

## *Supporting Information*

### **Two additive-induced isomeric aluminoborates templated by methylamine**

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**Fig. S1** IR spectra of **1** and **2**, respectively.

**Fig. S2** The asymmetric unit of compound **1**.

**Fig. S3** View of the coordination environments of all the B and Al atoms in compound **1**.

**Fig. S4** View of the anionic framework of **1**, showing cone-shaped 10-ring channels along the [110] (**a**) and [-110] (**b**) directions.

**Fig. S5** View of the unclosed 10-ring channels along the [110] (**a**) and [-110] (**b**) directions in compound **1**.

**Fig. S6** View of the templates and guest water molecules located in the 10-ring channel, interacted with the walls via hydrogen bonds in compound **1**.

**Fig. S7** IR spectra (**a**) and powder X-ray diffraction patterns (**b**) of compound **1** (black line), Na<sup>+</sup>- (red line), K<sup>+</sup>- (blue line) and Ag<sup>+</sup>-exchange (cyan) samples.

**Fig. S8** View of the coordination environments of all the B and Al atoms in compound **2**.

**Fig. S9** IR spectra (**a**) and powder X-ray diffraction patterns (**b**) of compound **2** (black line), Na<sup>+</sup>- (red line), K<sup>+</sup>- (blue line) and Ag<sup>+</sup>-exchange (cyan) samples.

**Fig. S10** View of three different shaped 11-ring channels in **2**, propagated along the [001], [110] and [112] directions, respectively.

**Fig. S11** View of the 10-ring channels in **2**, running along the [101] direction.

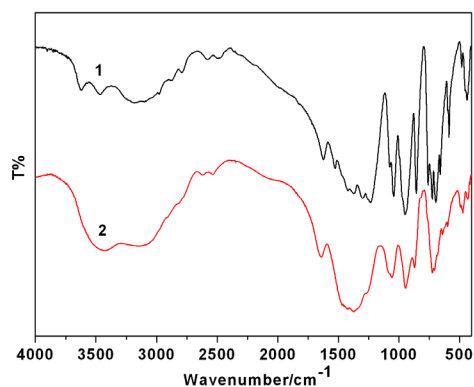


Fig. S1 IR spectra of **1** and **2**, respectively.

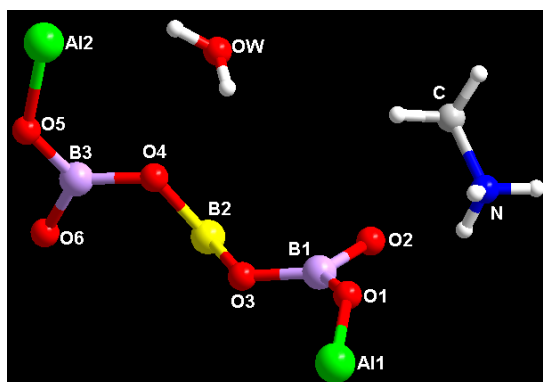
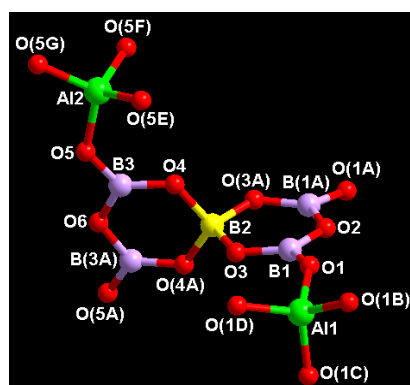
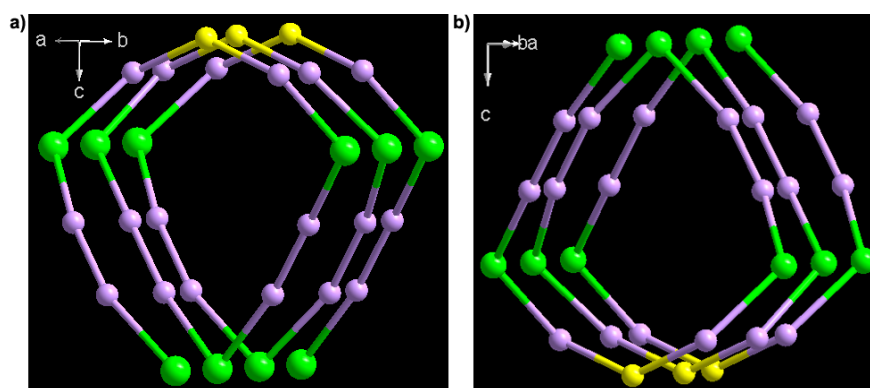
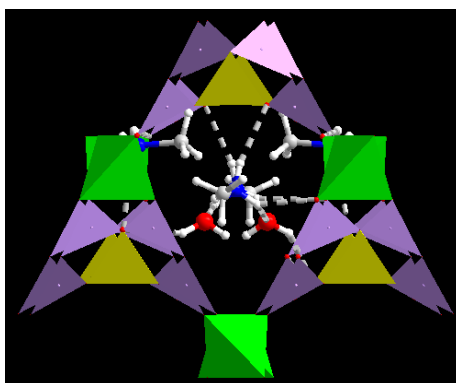


Fig. S2 The asymmetric unit of compound **1**.

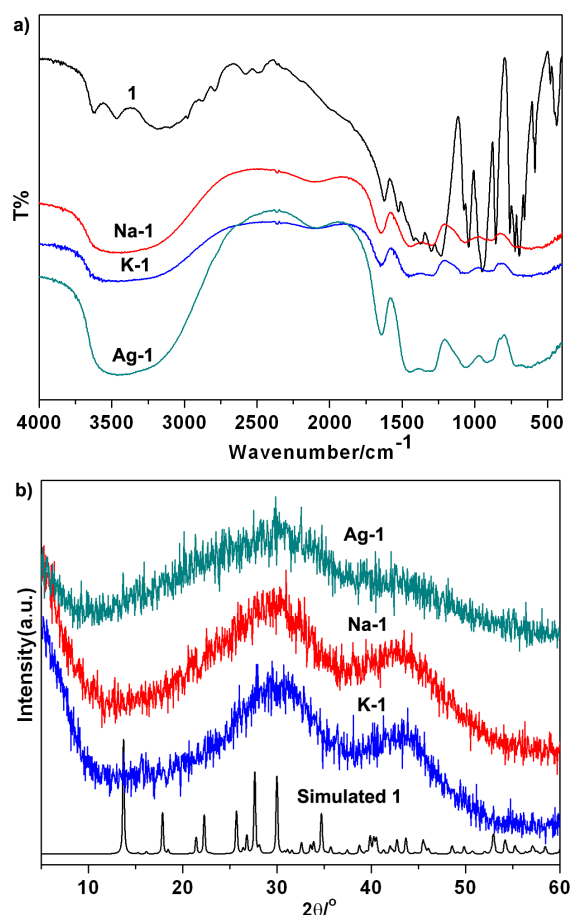




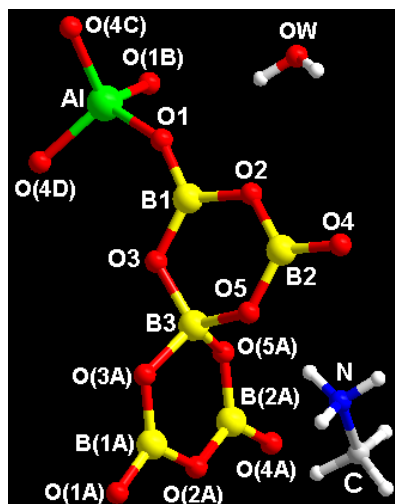
**Fig. S5** View of the unclosed 10-ring channels along the [110] (a) and [-110] (b) directions in compound 1. Color code: B2, yellow; B1, B3, purple; A1, green.



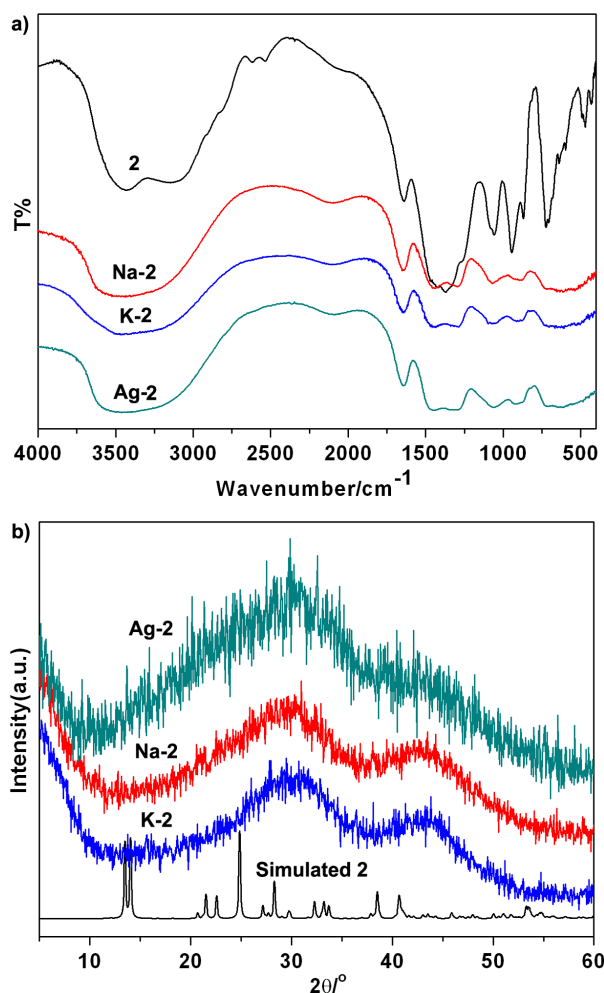
**Fig. S6** View of the templates and guest water molecules located in the 10-ring channel, interacted with the walls via hydrogen bonds in compound 1.



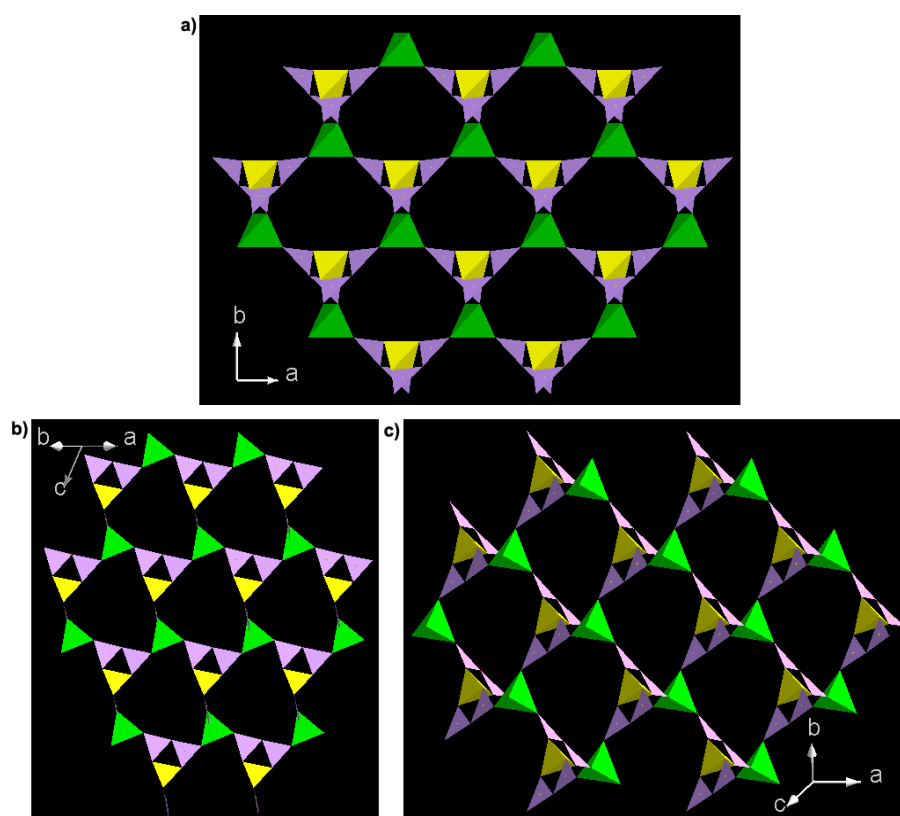
**Fig. S7** IR spectra (a) and powder X-ray diffraction patterns (b) of compound 1 (black line), Na<sup>+</sup>- (red line), K<sup>+</sup>- (blue line) and Ag<sup>+</sup>-exchange (cyan) samples.



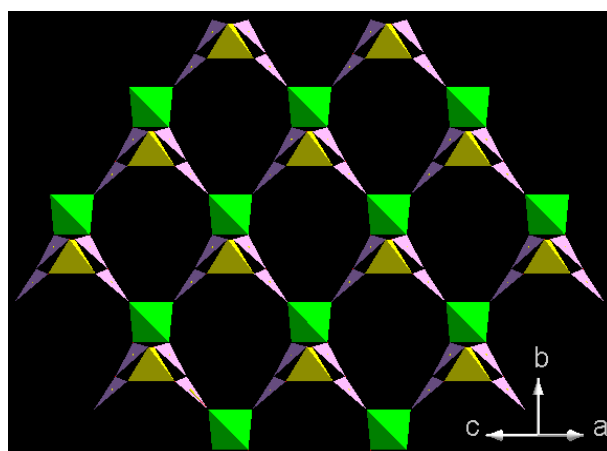
**Fig. S8** View of the coordination environments of all the B and Al atoms in compound **2**. Symmetry codes for **2**: #A  $-x+1, y, -z+3$ , #B  $-x, y, -z+2$ , #C  $-x+1/2, y+1/2, -z+2$ , #D  $x-1/2, y+1/2, z$ .



**Fig. S9** IR spectra (a) and powder X-ray diffraction patterns (b) of compound **2** (black line), Na<sup>+</sup>- (red line), K<sup>+</sup>- (blue line) and Ag<sup>+</sup>-exchange (cyan) samples.



**Fig. S10** View of three different shaped 11-ring channels in **2**, propagated along [001], [110] and [112] directions, respectively. Colour code: B<sub>3</sub>O<sub>4</sub>, yellow; B<sub>1</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, purple; AlO<sub>4</sub>, green.



**Fig. S11** View of the 10-ring channels in **2**, running along [101] direction. Colour code: B<sub>3</sub>O<sub>4</sub>, yellow; B<sub>1</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, purple; AlO<sub>4</sub>, green.