# Amine-templated Graphite and Diamond Nets in a Family of Aluminoborates

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# ELECTRONIC SUPPORTING INFORMATION

**Table S1:** Selected bond angles observed in $[(C_6H_{18}N_2)(AlB_6O_{13}H_3)]$, **I**; $[(C_5H_{16}N_2)(AlB_5O_{10})].2H_2O$, **II;** $[(C_5H_{16}N_2)(AlB_5O_{10})]$, **III** and $[(C_5H_{17}N_3)(AlB_5O_{10})].H_2O$, **IV.**

| **Moiety** | **Angle ($^o$)** | **Moiety** | **Angle ($^o$)** |
|---|---|---|---|
| Compound **I** | | | |
| O(1)-Al(1)-O(2) | 108.98(18) | O(3)-B(3)-O(11) | 118.9(4) |
| O(1)-Al(1)-O(3) | 107.03(17) | O(3)-B(3)-O(9) | 122.4(3) |
| O(1)-Al(1)-O(4) | 111.59(16) | O(11)-B(3)-O(9) | 118.7(4) |
| O(2)-Al(1)-O(4) | 108.39(16) | O(4)-B(4)-O(13) | 125.8(5) |
| O(3)-Al(1)-O(2) | 111.51(18) | O(4)-B(4)-O(12) | 116.3(5) |
| O(3)-Al(1)-O(4) | 108.36(16) | O(13)-B(4)-O(12) | 117.9(4) |
| B(1)-O(1)-Al(1) | 149.6(3) | O(8)-B(5)-O(7) | 118.9(4) |
| B(2)#1-O(2)-Al(1) | 148.4(3) | O(8)-B(5)-O(5) | 122.9(4) |
| B(3)-O(3)-Al(1) | 150.4(3) | O(7)-B(5)-O(5) | 118.1(4) |
| B(4)-O(4)-Al(1) | 138.3(3) | O(11)-B(6)-O(10) | 112.7(3) |
| O(1)-B(1)-O(5) | 115.5(4) | O(11)-B(6)-O(6)#4 | 108.9(4) |
| O(1)-B(1)-O(6) | 126.4(4) | O(10)-B(6)-O(6)#4 | 108.6(4) |
| O(6)-B(1)-O(5) | 118.1(4) | O(11)-B(6)-O(8)#4 | 108.6(4) |
| O(2)#3-B(2)-O(10) | 123.9(4) | O(10)-B(6)-O(8)#4 | 107.9(4) |
| O(2)#3-B(2)-O(9) | 117.3(4) | O(6)#4-B(6)-O(8)#4 | 110.2(4) |
| O(10)-B(2)-O(9) | 118.8(4) | | |
| Compound **II** | | | |
| O(1)-Al(1)-O(2) | 114.7(3) | O(2)#5-B(2)-O(8) | 120.2(6) |
| O(1)-Al(1)-O(3) | 110.0(2) | O(5)-B(2)-O(8) | 118.0(5) |
| O(1)-Al(1)-O(4) | 110.6(3) | O(3)-B(3)-O(10)#6 | 115.9(5) |
| O(2)-Al(1)-O(4) | 108.6(2) | O(7)-B(3)-O(3) | 124.1(6) |
| O(3)-Al(1)-O(2) | 106.0(3) | O(7)-B(3)-O(10)#6 | 120.0(5) |

| | | | |
|---|---|---|---|
| O(3)-Al(1)-O(4) | 106.6(2) | O(4)-B(4)-O(6) | 120.6(6) |
| B(1)-O(1)-Al(1) | 154.4(5) | O(4)-B(4)-O(10) | 120.9(6) |
| B(2)#1-O(2)-Al(1) | 157.1(5) | O(6)-B(4)-O(10) | 118.4(6) |
| B(3)-O(3)-Al(1) | 157.1(5) | O(6)#7-B(5)-O(7)#8 | 111.9(4) |
| B(4)-O(4)-Al(1) | 148.2(4) | O(6)#7-B(5)-O(9) | 110.7(5) |
| O(8)-B(1)-O(1) | 120.8(6) | O(7)#8-B(5)-O(9) | 107.6(4) |
| O(9)-B(1)-O(1) | 118.6(5) | O(6)#7-B(5)-O(5) | 109.4(4) |
| O(9)-B(1)-O(8) | 120.6(6) | O(7)#8-B(5)-O(5) | 107.7(5) |
| O(2)#5-B(2)-O(5) | 121.6(5) | O(9)-B(5)-O(5) | 109.4(4) |
| Compound **III** | | | |
| O(1)-Al(1)-O(1)#1 | 109.74(16) | O(5)-B(1)-O(4) | 118.4(3) |
| O(1)-Al(1)-O(2)#1 | 109.12(11) | O(2)-B(2)-O(3) | 122.0(3) |
| O(1)#1-Al(1)-O(2)#1 | 110.57(10) | O(2)-B(2)-O(4)#2 | 119.3(3) |
| O(1)-Al(1)-O(2) | 110.57(10) | O(4)#2-B(2)-O(3) | 118.7(3) |
| O(1)#1-Al(1)-O(2) | 109.12(11) | O(3)#4-B(3)-O(3)#3 | 110.0(4) |
| O(2)#1-Al(1)-O(2) | 107.70(19) | O(3)#4-B(3)-O(5)#5 | 110.58(11) |
| B(1)-O(1)-Al(1) | 137.4(2) | O(3)#3-B(3)-O(5)#5 | 108.62(12) |
| B(2)-O(2)-Al(1) | 142.3(2) | O(3)#4-B(3)-O(5) | 108.62(12) |
| O(1)-B(1)-O(5) | 118.2(3) | O(3)#3-B(3)-O(5) | 110.58(11) |
| O(1)-B(1)-O(4) | 123.4(3) | O(5)#5-B(3)-O(5) | 108.4(4) |
| Compound **IV** | | | |
| O(1)-Al(1)-O(2) | 109.25(9) | O(2)-B(2)-O(10) | 117.8(2) |
| O(1)-Al(1)-O(3) | 111.10(9) | O(8)-B(2)-O(10) | 119.5(2) |
| O(1)-Al(1)-O(4) | 106.92(9) | O(3)#4-B(3)-O(9) | 118.5(2) |
| O(2)-Al(1)-O(4) | 111.67(8) | O(3)#4-B(3)-O(10) | 121.7(2) |
| O(3)-Al(1)-O(2) | 106.40(9) | O(9)-B(3)-O(10) | 119.7(2) |
| O(3)-Al(1)-O(4) | 111.53(9) | O(4)#5-B(4)-O(7) | 119.2(2) |

| | | | |
|---|---|---|---|
| B(1)-O(1)-Al(1) | 155.31(16) | O(4)#5-B(4)-O(6) | 121.4(2) |
| B(2)-O(2)-Al(1) | 144.29(15) | O(7)-B(4)-O(6) | 119.4(2) |
| B(3)#1-O(3)-Al(1) | 140.38(18) | O(5)#6-B(5)-O(7)#6 | 111.35(17) |
| B(4)#2-O(4)-Al(1) | 132.72(15) | O(5)#6-B(5)-O(9) | 109.0(2) |
| O(1)-B(1)-O(5) | 122.3(2) | O(7)#6-B(5)-O(9) | 108.95(19) |
| O(1)-B(1)-O(6) | 119.6(2) | O(5)#6-B(5)-O(8) | 107.75(19) |
| O(5)-B(1)-O(6) | 118.0(2) | O(7)#6-B(5)-O(8) | 108.8(2) |
| O(2)-B(2)-O(8) | 122.7(2) | O(9)-B(5)-O(8) | 110.99(17) |

Symmetry transformations used to generate equivalent atoms. **I**: #3 x, y+1, z; #4 x+1/2, -y+1/2, z+1/2. **II**: #5 -x, y-1/2, -z+1; #6 -x+1, y+1/2, -z+2; #7 x-1, y, z; #8 -x, y-1/2, -z+2. **III**: #1 -x, y, -z; #2 x+1/2, y-1/2, z; #3 x-1/2, y+1/2, z; #4 -x+1/2, y+1/2, -z+1; #5 -x, y, -z+1. **IV**: #4 -x+1, y+1/2, -z+1; #5 -x, y+1/2, -z; #6 x, y, z+1.

**Table S2**. Boron-oxygen bond lengths and the calculated bond strengths (S) at boron and at oxygen in the compounds **I – IV**.

| **Bond** | **Bond length (Å)** | **S($B^{3+}$) (v.u)** | **S($O^{2-}$) (v.u)** |
|---|---|---|---|
| Compound **I** | | | |
| B(1)-O(1) | 1.324 | 1.135 | 1.958 |
| B(1)-O(5) | 1.408 | 0.904 | 1.880 |
| B(1)-O(6) | 1.347 | 1.067 | 2.067 |
| | | | **∑S($O^{2-}$) = 5.905** |
| B(2)-O(2)#3 | 1.328 | 1.123 | 1.959 |
| B(2)-O(9) | 1.387 | 0.957 | 1.889 |
| B(2)-O(10) | 1.372 | 0.997 | 2.035 |
| | | | **∑S($O^{2-}$) = 5.883** |
| B(3)-O(3) | 1.332 | 1.111 | 1.936 |
| B(3)-O(9) | 1.397 | 0.932 | 1.889 |
| B(3)-O(11) | 1.377 | 0.984 | 2.028 |
| | | | **∑S($O^{2-}$) = 5.853** |
| B(4)-O(4) | 1.342 | 1.081 | 1.844 |
| B(4)-O(12) | 1.377 | 0.984 | 2.166 |
| B(4)-O(13) | 1.366 | 0.984 | 2.126 |
| | | | **∑S($O^{2-}$) = 6.136** |
| B(5)-O(5) | 1.380 | 0.976 | 1.880 |
| B(5)-O(7) | 1.363 | 1.021 | 2.202 |
| B(5)-O(8) | 1.329 | 1.120 | 2.059 |
| | | | **∑S($O^{2-}$) = 6.141** |
| B(6)-O(6)#4 | 1.472 | 1.000 | 2.067 |
| B(6)-O(8)#4 | 1.495 | 0.939 | 2.059 |
| B(6)-O(10) | 1.458 | 1.038 | 2.035 |

| | | | |
|---|---|---|---|
| B(6)-O(11) | 1.456 | 1.044 | 2.028 |
| | | | **$\sum S(O^{2-})$ = 8.189** |
| Compound **II** | | | |
| B(1)-O(1) | 1.362 | 1.024 | 1.862 |
| B(1)-O(8) | 1.352 | 1.052 | 1.984 |
| B(1)-O(9) | 1.348 | 1.064 | 2.037 |
| | | | **$\sum S(O^{2-})$ = 5.883** |
| B(2)-O(2)#5 | 1.314 | 1.166 | 1.989 |
| B(2)-O(5) | 1.374 | 0.992 | 1.952 |
| B(2)-O(8) | 1.397 | 0.932 | 1.984 |
| | | | **$\sum S(O^{2-})$ = 5.925** |
| B(3)-O(3) | 1.370 | 1.002 | 1.829 |
| B(3)-O(7) | 1.349 | 1.061 | 2.034 |
| B(3)-O(10)#6 | 1.413 | 0.892 | 1.852 |
| | | | **$\sum S(O^{2-})$ = 5.715** |
| B(4)-O(4) | 1.321 | 1.144 | 1.930 |
| B(4)-O(6) | 1.352 | 1.052 | 2.119 |
| B(4)-O(10) | 1.386 | 0.960 | 1.852 |
| | | | **$\sum S(O^{2-})$ = 5.901** |
| B(5)-O(5) | 1.487 | 0.960 | 1.952 |
| B(5)-O(6)#7 | 1.448 | 1.067 | 2.119 |
| B(5)-O(7)#8 | 1.482 | 0.973 | 2.034 |
| B(5)-O(9) | 1.482 | 0.973 | 2.037 |
| | | | **$\sum S(O^{2-})$ = 8.142** |
| Compound **III** | | | |
| B(1)-O(1) | 1.333 | 1.108 | 1.905 |
| B(1)-O(4) | 1.388 | 0.955 | 1.912 |

| | | | |
|---|---|---|---|
| B(1)-O(5) | 1.370 | 1.002 | 1.980 |
| | | | **$\sum S(O^{2-}) = 5.797$** |
| B(2)-O(2) | 1.330 | 1.117 | 1.907 |
| B(2)-O(3) | 1.388 | 0.955 | 2.004 |
| B(2)-O(4)#2 | 1.387 | 0.957 | 1.912 |
| | | | **$\sum S(O^{2-}) = 5.823$** |
| B(3)-O(3)#3 | 1.454 | 1.049 | 2.004 |
| B(3)-O(3)#4 | 1.454 | 1.049 | 2.004 |
| B(3)-O(5) | 1.480 | 0.978 | 1.980 |
| B(3)-O(5)#5 | 1.480 | 0.978 | 1.980 |
| | | | **$\sum S(O^{2-}) = 7.968$** |
| Compound **IV** | | | |
| B(1)-O(1) | 1.319 | 1.150 | 1.958 |
| B(1)-O(5) | 1.379 | 0.978 | 1.997 |
| B(1)-O(6) | 1.396 | 0.934 | 1.879 |
| | | | **$\sum S(O^{2-}) = 5.834$** |
| B(2)-O(2) | 1.340 | 1.087 | 1.887 |
| B(2)-O(8) | 1.370 | 1.002 | 2.007 |
| B(2)-O(10) | 1.394 | 0.939 | 1.899 |
| | | | **$\sum S(O^{2-}) = 5.793$** |
| B(3)-O(3)#4 | 1.339 | 1.090 | 1.887 |
| B(3)-O(9) | 1.361 | 1.027 | 2.040 |
| B(3)-O(10) | 1.386 | 0.960 | 1.899 |
| | | | **$\sum S(O^{2-}) = 5.826$** |
| B(4)-O(4)#5 | 1.337 | 1.096 | 1.884 |
| B(4)-O(6) | 1.392 | 0.945 | 1.879 |
| B(4)-O(7) | 1.365 | 1.016 | 2.035 |

| | | | |
|---|---|---|---|
| | | | **$\sum S(O^{2-})$ = 5.798** |
| B(5)-O(5)#6 | 1.465 | 1.019 | 1.997 |
| B(5)-O(7)#6 | 1.465 | 1.019 | 2.035 |
| B(5)-O(8) | 1.470 | 1.005 | 2.007 |
| B(5)-O(9) | 1.467 | 1.013 | 2.040 |
| | | | **$\sum S(O^{2-})$ = 8.079** |

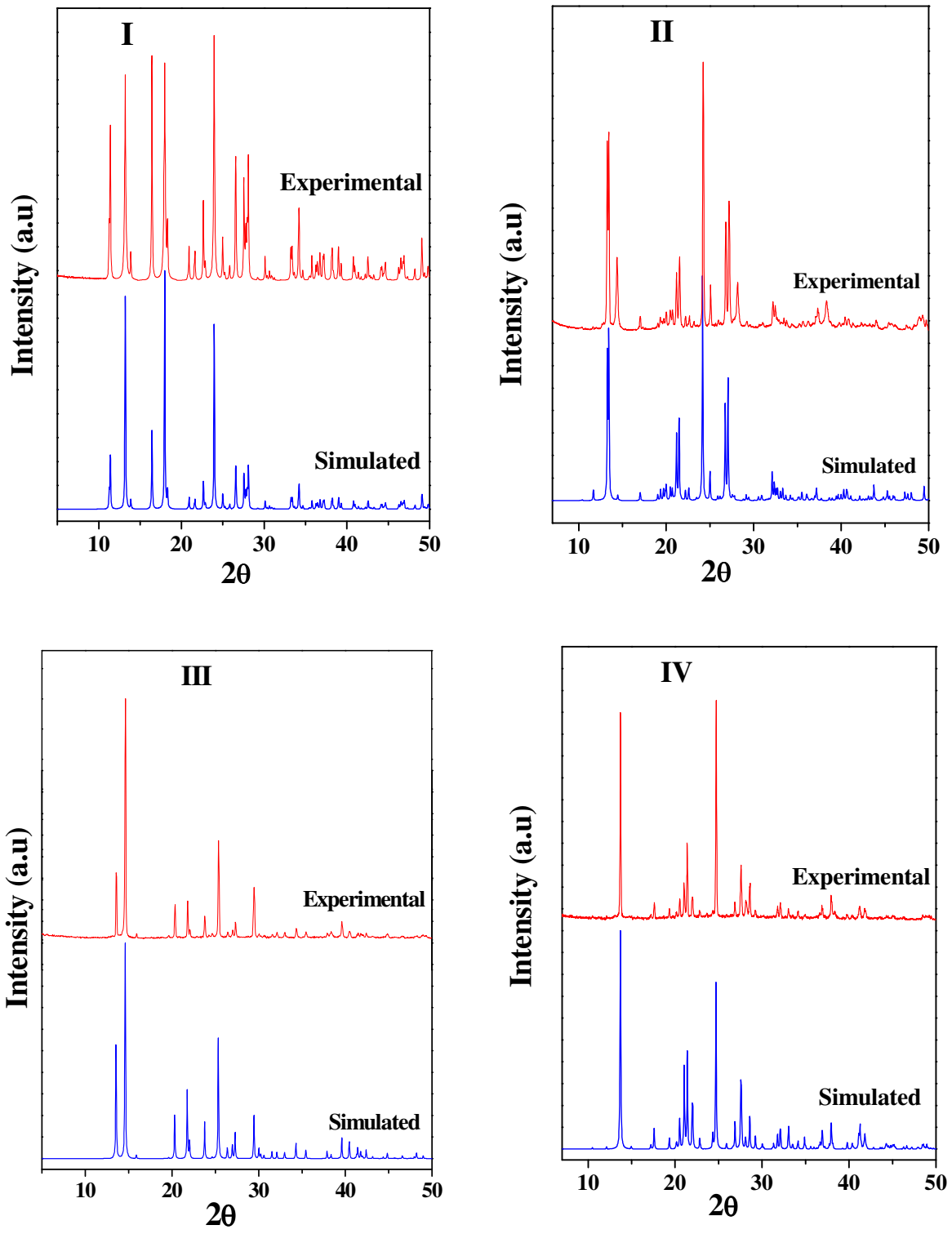



Fig. S1: Powder XRD (CuKα) pattern of the compounds **I–IV**.

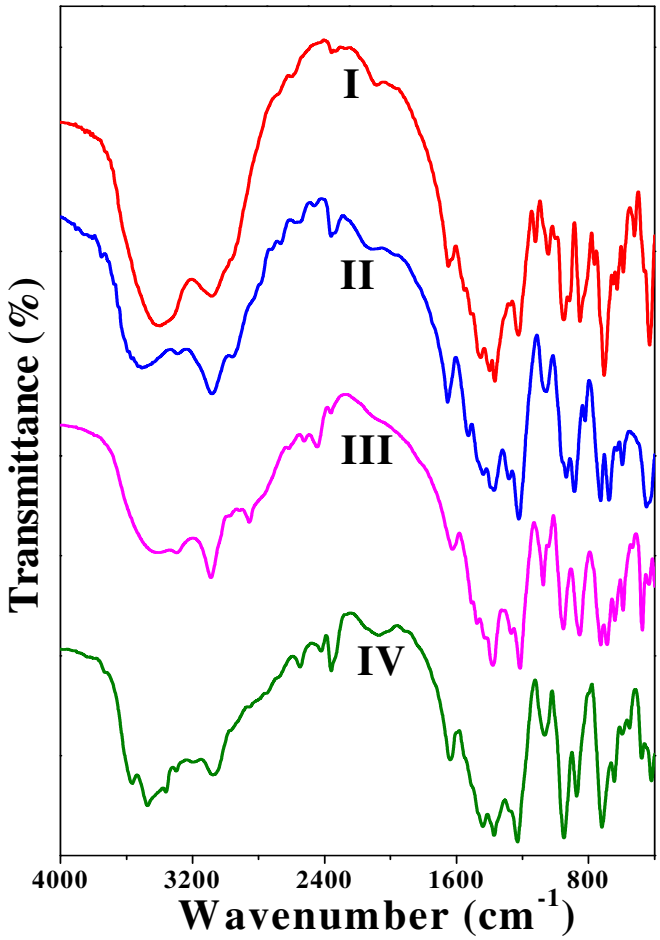



Fig. S2: IR spectra of **I– IV.**

IR spectra of all the compounds were more or less similar and can be described in terms of six distinct regions. (i) The compounds **I**, **II** and **IV** have a band at 3500-3400 $cm^{-1}$ region, indicative of the presence of the water molecules and -OH group associated with the borate unit; (ii) A band at 3073 $cm^{-1}$ region can be assigned to the symmetric stretching vibrations of N-H group of protonated amine molecules; (iii) The bands in the region 1650 – 1450 $cm^{-1}$ can be assigned to the N-H and C-H symmetric bond-bending vibrations as well as to the asymmetric stretching vibrations modes of the amine molecules; (iv) The strong bands at 1380 and 1220 $cm^{-1}$ region can be assigned to the trigonal borate units; (v) The bands in the region of 1124 – 1065 $cm^{-1}$ are due to the tetrahedral borate units and (vi) The bands in the region of 950-720 $cm^{-1}$ can be correlated with the Al-O stretching vibrations of tetrahedral $AlO_4$ groups.

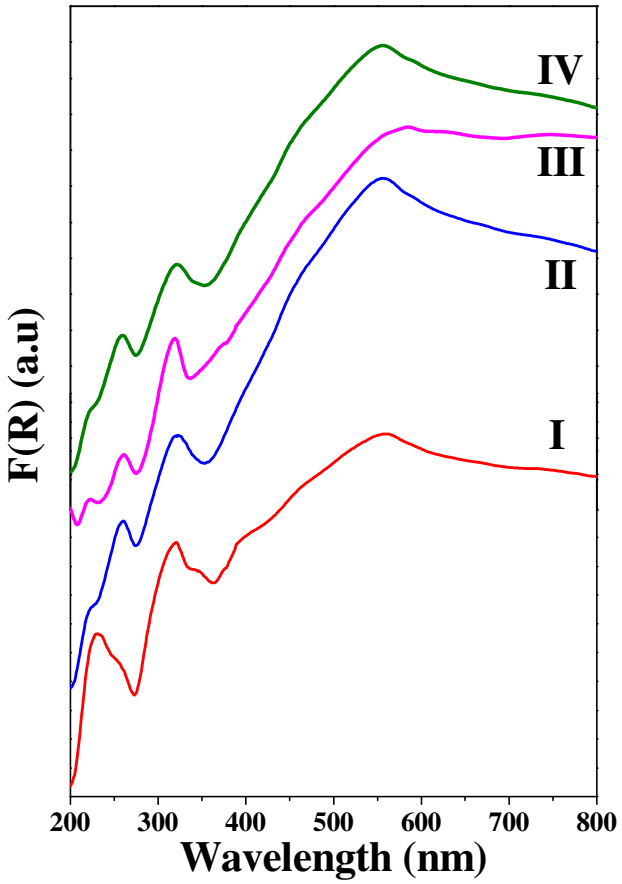



Fig. S3: The diffuse reflectance spectra of the compounds **I—IV** in Kubelka-Munk units. F(R) is the Kubelka-Munk function, where $F(R) = (1-R)^2/2R$, R is the experimentally observed reflectance.

**Experimental**: The powdered sample was placed inside a cuvette (75 mm × 80 mm × 20 mm) and the spectra were recorded in the diffuse reflectance mode using an integrating sphere of radius 50 mm. The Spectralon® was the coating material of the sphere to obtain the highest diffuse reflectance for the compounds

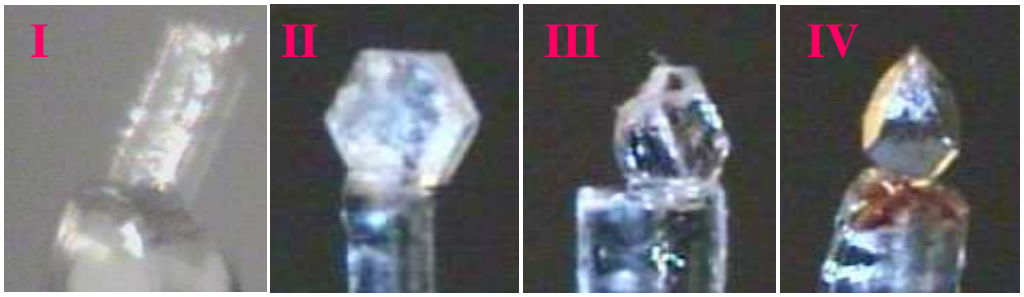
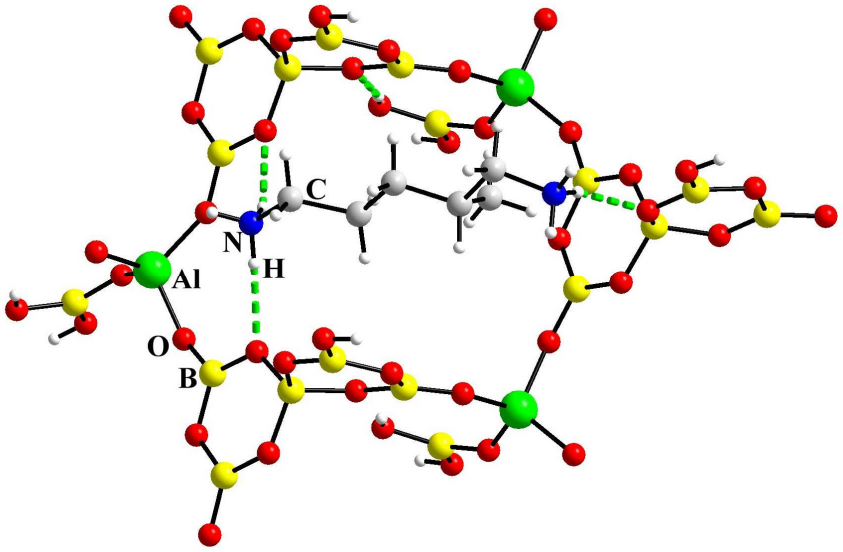
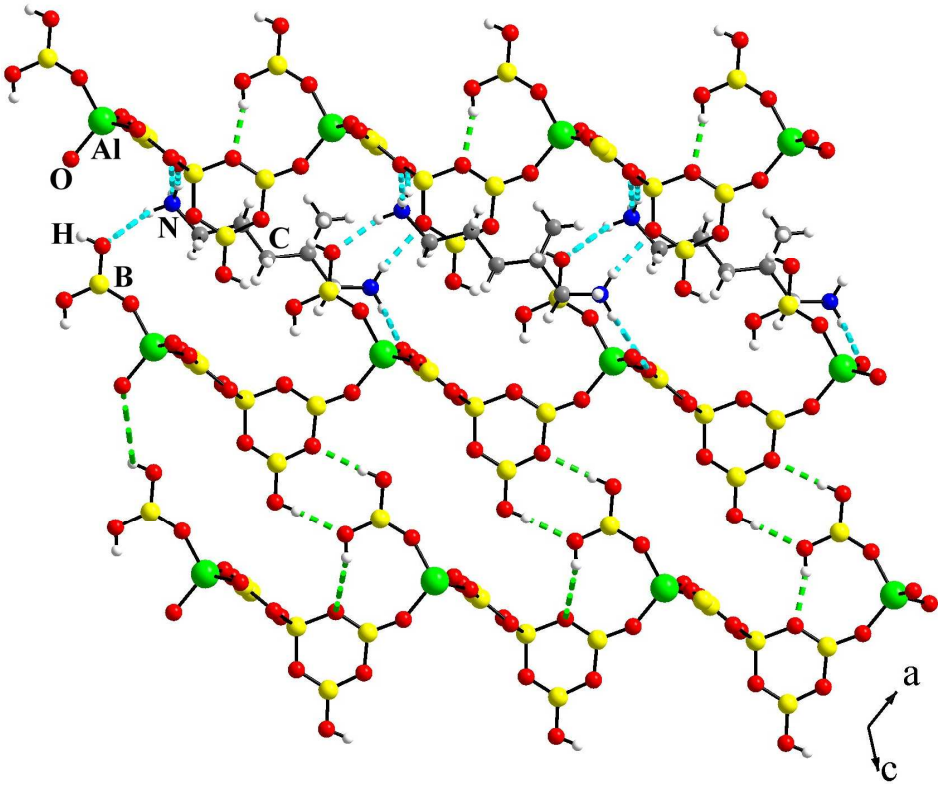



Fig. S4: Photos of single crystal of the compounds **I–IV.**

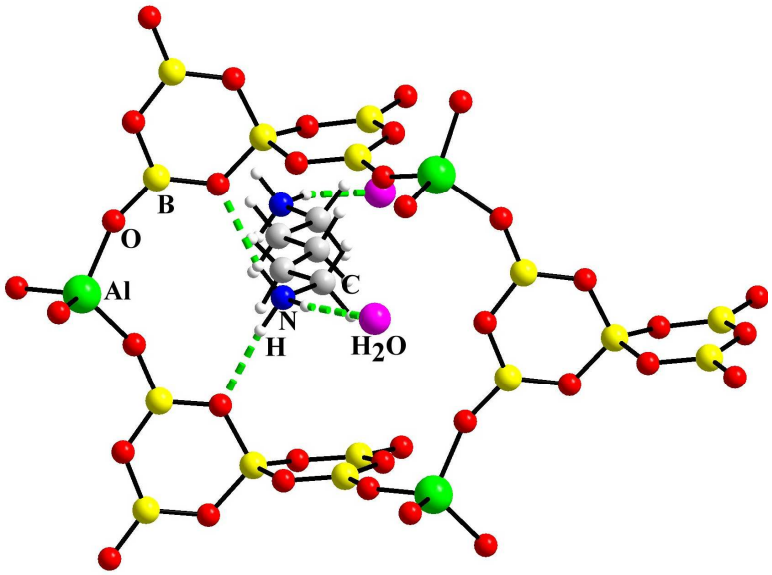



(a)

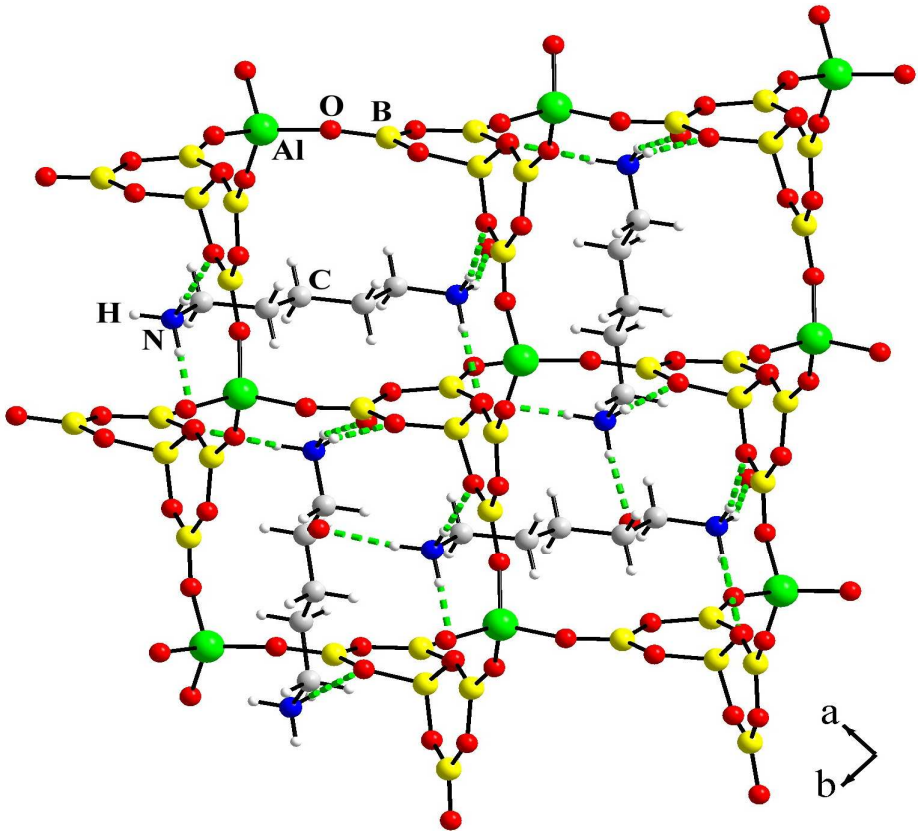



(b)

Fig. S5: (a) The 11 membered-ring observed by the connectivity between $Al^{3+}$ ions and $[B_5O_{10}H]$ units in the compound **I**. (b) The three-dimensional stacking of the layers is formed by the hydrogen bonding interactions of B-O-H units and amine molecules. The dotted line shows the observed hydrogen bonds.

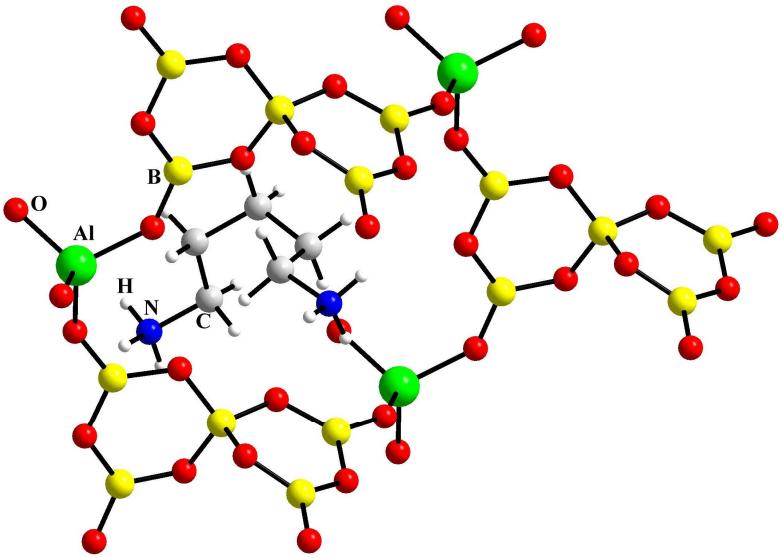



(b)

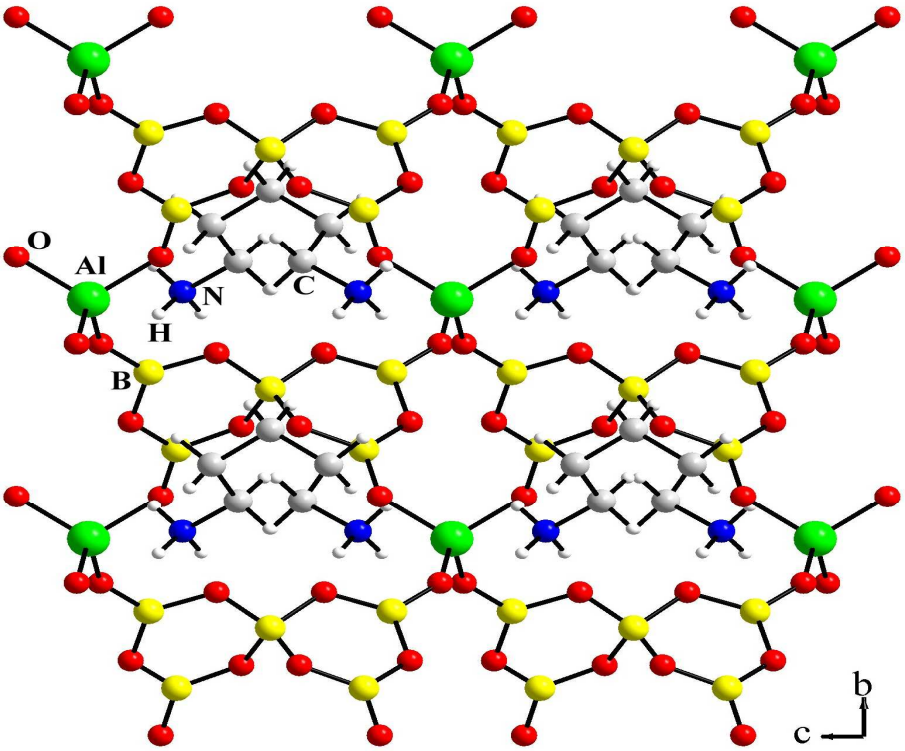



(b)

Fig. S6: (a) The 11 membered-ring observed by the connectivity between $Al^{3+}$ ions and $[B_5O_{10}]$ units in the compound **II**. (b) The figure shows the hydrogen bonding interactions of the amine molecules inside the channels in the '*ab*' plane. The dotted line shows the observed hydrogen bonds.

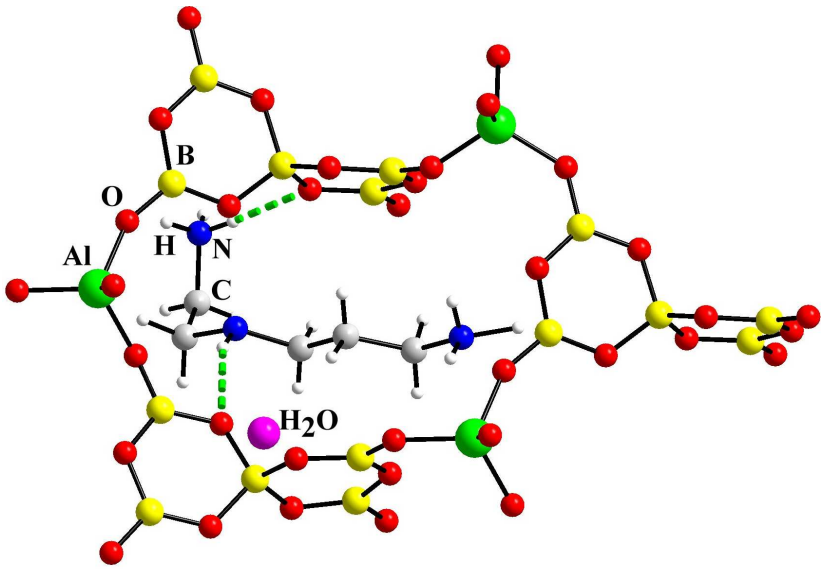



(a)

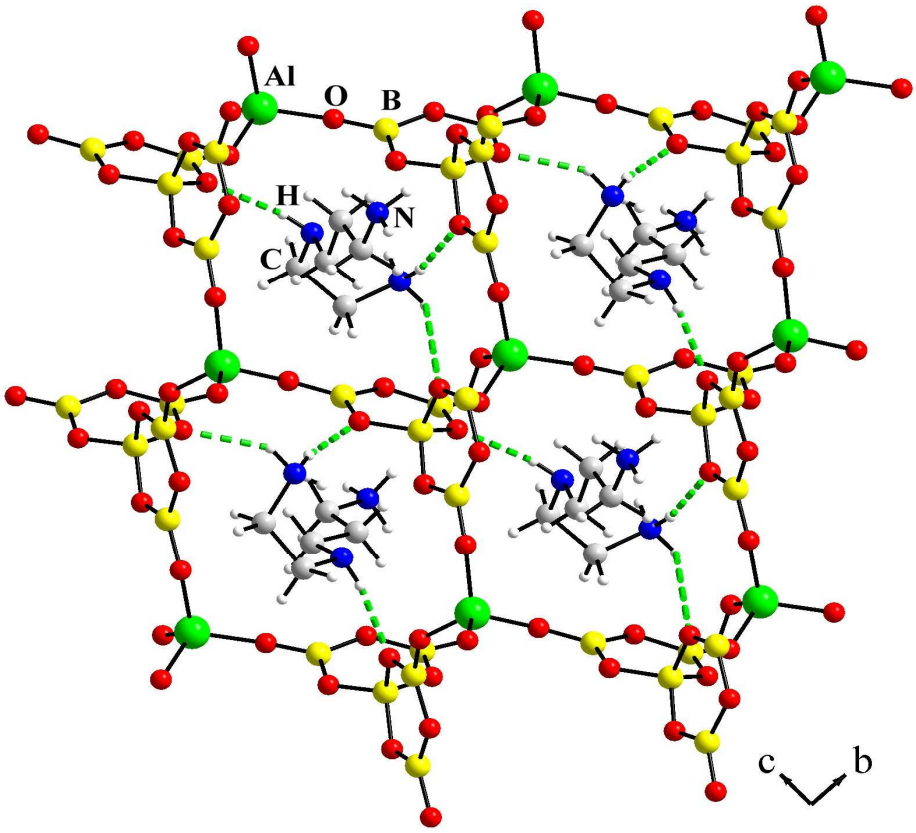



(b)

Fig. S7: (a) The 11 membered-ring observed by the connectivity between $Al^{3+}$ ions and $[B_5O_{10}]$ units in the compound **III**. (b) The figure shows the orientation of the amine molecules inside the one-dimensional channels in the '*bc*' plane.




(a)




(b)

Fig. S8: (a) The 11 membered-ring observed by the connectivity between $Al^{3+}$ ions and $[B_5O_{10}]$ units in the compound **IV**. (b) The figure shows the hydrogen bonding interactions of the amine molecules inside the channels in the '*bc*' plane. The dotted line shows the observed hydrogen bonds.

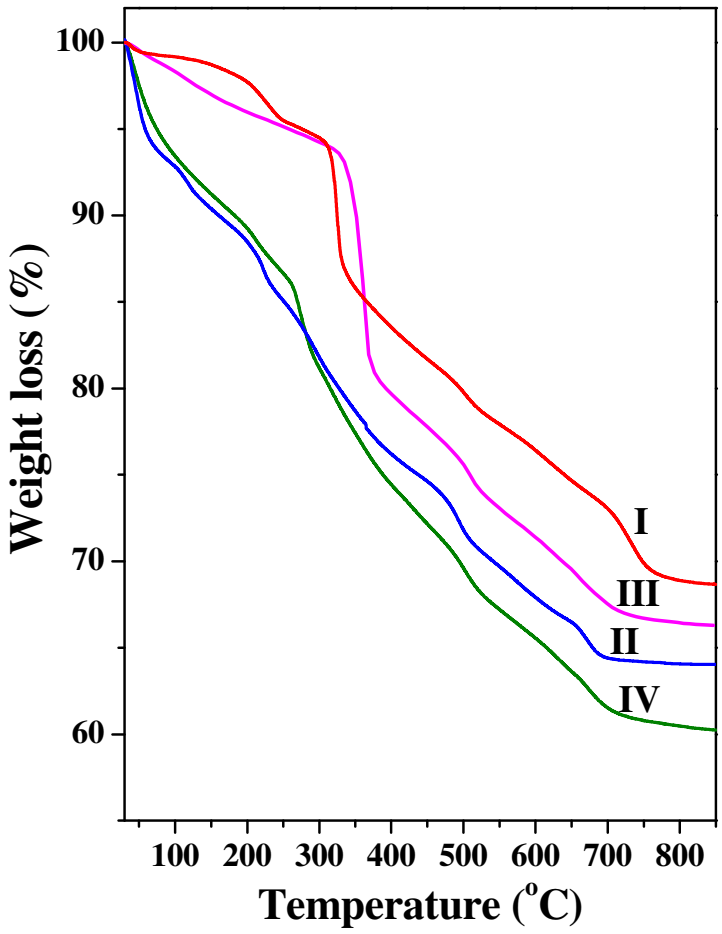
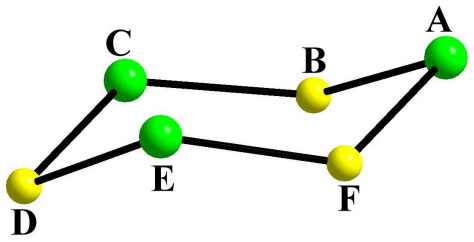
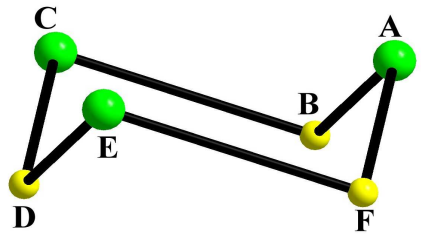


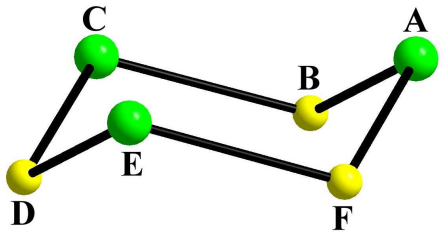

Fig. S9: TGA studies (in oxygen atmosphere) of **I-IV.**



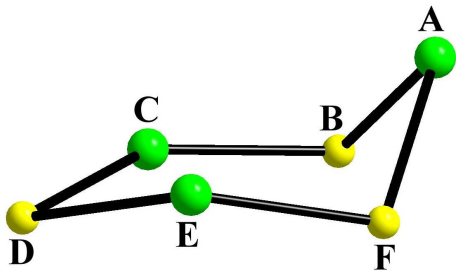

(**II**)




(**III**)



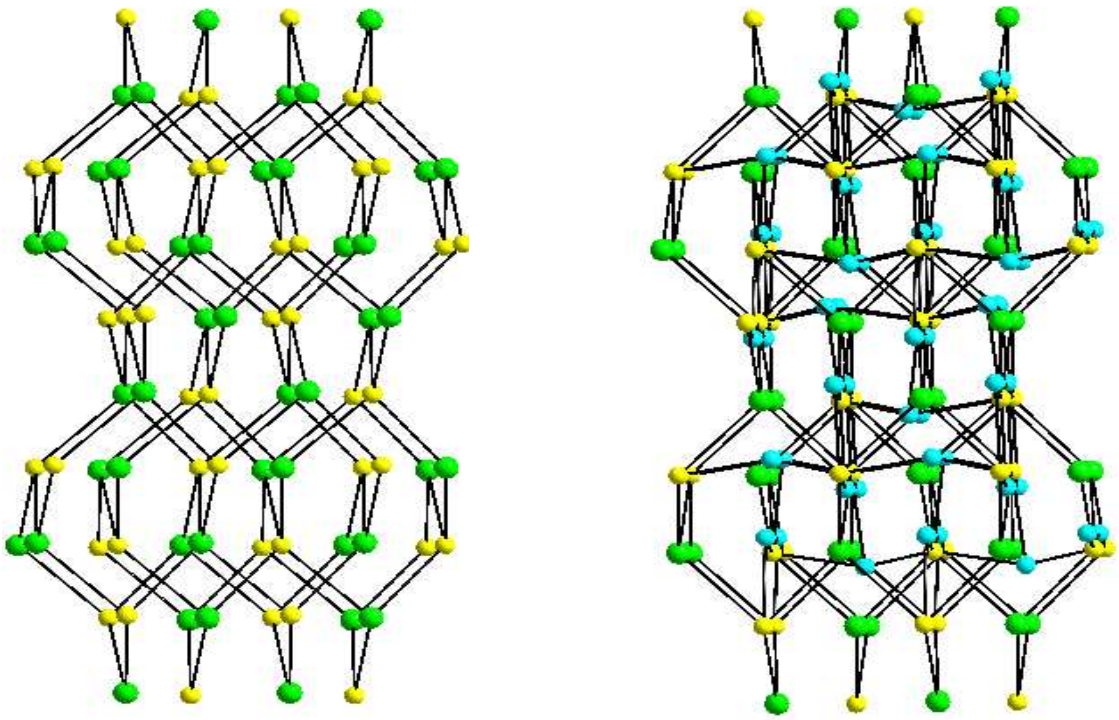

(**IV**)




$[CH_3NH_2(CH_2)_3NH_3][AlB_5O_{10}]$

| Dihedral Angle (deg) | $[(C_5H_{16}N_2)(AlB_5O_{10})].2H_2O$, **II** | $[(C_5H_{16}N_2)(AlB_5O_{10})]$, **III** | $[(C_5H_{17}N_3)(AlB_5O_{10})].H_2O$, **IV** | $[CH_3NH_2(CH_2)_3NH_3][AlB_5O_{10}]$ |
|---|---|---|---|---|
| <A-B-E-D | 176.0 | 180.0 | 180.0 | 153.0 |
| <B-C-F-E | 175.7 | 180.0 | 179.1 | 172.3 |
| <A-F-C-D | 180.0 | 180.0 | 178.0 | 150.0 |

Fig. S10: The observed six-membered building units and their dihedral angles between the opposite nodes for the diamond structures of compounds **I—IV** and $[CH_3NH_2(CH_2)_3NH_3][AlB_5O_{10}]$ (earlier reported).



(a) (b)

Fig. S11: (a) The connectivity involving Al centers and $B_5O_{10}$ units forming two-fold inter-penetrated diamond net in $[Li_2AlB_5O_{10}]$. (b) The observed 3,4,10-connected net in the compound $[Li_2AlB_5O_{10}]$. The Schläfli symbol of the net is $(4^3)_2(4^2.6^4)(4^8.6^{33}.8^4)$. The green atom corresponds to Al center, yellow atom corresponds to $B_5O_{10}$ unit and cyan atom corresponds to Li center.