Electronic Supplementary Information

Syntheses, structures and properties of two new members of the pentaborate family: $NaKB_5O_8(OH)\cdot H_2O$ and $KB_5O_8\cdot 2H_2O$

Xiaojing Li,‡[a,b] Luyong Zhang,‡[a,b] Fuming Li,[a,b] Zhihua Yang,[a,b] Xueling Hou *[a,b] and Fangfang Zhang *[a,b]

[a]Research Center for Crystal Materials; State Key Laboratory of Functional Materials and Devices for Special Environmental Conditions; Xinjiang Key Laboratory of Functional Crystal Materials; Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 40-1 South Beijing Road, Urumqi 830011, China.

[b]Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.

‡These authors contributed equally to this work.

*Corresponding authors, E-mails: xlhou@ms.xjb.ac.cn, ffzhang@ms.xjb.ac.cn

Table S1. Crystal data and structure refinement for **I** and **II**.

	I	**II**
Empirical formula	$NaKB_5O_8(OH)\cdot H_2O$	$KB_5O_8\cdot 2H_2O$
Formula weight	279.16	257.18
Crystal system	Triclinic	Orthorhombic
Space group	*P***Error!**	*Fddd*
a (Å)	6.6157(5)	11.883(3)
b (Å)	6.6221(5)	13.115(3)
c (Å)	11.1837(8)	21.624(5)
α (°)	78.713(3)	90
β (°)	76.654(2)	90
γ (°)	60.592(2)	90
Volume (Å^3)	413.33(5)	3370.1(14)
Z, Calculated density (g·cm^{-3})	2, 2.243	16, 2.028
Absorption coefficient (mm^{-1})	0.738	0.670
F(000)	276	2048
Theta range for data collection (°)	1.880 to 27.514	2.497 to 27.472
Limiting indices	$-8 \le h \le 8$	$-15 \le h \le 12$
	$-8 \le k \le 8$	$-15 \le k \le 16$
	$-14 \le l \le 14$	$-28 \le l \le 27$
Reflections collected / unique	6945 / 1899 [*R*(int) = 0.0560]	4890 / 969 [*R*(int) = 0.0492]
Completeness (%)	99.7	99.7
Data / restraints / parameters	1899 / 0 / 154	969 / 0 / 74
Goodness-of-fit on F^2	1.081	1.074
Final *R* indices [$F_o^2 > 2\sigma(F_o^2)$][a]	$R_1 = 0.0348$, $wR_2 = 0.0756$	$R_1 = 0.0423$, $wR_2 = 0.1018$
R indices (all data)[a]	$R_1 = 0.0442$, $wR_2 = 0.0857$	$R_1 = 0.0567$, $wR_2 = 0.1099$
Largest diff. peak and hole (e·Å^{-3})	0.360 and −0.371	0.419 and −0.445

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Atomic coordinates (× 10^4), equivalent isotropic displacement parameters (Å^2 × 10^3), Wyckoff positions, and BVS calculations for **I**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyck.	x	y	z	U_{eq}	BVS[a]
K(1)	2i	6594(1)	1830(1)	788(1)	20(1)	1.23
Na(1)	2i	3058(2)	11037(2)	3977(1)	24(1)	1.17
B(1)	2i	2012(4)	6651(4)	4085(2)	16(1)	3.05
B(2)	2i	1439(4)	5467(4)	2289(2)	13(1)	3.06
B(3)	2i	3162(4)	8126(4)	1971(2)	13(1)	3.04
B(4)	2i	7580(4)	6513(4)	1673(2)	14(1)	3.06
B(5)	2i	10676(4)	2520(4)	1645(2)	13(1)	3.06
O(1)	2i	6899(3)	10342(3)	3866(2)	28(1)	0.44
O(2)	2i	1750(3)	6627(3)	5358(2)	26(1)	1.02
O(3)	2i	1411(3)	5267(3)	3652(1)	18(1)	1.91
O(4)	2i	3104(2)	6195(2)	1610(1)	12(1)	2.06
O(5)	2i	2777(3)	8084(3)	3354(1)	18(1)	2.04
O(6)	2i	5408(2)	8155(3)	1491(1)	16(1)	2.00
O(7)	2i	8992(3)	7104(3)	2074(2)	18(1)	1.87
O(8)	2i	8446(3)	4230(3)	1426(2)	21(1)	2.11
O(9)	2i	12110(2)	3097(2)	2028(1)	14(1)	2.20
O(10)	2i	11248(3)	330(3)	1486(1)	15(1)	2.03

[a]BVS are calculated by using the bond-valence model ($S_i = \exp[(R_o - R_i)/B]$, where R_o is an empirical constant, R_i is the length of bond *i* (in angstroms), and B = 0.37). The R_o parameters used are 1.371 for B-O, 2.132 for K-O, and 1.803 for Na-O, respectively.

Table S3. Atomic coordinates (× 10^4), equivalent isotropic displacement parameters (Å^2 × 10^3), Wyckoff positions, and BVS calculations for **II**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyck.	x	y	z	U_{eq}	BVS[a]
K(1)	16e	3233(1)	1250	1250	27(1)	1.08
B(1)	32h	3820(2)	307(2)	2652(1)	13(1)	3.03
B(2)	32h	36(2)	−1597(2)	478(1)	14(1)	3.07
B(3)	16f	1250	−752(3)	1250	14(1)	3.09
O(1)	32h	3035(1)	1055(1)	2506(1)	16(1)	2.12
O(2)	32h	4235(1)	−179(1)	2136(1)	16(1)	2.11
O(3)	32h	1614(1)	−104(1)	735(1)	16(1)	2.02
O(4)	32h	308(1)	−1412(1)	1071(1)	16(1)	1.85
O(5)	32h	5309(2)	1982(2)	1932(1)	54(1)	0.088

[a]BVS are calculated by using the bond-valence model ($S_i = \exp[(R_o - R_i)/B]$, where R_o is an empirical constant, R_i is the length of bond *i* (in angstroms), and B = 0.37). The R_o parameters used are 1.371 for B-O and 2.132 for K-O, respectively.

Table S4. Hydrogen coordinates (× 10^4), isotropic displacement parameters (Å^2 × 10^3), and Wyckoff positions for **I** and **II**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Compounds	Atoms	Wyck.	x	y	z	U_{eq}
I	H(1)	2i	1326	5436	5736	39
	H(2)	2i	7728	9377	3219	42
	H(3)	2i	7415	11457	3810	42
II	H(1)	32h	5502	2628	1812	81
	H(2)	32h	5491	1763	2324	81

Table S5. Selected bond lengths (Å) and angles (°) for **I**.

K(1)-O(9)#3	2.7461(15)	B(1)-O(2)	1.392(3)
K(1)-O(4)#2	2.7525(15)	B(2)-O(9)#3	1.476(3)
K(1)-O(4)	2.8347(15)	B(2)-O(4)	1.419(3)
K(1)-O(10)	2.9795(15)	B(2)-O(7)#3	1.486(3)
K(1)-O(10)#4	2.8794(16)	B(2)-O(3)	1.502(3)
K(1)-O(6)#1	2.8282(15)	B(3)-O(4)	1.434(3)
K(1)-O(7)#1	2.9660(16)	B(3)-O(10)#6	1.490(3)
K(1)-O(8)	2.7006(15)	B(3)-O(6)	1.467(3)
Na(1)-O(9)#6	2.3732(17)	B(3)-O(5)	1.505(3)
Na(1)-O(3)#7	2.4402(18)	B(4)-O(6)	1.342(3)
Na(1)-O(5)	2.3005(17)	B(4)-O(7)	1.359(3)
Na(1)-O(2)#8	2.755(2)	B(4)-O(8)	1.390(3)
Na(1)-O(1)	2.3269(19)	B(5)-O(9)	1.355(3)
Na(1)-O(1)#5	2.407(2)	B(5)-O(10)	1.345(3)
B(1)-O(3)	1.361(3)	B(5)-O(8)	1.392(3)
B(1)-O(5)	1.343(3)		
O(9)#3-K(1)-O(4)#2	115.24(5)	O(5)-Na(1)-O(9)#6	86.96(6)
O(9)#3-K(1)-O(4)	50.47(4)	O(5)-Na(1)-O(3)#7	139.74(7)
O(9)#3-K(1)-O(10)#4	128.26(4)	O(5)-Na(1)-O(2)#8	90.51(6)
O(9)#3-K(1)-O(10)	135.74(5)	O(5)-Na(1)-O(1)#5	97.80(7)
O(9)#3-K(1)-O(6)#1	65.03(4)	O(5)-Na(1)-O(1)	114.00(7)
O(9)#3-K(1)-O(7)#1	98.57(5)	O(1)-Na(1)-O(9)#6	102.60(7)
O(4)#2-K(1)-O(4)	91.15(4)	O(1)#5-Na(1)-O(3)#7	111.56(7)
O(4)-K(1)-O(10)#4	138.98(4)	O(1)-Na(1)-O(3)#7	94.92(7)
O(4)#2-K(1)-O(10)	104.44(4)	O(1)-Na(1)-O(2)#8	155.12(7)
O(4)-K(1)-O(10)	112.76(4)	O(1)#5-Na(1)-O(2)#8	85.07(6)
O(4)#2-K(1)-O(10)#4	49.89(4)	O(1)-Na(1)-O(1)#5	87.27(7)
O(4)#2-K(1)-O(6)#1	122.56(5)	O(3)-B(1)-O(2)	118.0(2)
O(4)-K(1)-O(7)#1	133.29(5)	O(5)-B(1)-O(3)	123.7(2)
O(4)#2-K(1)-O(7)#1	135.54(5)	O(5)-B(1)-O(2)	118.3(2)
O(10)#4-K(1)-O(10)	92.01(4)	O(9)#3-B(2)-O(7)#3	110.58(17)
O(10)#4-K(1)-O(7)#1	86.82(4)	O(9)#3-B(2)-O(3)	104.72(16)
O(6)#1-K(1)-O(4)	115.35(4)	O(4)-B(2)-O(9)#3	110.58(17)
O(6)#1-K(1)-O(10)#4	83.52(4)	O(4)-B(2)-O(7)#3	113.35(18)
O(6)#1-K(1)-O(10)	109.32(4)	O(4)-B(2)-O(3)	110.97(17)
O(6)#1-K(1)-O(7)#1	47.43(4)	O(7)#3-B(2)-O(3)	106.20(17)
O(7)#1-K(1)-O(10)	61.91(4)	O(4)-B(3)-O(10)#6	108.77(16)
O(8)-K(1)-O(9)#3	111.11(5)	O(4)-B(3)-O(6)	112.32(18)
O(8)-K(1)-O(4)#2	90.19(5)	O(4)-B(3)-O(5)	111.60(17)
O(8)-K(1)-O(4)	67.53(4)	O(10)#6-B(3)-O(5)	108.14(17)
O(8)-K(1)-O(10)	47.98(4)	O(6)-B(3)-O(10)#6	108.49(17)
O(8)-K(1)-O(10)#4	117.24(5)	O(6)-B(3)-O(5)	107.41(16)
O(8)-K(1)-O(6)#1	146.19(5)	O(6)-B(4)-O(7)	119.5(2)

O(8)-K(1)-O(7)#1	104.24(5)	O(6)-B(4)-O(8)	121.37(19)
O(9)#6-Na(1)-O(3)#7	58.66(5)	O(7)-B(4)-O(8)	119.11(19)
O(9)#6-Na(1)-O(2)#8	82.01(6)	O(9)-B(5)-O(8)	120.06(19)
O(9)#6-Na(1)-O(1)#5	166.28(7)	O(10)-B(5)-O(9)	123.7(2)
O(3)#7-Na(1)-O(2)#8	66.28(6)	O(10)-B(5)-O(8)	116.18(19)

Symmetry transformations used to generate equivalent atoms:

#1 x, y−1, z

#2 −x+1, −y+1, −z

#3 x−1, y, z

#4 −x+2, −y, −z

#5 −x+1, −y+2, −z+1

#6 x−1, y+1, z

#7 x, y+1, z

#8 −x, −y+2, −z+1

Table S6. Selected bond lengths (Å) and angles (°) for **II**.

K(1)-O(1)#1	2.7381(17)	B(1)-O(2)	1.376(3)
K(1)-O(1)	2.7381(17)	B(1)-O(3)#2	1.336(3)
K(1)-O(2)#1	2.9331(17)	B(2)-O(1)#3	1.379(3)
K(1)-O(2)	2.9331(17)	B(2)-O(2)#4	1.366(3)
K(1)-O(3)#1	2.8448(18)	B(2)-O(4)	1.345(3)
K(1)-O(3)	2.8449(18)	B(3)-O(3)	1.465(3)
K(1)-O(5)	3.030(3)	B(3)-O(3)#5	1.465(3)
K(1)-O(5)#1	3.030(3)	B(3)-O(4)	1.467(3)
B(1)-O(1)	1.390(3)	B(3)-O(4)#5	1.467(3)
O(1)-K(1)-O(1)#1	170.12(8)	O(3)#1-K(1)-O(2)	114.71(5)
O(1)#1-K(1)-O(2)	137.95(5)	O(3)-K(1)-O(2)#1	114.71(5)
O(1)-K(1)-O(2)#1	137.95(5)	O(3)#1-K(1)-O(3)	94.90(8)
O(1)#1-K(1)-O(2)#1	47.73(5)	O(3)#1-K(1)-O(5)	99.33(6)
O(1)-K(1)-O(2)	47.73(5)	O(3)-K(1)-O(5)#1	99.33(6)
O(1)-K(1)-O(3)#1	67.17(5)	O(3)-K(1)-O(5)	159.83(6)
O(1)-K(1)-O(3)	105.75(5)	O(3)#1-K(1)-O(5)#1	159.83(6)
O(1)#1-K(1)-O(3)	67.17(5)	O(5)-K(1)-O(5)#1	71.04(10)
O(1)#1-K(1)-O(3)#1	105.75(5)	O(2)-B(1)-O(1)	112.6(2)
O(1)#1-K(1)-O(5)	121.57(6)	O(3)#2-B(1)-O(1)	122.0(2)
O(1)#1-K(1)-O(5)#1	67.46(6)	O(3)#2-B(1)-O(2)	125.4(2)
O(1)-K(1)-O(5)#1	121.57(6)	O(2)#4-B(2)-O(1)#3	121.6(2)
O(1)-K(1)-O(5)	67.46(6)	O(4)-B(2)-O(1)#3	120.6(2)
O(2)-K(1)-O(2)#1	132.09(8)	O(4)-B(2)-O(2)#4	117.7(2)
O(2)-K(1)-O(5)	63.51(6)	O(3)#5-B(3)-O(3)	109.1(3)
O(2)-K(1)-O(5)#1	77.59(6)	O(3)#5-B(3)-O(4)#5	111.57(9)
O(2)#1-K(1)-O(5)	77.59(6)	O(3)-B(3)-O(4)	111.57(9)
O(2)#1-K(1)-O(5)#1	63.51(6)	O(3)-B(3)-O(4)#5	108.47(9)
O(3)-K(1)-O(2)	97.53(5)	O(3)#5-B(3)-O(4)	108.47(9)
O(3)#1-K(1)-O(2)#1	97.53(5)	O(4)#5-B(3)-O(4)	107.6(3)

Symmetry transformations used to generate equivalent atoms:

#1 x, −y+1/4, −z+1/4 #2 x+1/4, −y, z+1/4

#3 x−1/4, −y, z−1/4 #4 x−1/2, −y−1/4, −z+1/4

#5 −x+1/4, y, −z+1/4

Table S7. Hydrogen bond lengths (Å) and angles (°) for **I** and **II**. D, hydrogen bond donor; A, hydrogen bond acceptor.

Compounds	D-H···A	$d_{(D-H)}$ (Å)	$d_{(H\cdots A)}$ (Å)	$d_{(D-A)}$ (Å)	D-H···A (°)
I	O(2)-H(1)···O(3)#2	0.95	2.02	2.852(2)	144.1
	O(1)-H(3)···O(2)#1	0.94	2.04	2.895(2)	150.1
	O(1)-H(2)···O(7)	0.94	1.90	2.831(2)	167.5
	Symmetry transformations used to generate equivalent atoms:				
	#1 −x+1, −y+2, −z+1		#2 −x, −y+1, −z+1		
II	O(5)-H(1)···O(4)#1	0.92	2.51	3.260(3)	139.3
	O(5)-H(1)···O(4)#2	0.92	2.05	2.811(3)	139.7
	Symmetry transformations used to generate equivalent atoms:				
	#1 −x+3/4, y+1/2, −z+1/4		#2 x+1/2, y+1/2, z		

Table S8. Assignments of the absorption bands observed in the IR spectrum of **I**.

Absorption bands (cm^{-1})	Assignment
3473, 3397	asymmetric stretching of H-O
1639	the bending of group H-O-H
1356, 1262	asymmetric stretching of B-O in the $[BO_3]$
1136, 1089, 1043	asymmetric stretching of B-O in the $[BO_4]$
937, 883	symmetric stretching of B-O in the $[BO_3]$
828, 743	symmetric stretching of B-O in the $[BO_4]$
700, 624	out-of-plane bending modes of $[BO_3]$
565, 536	bending modes of $[BO_3]$ and $[BO_4]$

Table S9. Real-space atom-cutting analysis of the calculated birefringence of the title compounds. The cutting radii of Na, K, B, O, and H were set as 1.05, 1.50, 0.88, 1.12, and 0.32 Å, respectively.

Compounds	Cut units	Δ*n* (at 1064 nm)
I	None	0.0610
	Na	0.0589
	K	0.0601
	H_2O	0.0592
	$[BO_3]+[BO_2(OH)]+[BO_4]$	0.0158
II	None	0.0704
	K	0.0641
	H_2O	0.0619
	$[BO_3]+[BO_4]$	0.0128

Table S10. The birefringence and the density of π-conjugated units of the title compounds.

Compounds	Birefringence at 1064 nm (cal.)	π-conjugated units	The density of π-conjugated units ($Å^{-3}$)
I	0.061	$[BO_3]$, $[BO_2(OH)]$	0.0145
II	0.070	$[BO_3]$	0.0190

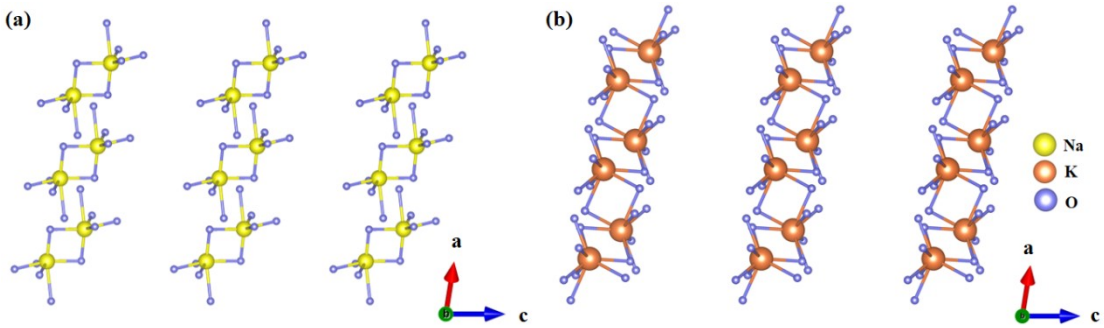

Figure S1. (a) The isolated $[Na_2O_{10}]$ dimers in **II**. (b) The $^1[KO_6]_\infty$ chains in **I**.

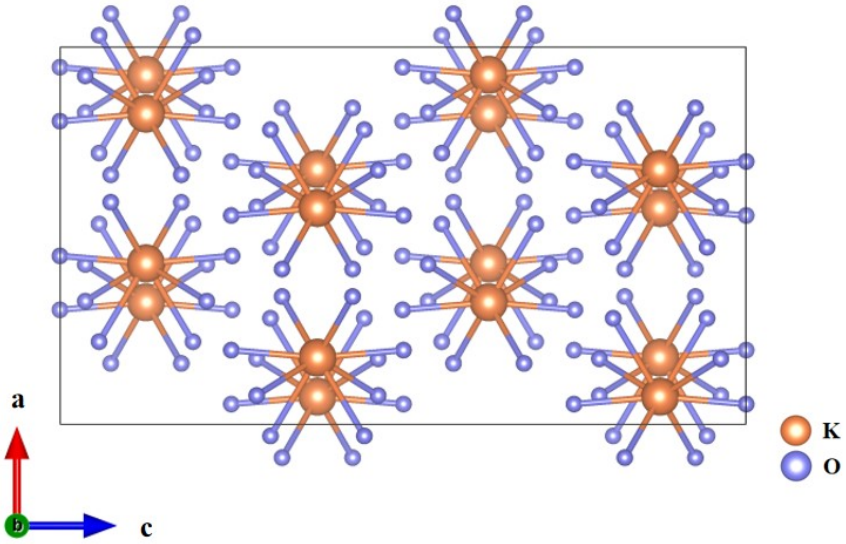

Figure S2. The isolated [KO_8] polyhedra in **II**.

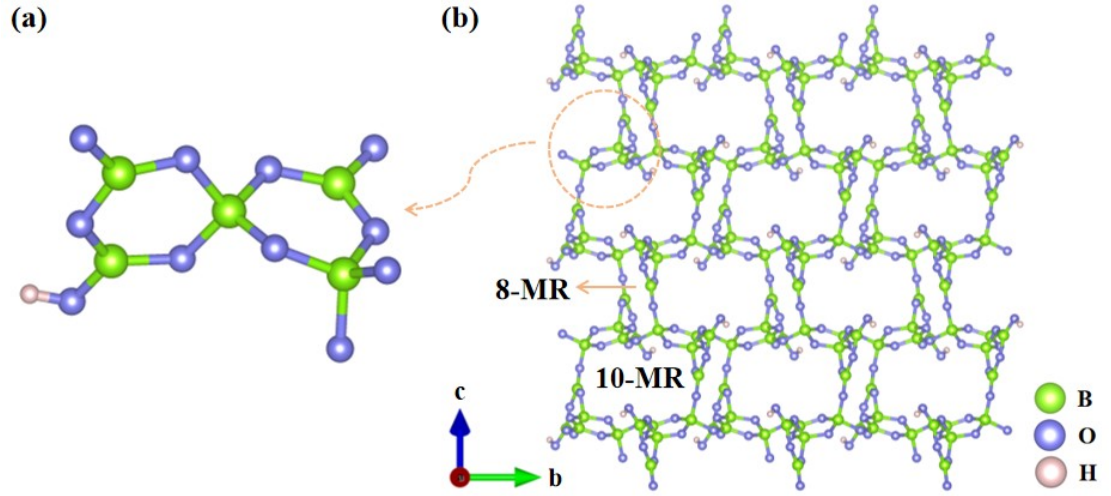

Figure S3. Crystal structure of $LiCsB_5O_8(OH)\cdot H_2O$. (a) $[B_5O_{10}(OH)]$ FBB. (b) The $^2[B_5O_8(OH)]_\infty$ layer with 8- and 10- membered rings (MRs).

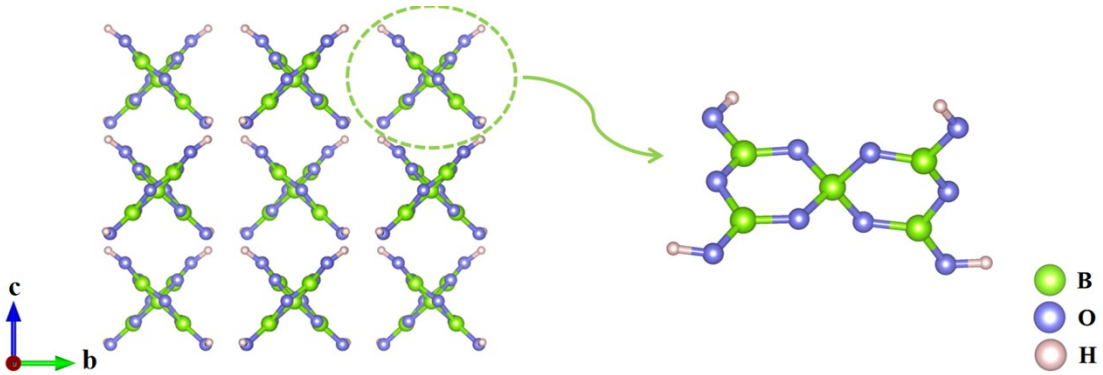

Figure S4. The isolated $[B_5O_6(OH)_4]$ FBBs in $KB_5O_8{\cdot}4H_2O$.

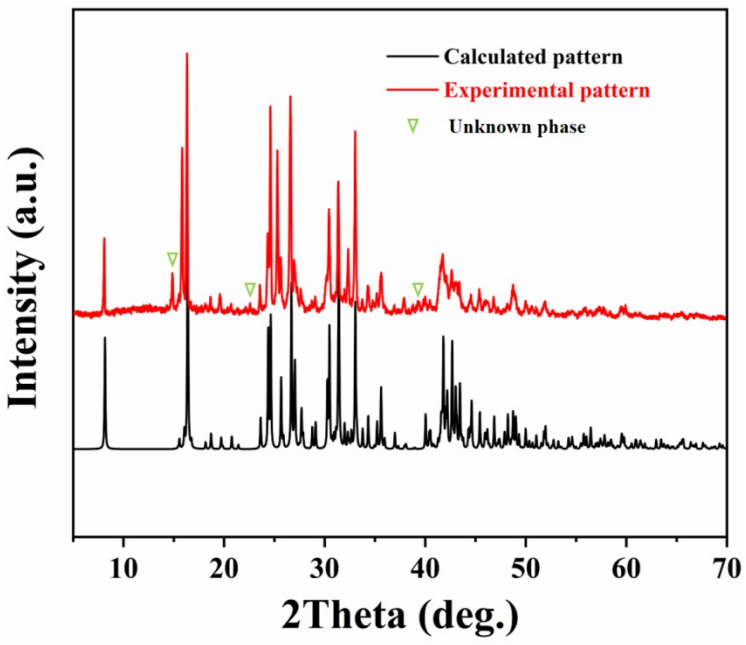

Figure S5. Calculated and experimental powder XRD patterns of **I**. The green inverted triangle symbols represent the impurity peaks of unknown phase.

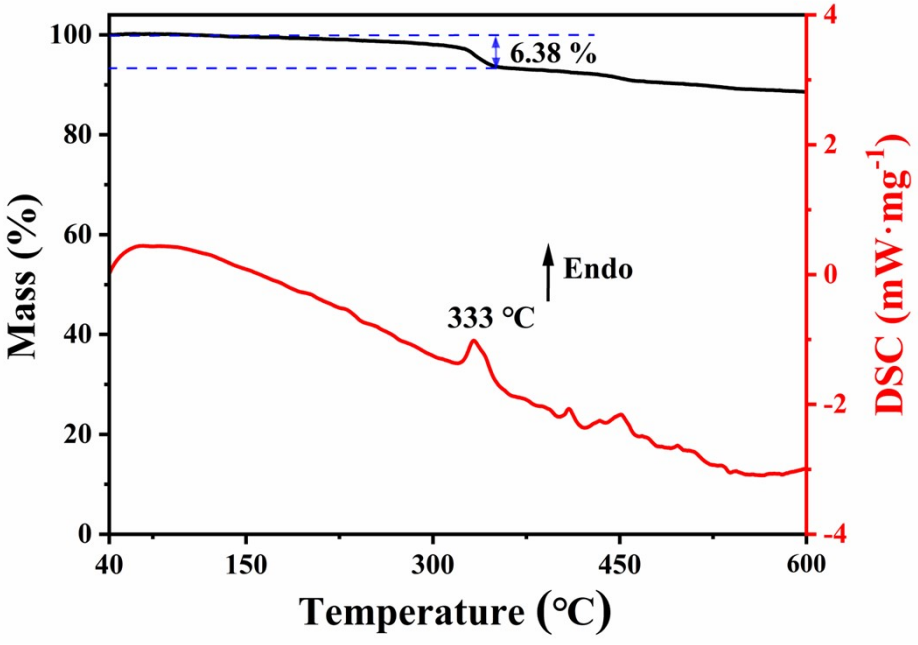

Figure S6. TG-DSC curves of **I**.

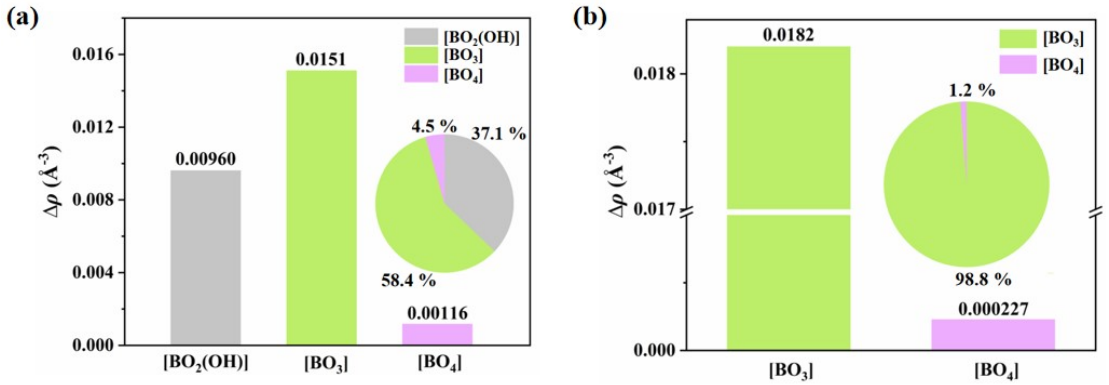

Figure S7. Bonding electron density difference (Δρ) of anionic groups calculated by adopting the REDA method for **I** (a) and **II** (b).