Supporting Information

Three mixed-alkaline-metal borates with $\{Li@B_{12}O_x(OH)_{24-x}\}$ ($x = 18, 22$) clusters: from isolated oxoboron cluster to unusual layer

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Table S1. Sample concentrations of compounds **1**–**3**

Compound	Sample concentration (mg/kg)				
	Li	Na	K	B	Cs
1	255.6871	6361.4677	1750.7031	4741.2692	—
2	271.9058	—	—	4881.6947	26734.1649
3	251.7427	—	—	4551.7548	25201.9072

For compound **1**:

the ratio of *n*(Li):*n*(Na):*n*(K):*n*(B)

= (255.6871/6.94):(6361. 4677/22.99):(1750.7031/39.10):(4741.2692/10.81)

= 36.84:276.71:44.77:438.60

= 1:7.51:1.22:11.91

For compound **2**:

the ratio of *n*(Li):*n*(Cs):*n*(B)

= (271.9058/6.94):(26734.1649/132.90):(4881.6947/10.81)

= 39.18:201.16:451.19

= 1:5.13:11.53

For compound **3**:

the ratio of *n*(Li):*n*(Cs):*n*(B)

= (251.7427/6.94):(25201.9072/132.90):(4551.7548/10.81)

= 36.27:189.63:421.07

= 1:5.23:11.61

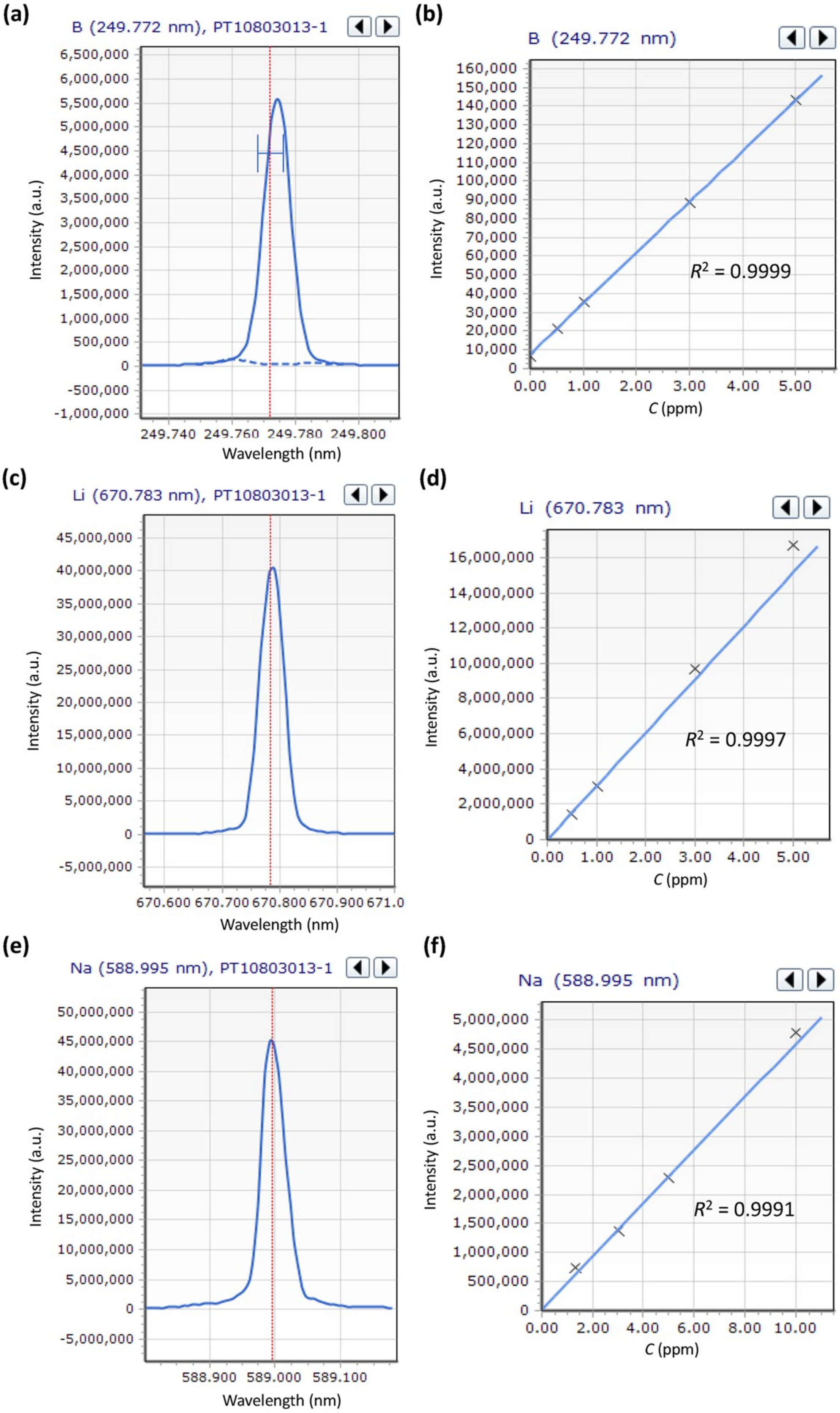

Fig. S1 ICP-OES spectra for compounds **1**–**3** (B, Li and Na)

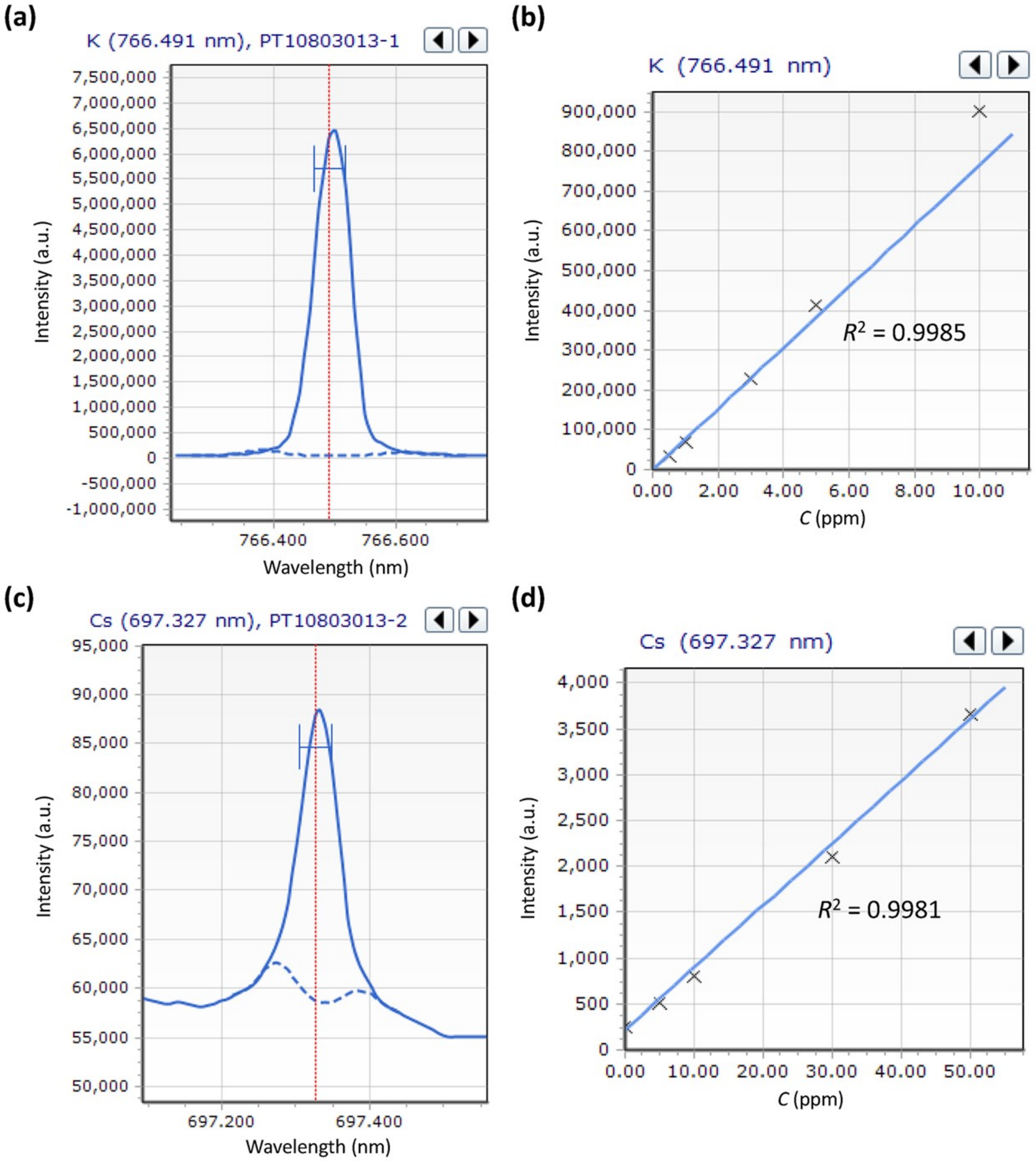

Fig. S2 ICP-OES spectra for compounds **1**–**3** (K and Cs)

Table S2. Selected H-bonding distances (Å) and angles (°) for **2**

D–H	d(D–H)	d(H···A)	∠DHA	d(D···A)	A	Symmetry
O1–H1	0.816	2.012	156	2.777	O13	[$-x + 1, y + 1/2, -z + 3/2$]
O21–H21	0.822	2.005	166	2.811	O10	[$-x + 2, y - 1/2, -z + 3/2$]
O25–H25A	0.853	1.987	174	2.837	O4	[$x, -y + 3/2, z - 1/2$]
O25–H25B	0.859	2.574	157	3.384	O5	
O25–H25B	0.859	2.571	145	3.309	O9	
O23–H23A	0.892	2.478	147	3.261	O18	
O24–H24A	0.851	2.327	132	2.963	O23	
O24–H24B	0.859	2.634	120	3.157	O22	[$-x + 1, y + 1/2, -z + 3/2$]
O24–H24B	0.859	2.288	137	2.978	O19	[$-x + 1, y + 1/2, -z + 3/2$]

Table S3. Selected H-bonding distances (Å) and angles (°) for **3**

D–H	d(D–H)	d(H···A)	∠DHA	d(D···A)	A	Symmetry
O7–H7	0.820	2.064	153	2.819	O3	[$x + 1, y, z$]
O18–H18	0.820	2.044	161	2.833	O11	[$x - 1, -y + 1, z - 1/2$]
O23–H23A	0.866	2.136	127	2.745	O24	[$x, -y + 1, z - 1/2$]
O24–H24C	0.850	1.818	173	2.663	O2	[$x, -y + 1, z + 1/2$]

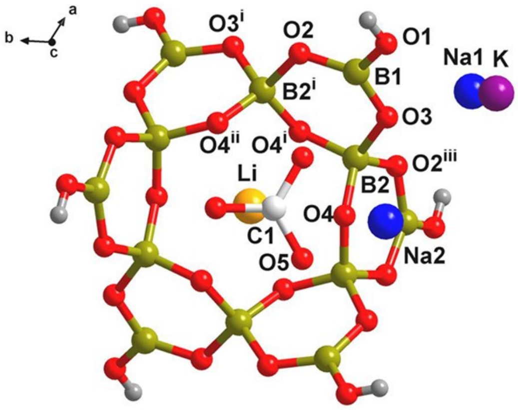

Fig. S3 The structure of compound **1**, symmetry codes: (i) 2/3 + *x* − *y*, 1/3 + *x*, 4/3 − *z*; (ii) 1 − *y*, 1 + *x* − *y*, *z*; (iii) −1/3 + *y*, 1/3 − *x* + *y*, 4/3 − *z*. The occupancies of Li, Na1, Na2 and K were 1/6, 1/3, 1 and 1/6, respectively

In crystallography, generally, atoms with similar atomic numbers have little difference in residual electron densities (Q peaks) due to their similar atomic masses, which are sometimes difficult to distinguish. For example, C (atomic number 6, similarly hereinafter) and N(7) or O(8) and F(9) need to prove the assignment of atomic type by means of reaction materials, elemental analysis or nuclear magnetic resonance.

In compound **1**, the three metals of Li(3), Na(11) and K(19) are in different periods in periodic table of elements. In addition to the different atomic radius, more importantly, the atomic masses of the elements are quite different. Reflected in the single crystal diffraction results, the electron cloud densities (Q peaks) of the three atoms will also be greatly different. Therefore, it is possible to distinguish Li, Na, and K from the residual electron densities (Q peaks).

If the Q peak that should be Li is assigned to Na or K, the *R* value and other parameters of compound **1** will increase significantly, and the data will not converge. Many NPD atoms may also appear on the oxoboron skeleton after wrongly assignment. In short, if the assignment of metals Li, Na and K are incorrect, it is difficult to obtain the reasonable structure data. In addition, the number of Li, Na and K are determined by the occupancy of their location, which is generally not changed. The occupancies of Li, Na1, Na2 and K were 1/6, 1/3, 1 and 1/6, respectively.

In summary, apart from ICP-OES spectra, we can confirm the assignment of Li, Na, and K through crystallographic methods.

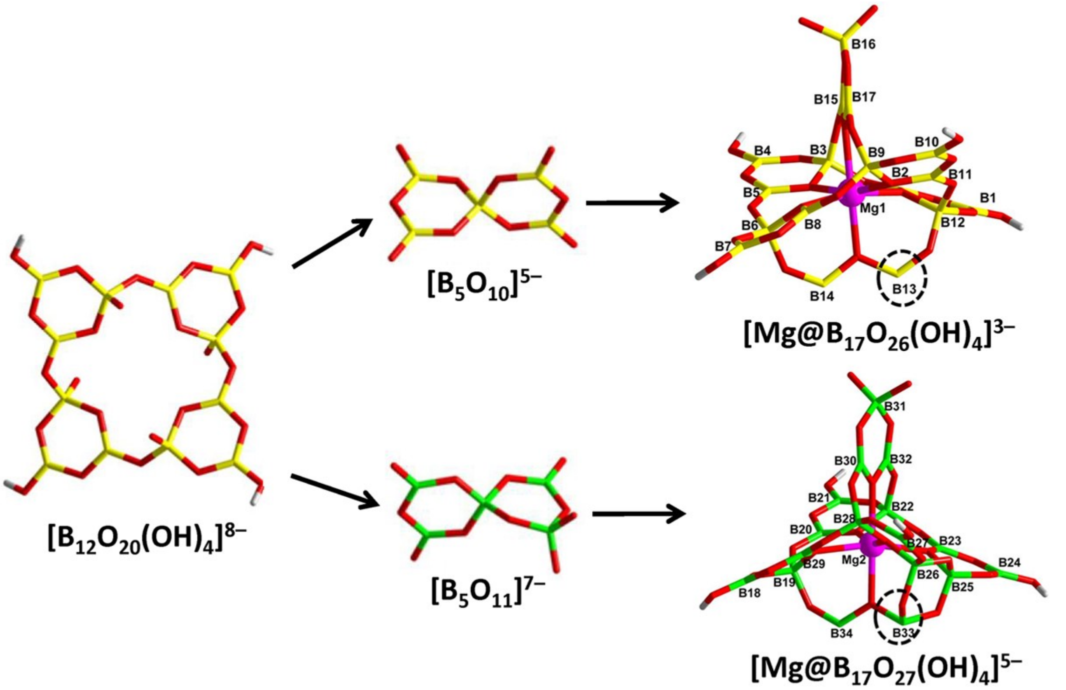

Fig. S4 View of the $[B_{12}O_{20}(OH)_4]^{8-}$, $[Mg@B_{17}O_{26}(OH)_4]^{3-}$, and $[Mg@B_{17}O_{27}(OH)_4]^{5-}$ clusters in **1a**.

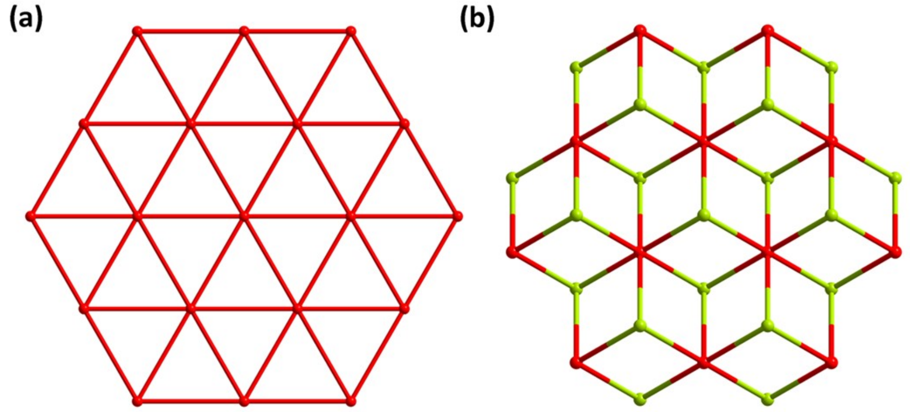

Fig. S5 View of (a) the hxl topology in **1b** and (b) kgd; Shubnikov plane (3.6.3.6)/ dual net in **1**, in which the Li@$B_{12}O_x$ clusters are shown as red nodes and carbonates are shown as lime nodes.

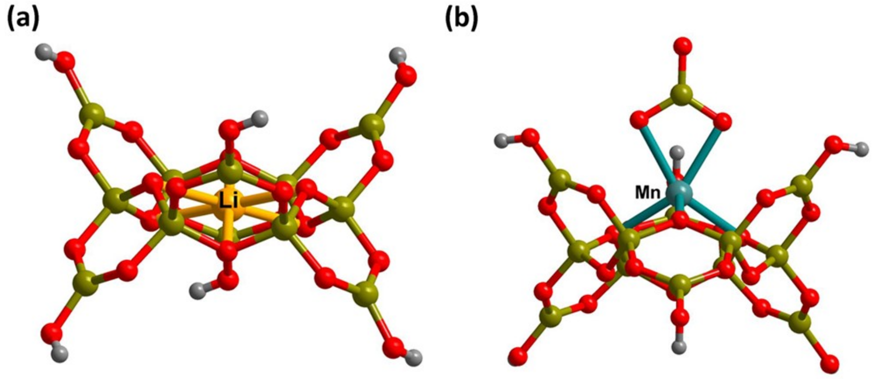

Fig. S6 (a, b) The position of Li (**1**) and Mn (**1c**) in $\{B_{12}O_x\}$ cluster.

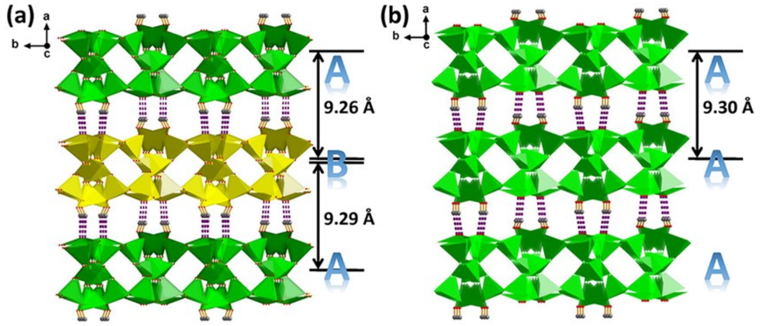

Fig. S7 The 3D supramolecular structure of **2**(a) and **3**(b) along the *c* axis. In **2**(a), the A- and B-layer are formed by Li1@$B_{12}O_x$-II and Li2@$B_{12}O_x$-II clusters, respectively. In **3**(b) the A-layer are formed by Li1@$B_{12}O_x$-II clusters.

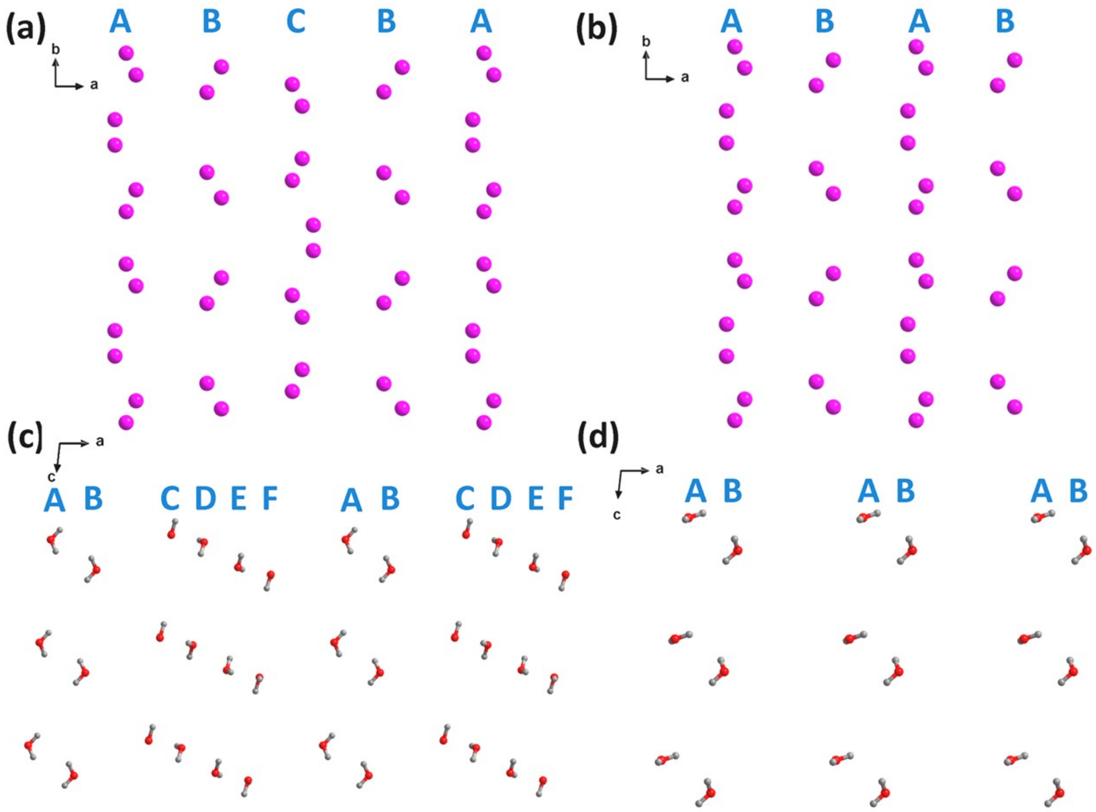

Fig. S8 The arrangements of Cs^+ in **2**(a) and **3**(b) and H_2O in **2**(c) and **3**(d).

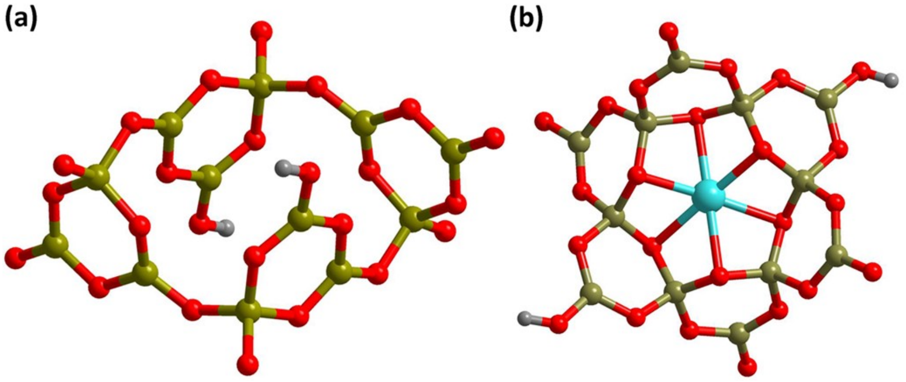

Fig. S9 View of $[B_{12}O_{22}(OH)_2]^{10-}$ cluster in **4** (a) and $[Li@B_{12}O_{22}(OH)_2]^{9-}$ in **2** and **3** (b).

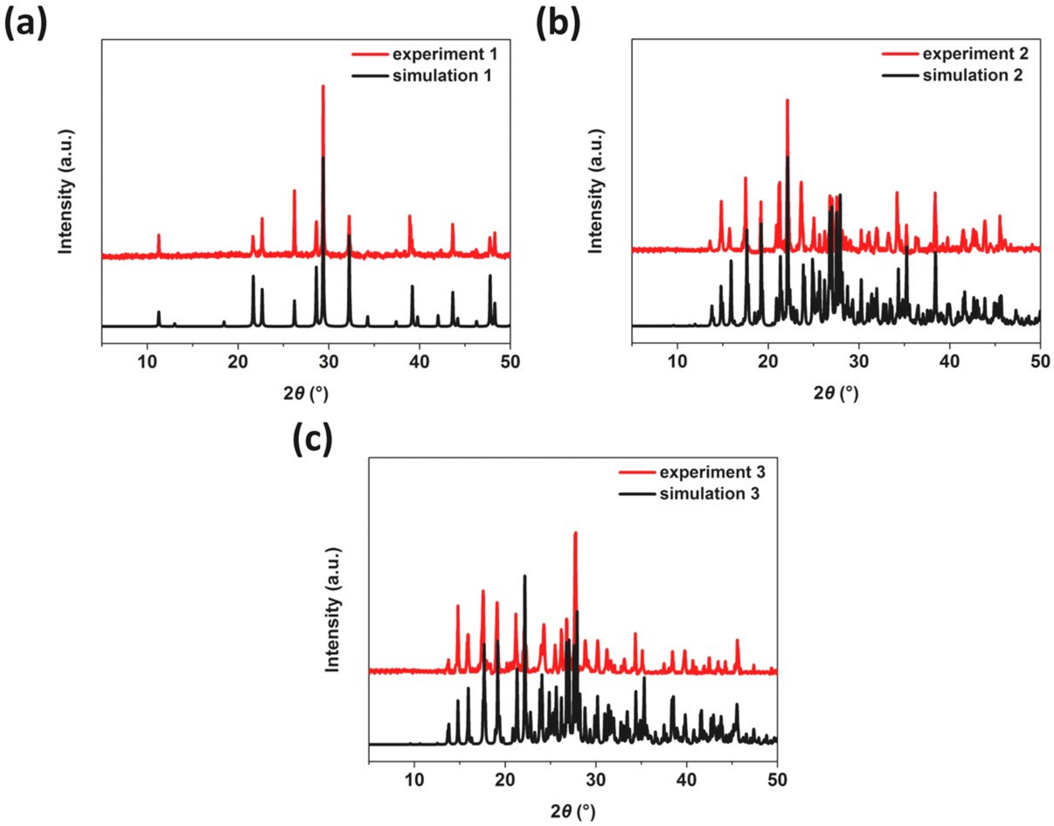

Fig. S10 PXRD patterns show the comparison between the experimental value and calculated ones for compounds **1**(a), **2**(b) and **3**(c).

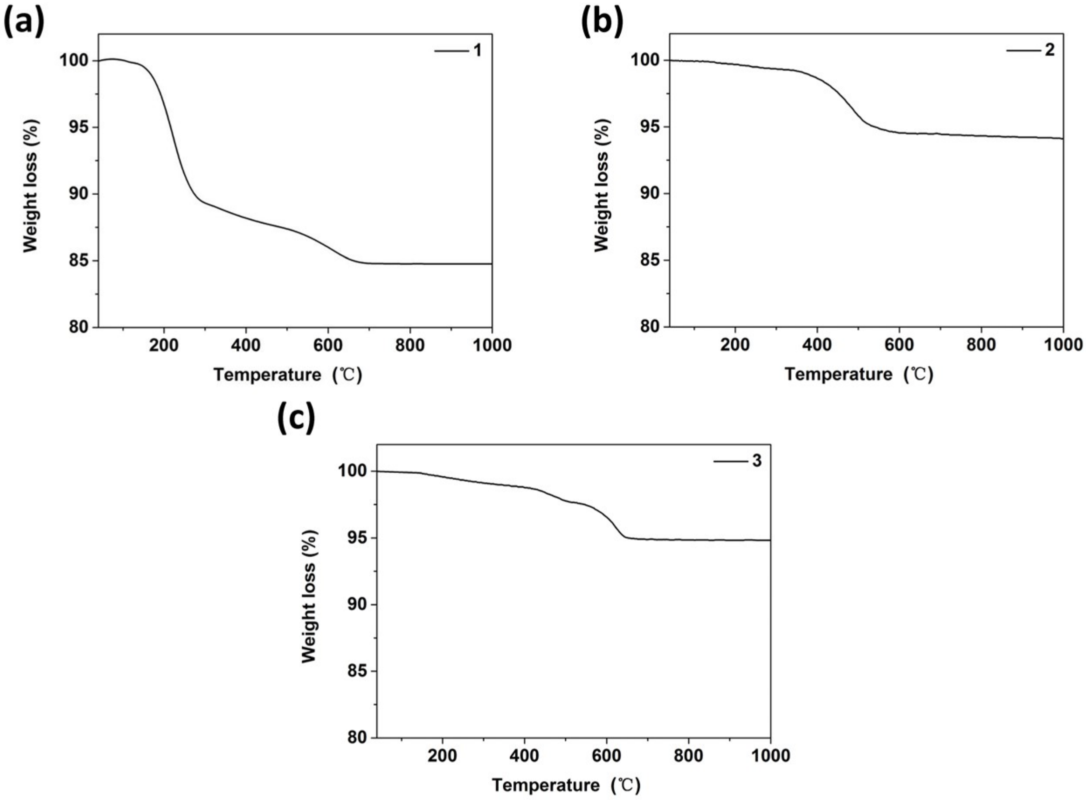

Fig. S11 TG curves for compounds **1**(a), **2**(b) and **3**(c).

The Thermgravimetric (TG) curves of compound **1**–**3** show a one-step weight loss process and the can be stable up to about 170, 200 and 190°C, respectively (Fig. S11). For **1**, the weight loss 15.6 % (cal. 16.3 %) in the temperature range 180–650°C is attributed to the removal of CO_2 molecule and dehydration of the hydroxyls. In the temperatures range from 190 to 630 °C, there is small weight loss of 5.5% and 5.2% for **2** and **3**, indicating the decomposition of crystalline water and hydroxyl groups, which are close to the calculated values of 6.0 and 6.0% for **2** and **3**, respectively.

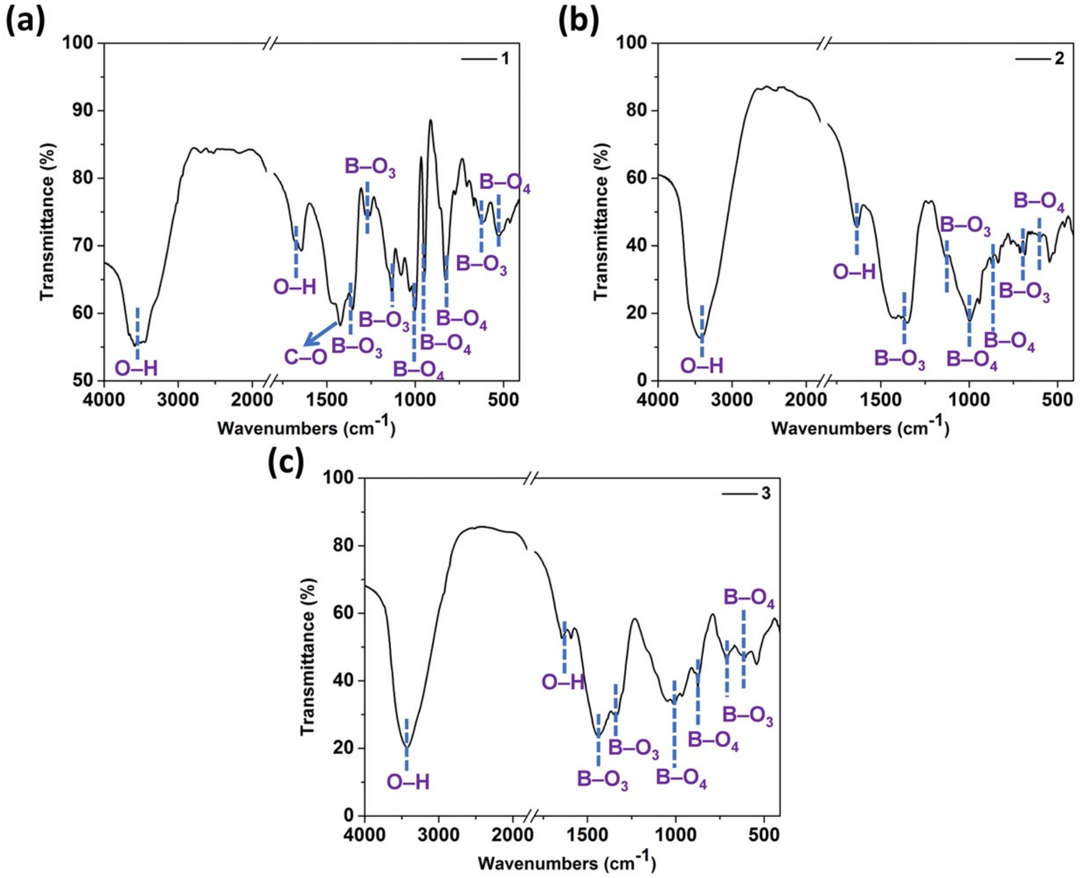

Fig. S12 IR spectra for compounds **1**(a), **2**(b) and **3**(c).

As for the IR spectra in **1**–**3** (Fig. S12), the absorption bands around 3600–3000 cm^{-1} and the 1645–1600 cm^{-1} are related to vibrations of the O–H bonds of H_2O and hydroxyl. The stretching of BO_3 and BO_4 units are located at 1420–1338 cm^{-1}, 1280–1230 cm^{-1}, 1000–943 cm^{-1} and 750–670 cm^{-1}, respectively. The band near 1427 is associated with asymmetric stretching vibrations of CO_3 units (elemental analyses also confirmed the existence of carbon element). The results of TGA, IR spectra, elemental analyses and ICP-OES are agreement with the single-crystal structures of **1**–**3**.

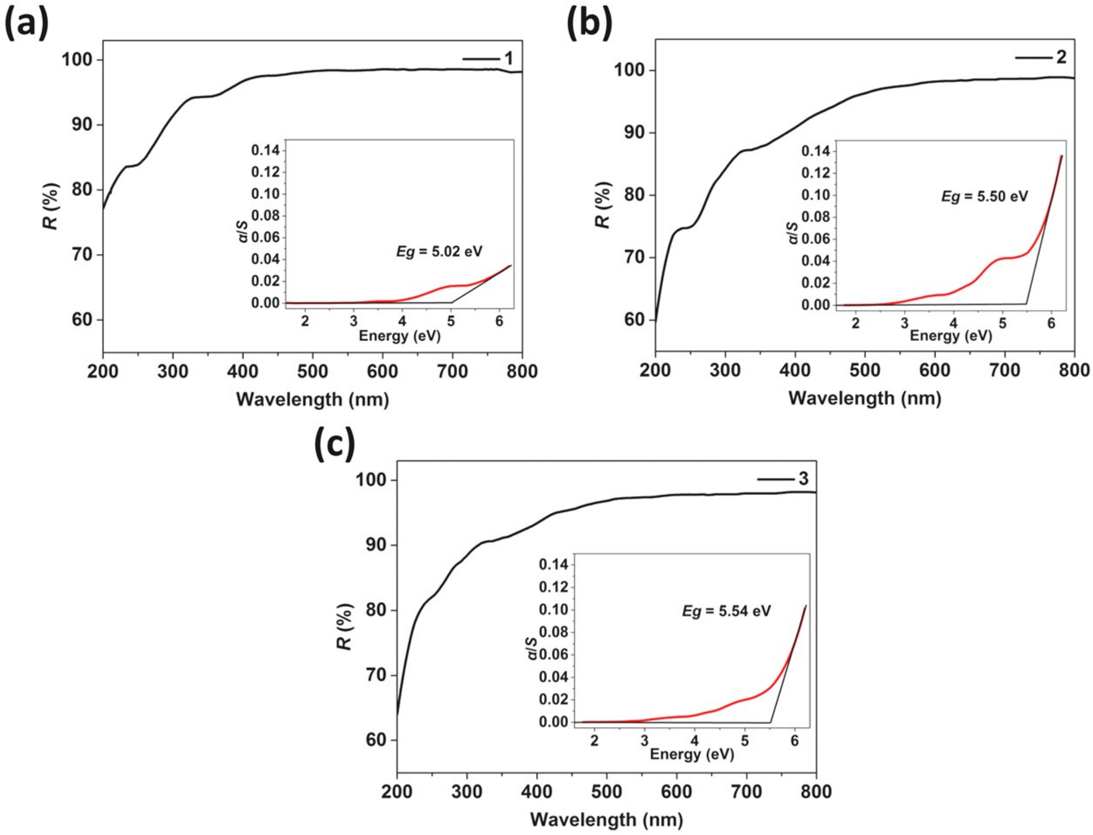

Fig. S13 UV/Vis diffuse reflectance spectra of compounds **1**(a), **2**(b) and **3**(c). Inset: plots of the absorption data (*α*/*S*) *vs*. Energy (*E*).