Supporting Information

Linking 1-D Transition-Metal Coordination Polymers and Different Inorganic Boron Oxides to Construct a Series of 3-D Inorganic-Organic Hybrid Borates

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Table S1. Selected bond lengths (Å) of **1**[a].

Zn(1)-O(6)	2.0262(13)	B(2)-O(6)	1.484(3)
Zn(1)-N(1)	2.0370(18)	B(3)-O(7)	1.366(3)
Zn(1)-N(2)	2.0478(17)	B(3)-O(8)	1.367(3)
Zn(1)-O(3)	2.1572(14)	B(3)-O(5)	1.369(3)
Zn(1)-O(10A)	2.2567(13)	B(4)-O(9)	1.437(3)
B(1)-O(1)	1.347(3)	B(4)-O(8)	1.476(3)
B(1)-O(2)	1.359(3)	B(4)-O(6)	1.485(3)
B(1)-O(3)	1.378(3)	B(4)-O(10)	1.504(2)
B(2)-O(2)	1.457(3)	B(5)-O(9B)	1.352(3)
B(2)-O(4)	1.468(2)	B(5)-O(4)	1.363(3)
B(2)-O(5)	1.480(3)	B(5)-O(10)	1.371(3)

[a]Symmetry codes: A: -*x* + 1, *y* + 1/2, -*z* - 1/2; B: -*x* + 1,y - 1/2,-*z* - 1/2.

Table S2. Hydrogen bond lengths (Å) and bond angles (°) in compound **1**[a].

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠DHA(°)
O(1)-H(1A) ··· O(4) #1	0.778	1.89	2.665	174.47
O(3)-H(3A) ··· O(2) #2	0.74	1.965	2.7	172.27
O(7)-H(7A) ··· O(5) #3	0.789	2.008	2.795	174.82
N(1)-H(1N) ··· O(7) #4	0.908	2.269	3.161	167.14
N(1)-H(2N) ··· O(8) #5	0.866	2.29	3.083	152.15
N(2)-H(3N) ··· O(9) #5	0.877	2.167	2.918	143.4

[a]Symmetry codes: #1: -*x*, *y* + 1/2, -*z* - 1/2; #2: -x, *y* + 1/2, -*z* - 1/2; #3: -*x*, -*y* - 1, -*z* - 1; #4: x, -y - 1/2, *z* + 1/2; #5: -*x* + 1, *y* + 1/2, -*z* - 1/2.

Table S3. Selected bond lengths (Å) of **2**[a].

Cd-N(1)	2.241(4)	B(3)-O(10C)	1.354(6)
Cd-N(2)	2.247(4)	B(3)-O(9)	1.370(6)
Cd-O(2)	2.294(3)	B(3)-O(11)	1.376(5)
Cd-O(7)	2.307(3)	B(4)-O(10)	1.439(5)
Cd-O(9A)	2.324(3)	B(4)-O(6)	1.480(6)
Cd-O(4B)	2.686(3)	B(4)-O(2)	1.490(5)
B(1)-O(5)	1.347(6)	B(4)-O(9)	1.508(5)
B(1)-O(4)	1.363(6)	B(5)-O(2)	1.465(5)
B(1)-O(7)	1.367(6)	B(5)-O(5)	1.465(5)
B(2)-O(6)	1.365(6)	B(5)-O(11)	1.486(5)
B(2)-O(3)	1.365(6)	B(5)-O(8)	1.496(6)
B(2)-O(8)	1.368(6)		

[a]Symmetry codes: A: -*x* + 1, *y* - 1/2, -*z* - 1/2; B: -*x*, *y* - 1/2, -*z* - 1/2; C: -*x* + 1, *y* + 1/2, -*z* - 1/2.

Table S4. Hydrogen bond lengths (Å) and bond angles (°) in compound **2**[a].

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠DHA(°)
O(3)-H(3A) ··· O(8) #1	0.729	2.098	2.804	163.22
O(4)-H(4) ··· O(11) #2	0.774	1.941	2.714	178.14
O(7)-H(7) ··· O(5) #2	0.93	1.757	2.635	156.21
N(1)-H(1B) ··· O(9) #3	0.89	2.403	3.128	138.78
N(1)-H(1D) ··· O(9) #4	0.89	2.257	3.108	160.09
N(2)-H(2C) ··· O(9) #3	0.89	2.315	2.988	132.33

[a]Symmetry codes: #1: -*x*, -*y* - 1, -*z* - 1; #2: -*x*, *y* - 1/2, -*z* - 1/2; #3 -*x* + 1, *y* - 1/2, -*z* - 1/2; #4; *x*, -*y* - 3/2, *z* + 1/2.

Table S5. Selected bond lengths (Å) of **3**[a].

Co(1)-O(4A)	1.945(3)	B(1)-O(2C)	1.364(5)
Co(1)-N(1B)	2.040(3)	B(1)-O(3)	1.376(5)
Co(1)-N(1)	2.041(3)	B(2)-O(1D)	1.438(4)
Co(1)-O(3)	2.252(2)	B(2)-O(2)	1.459(5)
Co(1)-O(3B)	2.252(2)	B(2)-O(4)	1.482(4)
B(1)-O(1)	1.356(5)	B(2)-O(3)	1.519(5)

[a]Symmetry codes: A: *y* - 1/2, -*x* + 1/2, *z* + 1/4; B: -*y*, -*x*, -*z* - 1/2; C: *y*, *x*, -*z* - 1; D: *x* + 1/2, -*y* + 1/2, -*z* - 3/4.

Table S6. The known inorganic-organic hybrid borates.[a]

Ref.	Formula	Metal-organic component	Inorganic component	Final framework
1	$[Zn(B_4O_8H_2)(C_3H_{10}N_2)]$	isolated metal complex	1D borate chain	1D hybrid chain
	$[Zn(B_4O_8H_2)(C_3H_{10}N_2)\cdot 3H_2O$	1D coordination polymer	1D borate chain	2D hybrid layer
	$[Zn(B_5O_{10}H_3)(C_{10}H_{24}N_4)]\cdot 3H_2O$	1D coordination polymer	1D borate chain	2D hybrid layer
	$[Zn_2(B_8O_{15}H_2)(C_3H_{10}N_2)_2]$	1D coordination polymer	2D borate layer	3D hybrid framework
2	$[Cu(enMe)_2]_3\{Al_2[B_5O_8(OH)_2]_4\}\cdot H_2O$	isolated metal complex	2D aluminoborate framework	2D hybrid framework
	$[Cu(en)_2][AlB_5O_{10}]$	isolated metal complex	3D aluminoborate framework	3D hybrid framework
3	$Zn_4(dah)(BO_3)_2(B_3O_7H_2)\cdot H_3O\cdot 1.5H_2O$	isolated metal complex	isolated BO_3 triangle and $B_3O_7H_2$ cluster	3D hybrid framework
4	$[Zn(dap)_2][AlB_5O_{10}]$	2D coordination polymer	3D aluminoborate framework	3D interpenetrated framework
5	$[Zn(en)_2][AlB_5O_{10}]$	isolated metal complex	3D aluminoborate framework	3D hybrid framework
6	$Zn(1,3\text{-}DAP)[B_4O_7]$	1D coordination polymer	3D borate framework	3D hybrid framework
7	$[EAH]_2\{(py)_2Cd@[B_{14}O_{20}(OH)_6]\}$	isolated metal complex	0D borate cluster	isolate hybrid cluster
	$[PAH]_2\{(py)_2Cd@[B_{14}O_{20}(OH)_6]\}$	isolated metal complex	0D borate cluster	isolate hybrid cluster
	$[pyH]_2\{(py)_2Cd@[B_{14}O_{20}(OH)_6]\}$	isolated metal complex	0D borate cluster	isolate hybrid cluster
	$\{(AImH)_2Cd@[B_{14}O_{20}(OH)_6]\}$	isolated metal complex	0D borate cluster	isolate hybrid cluster

[a] Isolated metal complexes act as templates are excluded.

References:

1. Paul, A. K.; Sachidananda, K.; Natarajan, S. $[B_4O_9H_2]$ Cyclic Borate Units as the Building Unit in a Family of Zinc Borate Structures. Cryst. Growth Des., 2010, 10, 456-464.

2. Cheng, L.; Zhao, J. W.; Yang, G. Y. Two Cu-Complex Directed Aluminoborates: From 2D Layers to 3D Frameworks, Dalton Trans., 2014, 43, 7324–7330.

3. Zhao, P.; Lin, Z. E.; Wei, Q.; Cheng, L.; Yang, G. Y. A Pillared-Layered Zincoborate with an Anionic Network Containing Unprecedented Zinc Oxide Chains. Chem. Commun., 2014, 50, 3592-3594.

4. Wei, L.; Wei, Q.; Lin, Z.; Meng, Q.; He, H.; Yang, B.; Yang, G. A 3D Aluminoborate Open Framework Interpenetrated by 2D Zinc−Amine Coordination-Polymer Networks in Its 11-Ring Channels. Angew. Chem., Int. Ed. 2014, 53, 7188−7191.

5. Liu, Y.; Pan, R.; Cheng, J.; He, H.; Yang, B.; Zhang, Q.; Yang, G. A Series of Aluminoborates Templated or Supported by Zinc−Amine Complexes. Chem. - Eur. J. 2015, 21, 15732−15739.

6. Pan, C. Y.; Zhong, L. J.; Zhao, F. H.; Yang, H. M.; Zhou, J. Zn(1,3DAP)$[B_4O_7]$: A rare Chiral Zeolitic Framework Constructed of Four-Connected $[B_4O_9]$ Clusters with a Single-Stranded Helical Channel. Chem. Commun. 2015, 51, 753−756.

7. Wei, Q.; Zhang, Y. J.; Song, Y.; Yang, G. Y.; Zou, X. A Series of Inorganic-Organic Hybrid CadmiumBorates with Novel Cd-Centred $[Cd@B_{14}O_{20}(OH)_6]^{2-}$ clusters. Dalton Trans., 2016, 45, 13937–13943.

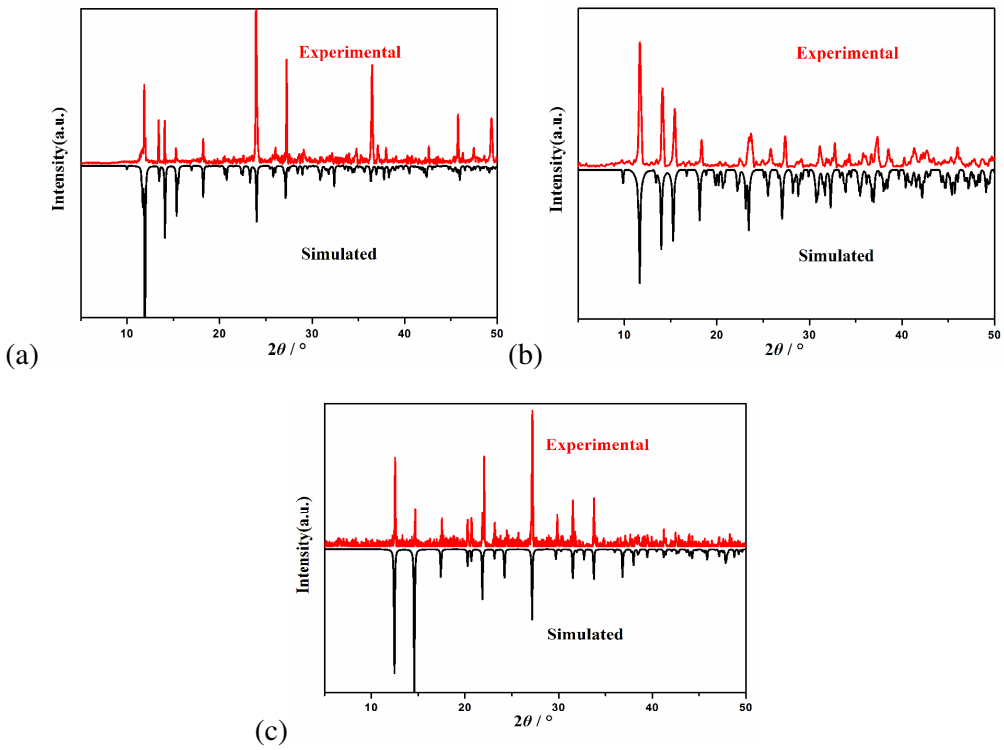

Figure S1. View of the powder X-ray diffractions of compounds **1**(a), **2**(b) and **3**(c).

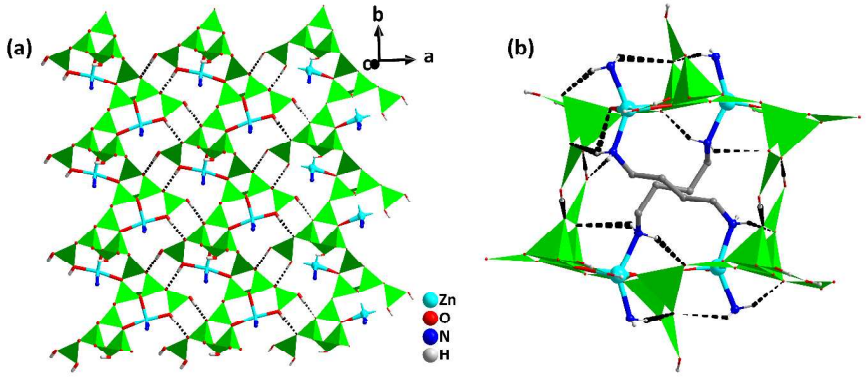

Figure S2. (a) View of the hydrogen interactions during the supramolecular zincoborate layer of **1**. (b) View of the N-H... O hydrogen bond of **1**.

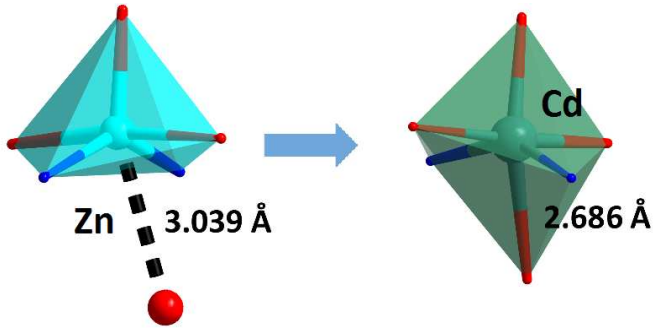

Figure S3. ZnO_3N_2 trigonal bipyramidal in **1** and CdO_4N_2 octahedron with a longish Cd-O bond in **2**.

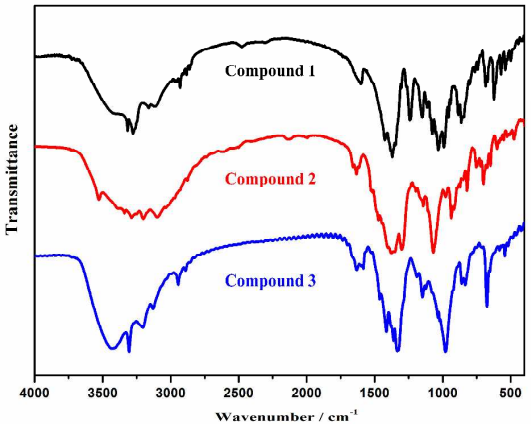

Figure S4. IR spectrums of **1**-**3**.

The IR spectra of **1-3** show that the stretching vibrations of the O-H, N-H, and C-H bonds are at the broad bands of about 3430, 3305 and 2945 cm^{-1}, respectively. The asymmetric vibration bands of N-H and C-H appear in the region of 1646-1607 cm^{-1}, respectively. The appearance of the resonance signal confirms that the organic components exist in the samples. The B-O asymmetric stretching of BO_3 and BO_4 groups are in the range of 1430-1285 cm^{-1} and 1130-1000 cm^{-1}, respectively. The bands occurring from 920 to 800 cm^{-1} can be attributed to the symmetric stretching modes of BO_3 and BO_4 groups.

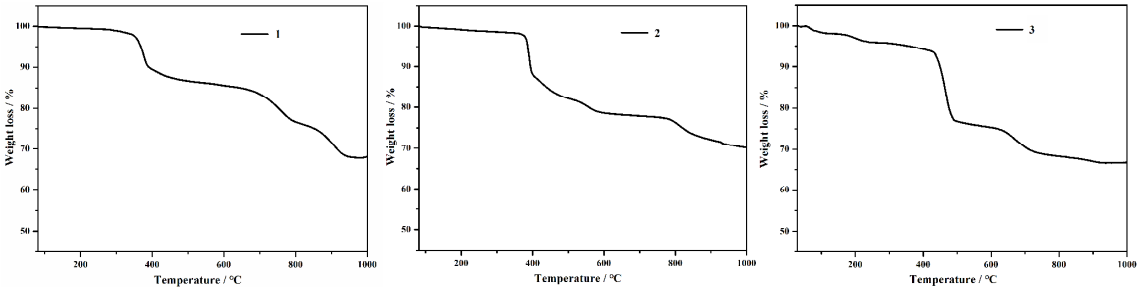

Figure S5. Thermogravimetric curves of **1**-**3**.

The samples can stable up to 340 ^{o}C for 1-2 and 430 ^{o}C for 3. The curves of 1-2 show a weight loss of 30.5% and 26.9% between 340 to 800 ^{o}C, which are in good agreement with the calculated values of 31.1% and 27.6% for 1-2, the weight loss can attribute to the removal of the guest organic amines and the dehydration of hydroxyl groups. The following weight loss might be attributed to the gradual volatilization of boron oxide. The curve of 3 shows a sharp weight loss between 430 ^{o}C to 1000 ^{o}C was attribute to the removal of organic amines, the total weight loss is 26.8%, and is similar to the calculated values of 25.7%.

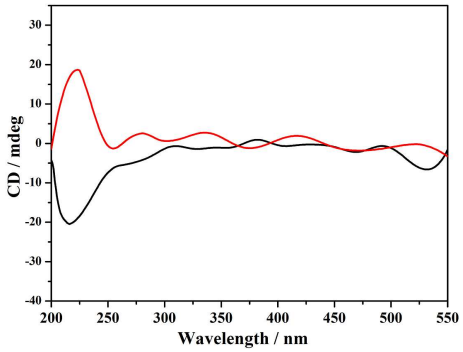

Figure S6. Solid-state CD spectra of **3**.