5. (a) View of the $[Zn(ma)(en)_2]^{2+}$ cations and 13-ring channels delimited by $-AlO_4$-**3**BO_3-AlO_4-**4**$BO_{3/4}$-AlO_4-**3**$BO_{3/4}$- linkage with free diameter of about 8.2×11.7 $Å^2$ in **2**. (b) View of the $[Zn(dien)_2]^{2+}$ cations and 13-ring opening, which is constructed by -AlO_4-**2**BO_3-AlO_4-**4**$BO_{3/4}$-AlO_4-**4**$BO_{3/4}$- linkage with diameter of about 8.7×10.3 $Å^2$ in **2a**. (c) View of the 3-D framework showing 7L and 9R helical channels along the [101] direction in **2**. (d) View of the 3-D framework showing two pairs of 7L/7R and 9L/9R helical channels along the [101] direction in **2a**.

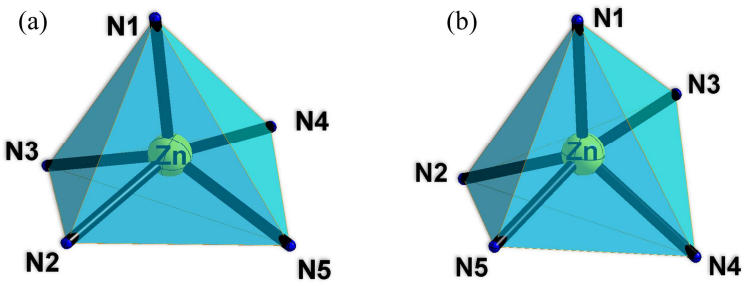


Figure S6. The coordination environments of Zn atoms in compounds **1** (a) and **2** (b).

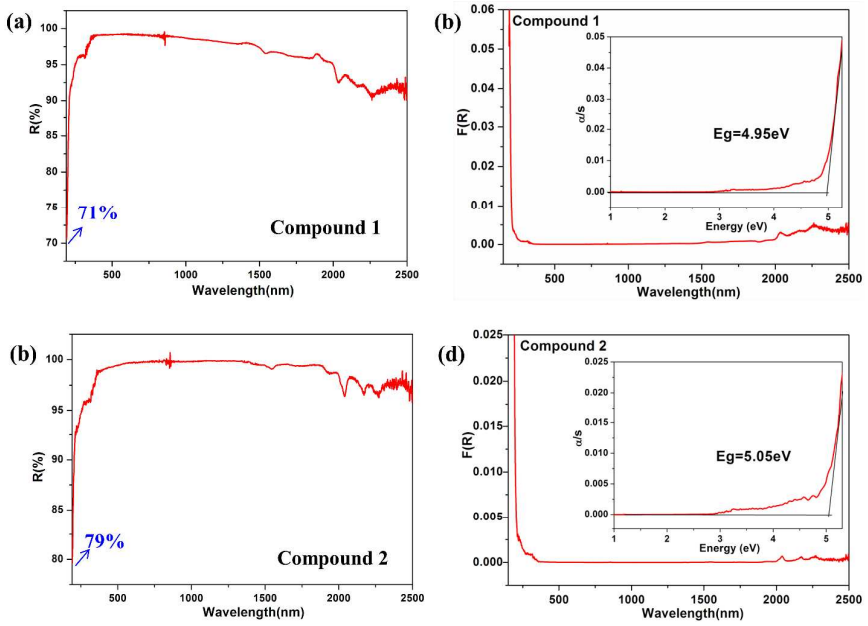


Figure S7. UV-vis-NIR optical diffuse reflectance spectra of compounds **1** (a,c) and **2** (b,d).

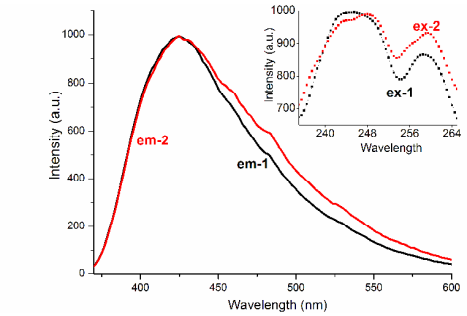


Figure S8. The emission and excitation (inserted graph) spectra of compounds **1** (black) and **2** (red).

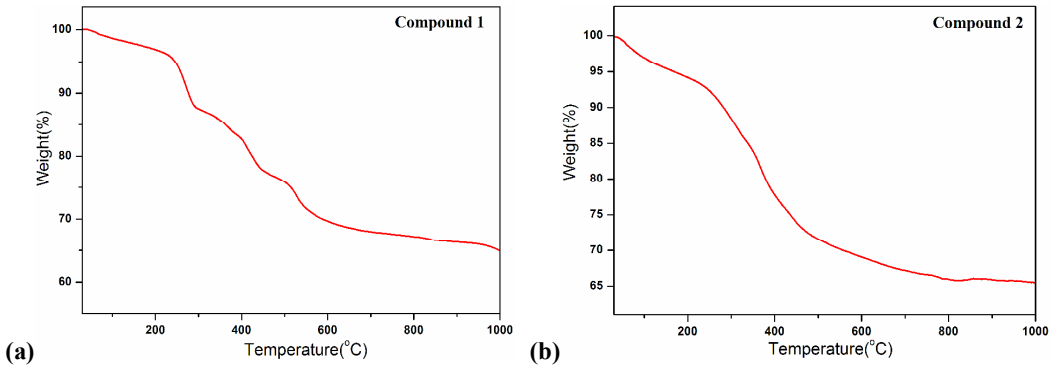


Figure S9. TG curves of compounds **1** (a) and **2** (b).

The thermal behaviors of **1** and **2** are shown in Figure S9. For **1**, the total weight loss from 30 to 700 °C corresponds to the removal of one ma and two en molecules. The observed loss of 33.15% matches well with the theoretical value (33.00%). **1** and **2** show similar thermal behavior. The TG curve of **2** shows a gradual weight loss of 32.40% up to 700°C, which is attributed to the gradual decomposition of organic amines and hydroxyl group, corresponding to the calculated value (31.92%).

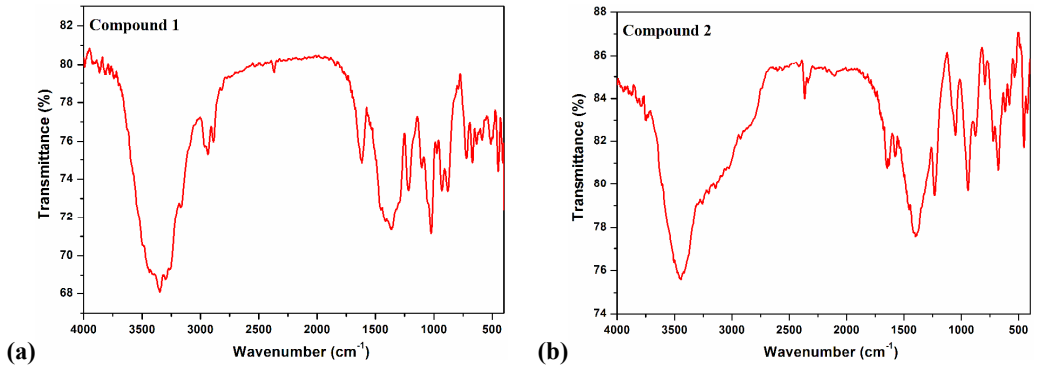


Figure S10. IR spectra of compounds **1** (a) and **2** (b).

The IR spectra of **1** and **2** are nearly identical and both exhibit a series of strong absorption bands. The broad absorption band around 3450-3340 cm^{-1} is related to the stretching vibrations of O–H, N–H and C–H bonds. The band at 1650-1606 cm^{-1} is assigned to N–H and C–H bending mode. The intense bands at 1440−1210 and 1150−1010 cm^{-1} can be assigned to the B−O asymmetrical stretch of the BO_3 and BO_4 groups, respectively. While the band around 975−880 cm^{-1} is associated with the symmetric stretching vibrations of BO_3 and BO_4 units. In addition, the bending vibrations of the two units are observed in the range of 720−630 cm^{-1}.[1] The bands around 510 and 445 cm^{-1} are due to the stretching-bending vibrations of AlO_4 units.[2] The results are consistent with those of the structural analyses.

(1) (a) Xu, X.; Hu, C. L.; Kong, F.; Zhang, J. H.; Mao, J. G.; Sun, J. $Cs_2GeB_4O_9$: a New Second-Order Nonlinear-Optical Crystal. *Inorg. Chem.* **2013**, *52*, 5831-5837. (b) Cheng, L.; Yang, G. Y. A novel aluminoborate open-framework $[In(dien)_2][Al_2B_7O_{16}H_2]$ with large chiral cavities templated by chiral main group metal complexes. *Chem. Commun.* **2014**, *50*, 344-346.

(2) Yu, H.; Pan, S.; Wu, H.; Yang, Z.; Dong, L.; Su, X.; Zhang, B.; Li, H. Effect of Rigid Units on the Symmetry of the Framework: Design and Synthesis of Centrosymmetric $NaBa_4(B_5O_9)_2F_2Cl$ and Noncentrosymmetric $NaBa_4(AlB_4O_9)_2Br_3$. *Cryst. Growth Des.* **2013**, *13*, 3514-3521.