

Supporting Materials:

## Synthesis and Structure of an Aluminoborate Consisting of 12-membered Borate Rings and Aluminate Clusters.

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Table S1 Crystallographic data of PKU-8

Formula	$[H_{18}Al_7B_{12}O_{36}]Cl_3$	
Formula mass (g/mol)	1019.07	
Crystal system	Rhombohedral	
Space group	<i>R</i> 3	
<i>a</i> /Å	15.0613(1)	
<i>c</i> /Å	14.0134(2)	
<i>V</i> /Å <sup>3</sup>	2752.962(54)	
<i>Z</i>	3	
Density	1.844	
Diffraction technique	Powder diffraction	
$\lambda$ /Å	1.5405	
Structure determination and refinement	TOPAS with Pseudovoigt peak function	
GOF	3.422	
Final <i>R</i> indices	<i>R</i> <sub>p</sub> = 0.0398, <i>R</i> <sub>w</sub> = 0.0557, <i>R</i> <sub>B</sub> = 0.0285	

Table S2 Atomic parameters, BVS, bond distances and angles in PKU-8, the possible hydroxyl groups are expressed in red

	x	y	z	occ	B	BVS	hydroxyl
Al1	0	0	0.75	1	1.954(66)	2.47	
Al2	0.8035(12)	0.9939(11)	0.7389(15)	1	1.954(66)	3.28	
Al3	0.0039(11)	0.1956(13)	0.7346(12)	1	1.954(66)	2.75	
O1	0.3944(17)	0.5920(19)	0.3370(16)	1	1.388(57)	1.46	OH
O2	0.2642(22)	0.7260(21)	0.4793(15)	1	1.388(57)	1.27	OH
O3	0.3299(20)	0.0909(21)	0.5440(21)	1	1.388(57)	1.84	
O4	0.2649(19)	0.9480(21)	0.6569(22)	1	1.388(57)	1.18	OH
O5	0.0800(23)	0.7170(23)	0.4900(27)	1	1.388(57)	1.26	OH
O6	0.9040(22)	0.6520(20)	0.5430(20)	1	1.388(57)	1.83	

O7	0.4620(29)	0.5429(30)	0.4730(14)	1	1.388(57)	2.18		
O8	0.0440(20)	0.7399(22)	0.6559(25)	1	1.388(57)	1.30	OH	
O9	0.5810(20)	0.5650(17)	0.5909(17)	1	1.388(57)	1.85		
O10	0.2840(23)	0.9199(24)	0.4890(25)	1	1.388(57)	1.27	OH	
O11	0.4179(18)	0.4239(17)	0.5960(20)	1	1.388(57)	2.18		
O12	0.2019(25)	0.7900(27)	0.3369(15)	1	1.388(57)	1.70		
B2	0.1739(44)	0.8170(43)	0.2480(23)	1	1.98(17)	3.25		
B1	0.4879(55)	0.5100(53)	0.5530(23)	1	1.98(17)	3.14		
B3	0.3289(52)	0.9930(49)	0.5690(61)	1	1.98(17)	2.88		
B4	0.0079(51)	0.6690(51)	0.5710(65)	1	1.98(17)	3.22		
Cl1	0.5865(17)	0.1643(8)	0.3607(11)	1	6.54(27)			
Cl2	0.8323(6)	0.9174(12)	0.4435(11)	0.8	2.75(19)			
Ow1	0.8225(13)	0.4172(33)	0.6488(13)	0.8	10.32(39)			
Ow2	0.0902(9)	0.5512(27)	0.7533(13)	1	4.00(31)			
Ow3	0.630(11)	0.382(11)	0.5909(36)	0.36	9.7(17)			
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Bond	distance	bond	distance					
Al1 O2	1.893(36)	Al1 O1	2.096(30)					
Al2 O1	1.790(31)	Al3 O7	1.859(34)					
Al2 O8	1.839(39)	Al3 O10	1.898(42)					
Al2 O7	1.859(37)	Al3 O1	1.929(21)					
Al2 O5	1.893(44)	Al3 O4	1.930(36)					
Al2 O12	1.943(32)	Al3 O12	1.983(29)					
Al2 O2	1.956(30)	Al3 O2	2.088(27)					
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B1 O3	1.321(57)	B3 O10	1.477(84)					
B1 O6	1.327(37)	B3 O9	1.488(82)					
B1 O12	1.438(51)	B3 O4	1.501(83)					
B2 O9	1.332(67)	B3 O3	1.508(34)					
B2 O11	1.338(61)	B4 O11	1.341(86)					
B2 O7	1.360(72)	B4 O5	1.485(86)					
		B4 O6	1.506(84)					
		B4 O8	1.507(87)					
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Bond	angle	bond	angle					
O9 B1 O11	119.9(47)	O9 B3 O4	109.6(38)					
O9 B1 O7	119.6(52)	O9 B3 O3	109.6(17)					
O11 B1 O7	120.5(42)	O4 B3 O3	109.2(19)					
O3 B2 O6	120.8(16)	O11B4 O5	109.2(65)					
O3 B2 O12	122.9(12)	O11B4 O6	109.2(33)					
O6 B2 O12	116.0(20)	O11B4 O8	107.6(52)					
O10 B3 O9	111.6(62)	O5 B4 O6	112.9(41)					
O10 B3 O4	108.0(57)	O5 B4 O8	110.0(34)					
O10 B3 O3	108.8(18)	O6 B4 O8	108.0(62)					

**Figure S1** Rietveld fitting for powder X-ray diffraction pattern of PKU-8; the symbol • and solid line represent the observed and calculated patterns; the difference curve and calculated reflection positions are shown below the diffraction pattern

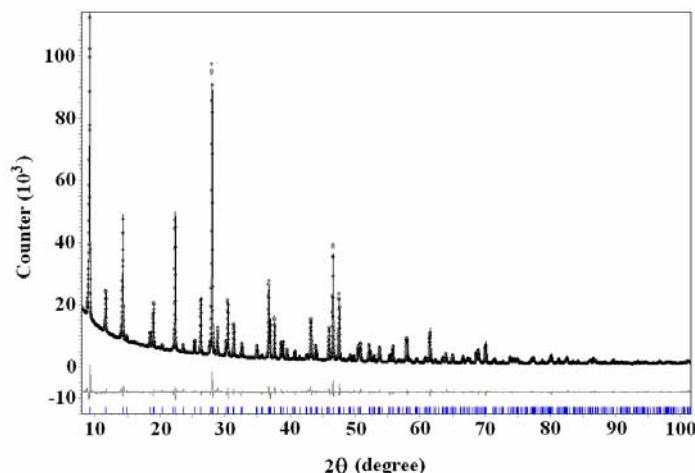


Figure S2. Products formed under different reaction conditions

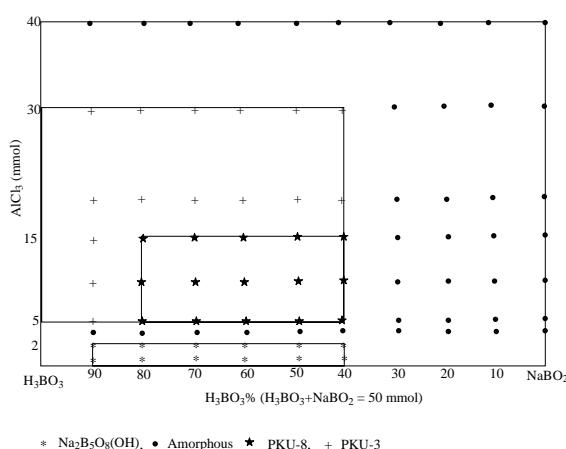


Figure S3. Electron diffraction pattern of PKU-8 along [0-10] direction and TEM image of the crystals

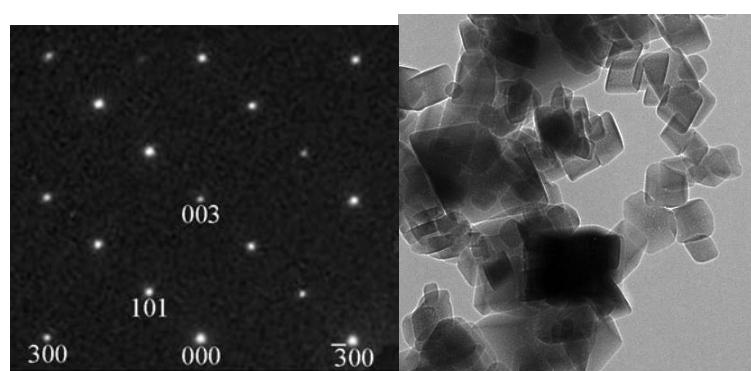


Figure S4. IR spectrum of PKU-8

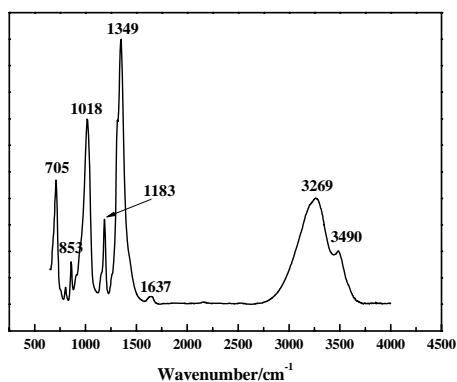


Figure S5. The MAS-NMR spectra of PKU-8, (A)  $^{11}\text{B}$  and  $^{27}\text{Al}$  and (B)  $^1\text{H}$

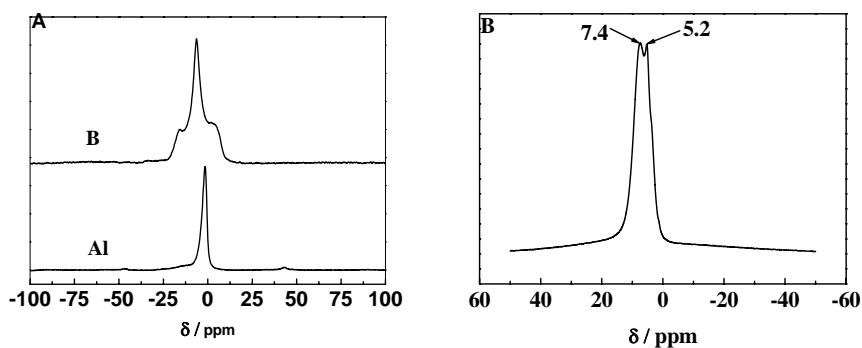


Figure S6. The XRD patterns of PKU-8 samples after heated at different temperatures

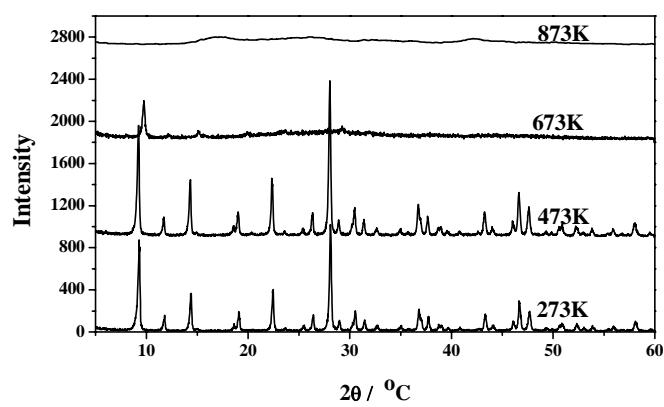


Figure S7. TGA-MS curves of PKU-8, which shows the temperature dependence of the weight-loss and the decomposed gas-phases (HCl and H<sub>2</sub>O)

