Temperature dependence of photoluminescence, hydrogen bonding and revealed for the first time in Templated family: synthesis, structure and properties of a Pentborate [Emmim][$B_5O_6(OH)_4$]

Kang Zhou,[a] Zhuo-Qing Chen, Zhi-Qiang Liu, Jun Li, Feng-Hua Zhao, Chun-Yang Pan*[a]

[a]*school of Chemical Engineering and Light Industry，Guangdong University of technology，Guangzhou, Guangdong 510006, China* Tel: +86-020-39322231 Fax: +86-020-39322231.

*Corresponding author: Chun-Yang Pan, E-mail: panchuny@gdut.edu.cn

Sample treatment

The title compound was divided into four parts (denoted A, B, C and D) after drying treatment. The samples B, C, and D were put in the Al_2O_3 crucible, and annealed to 100, 150 and 200℃ for 1 hour, and then cooled to room temperature.

Table S1 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) of [Emmim]·[$B_5O_6(OH)_4$](296K).

Atoms	x	y	z	Ueq
B1	-0.0634(4)	0.8834(4)	0.1869(5)	0.0416(11)
B2	-0.0596(4)	1.0864(4)	0.1870(4)	0.0423(11)
B3	0.1202(3)	0.9833(4)	0.2408(4)	0.0347(9)
B4	0.3064(4)	0.9314(4)	0.1425(4)	0.0384(10)
B5	0.3004(4)	0.9330(4)	0.3470(4)	0.0412(11)
O1	-0.1298(3)	0.7874(3)	0.1687(3)	0.0560(9)

O2	-0.1241(3)	1.1826(3)	0.1697(3)	0.0623(10)
O3	0.3762(3)	0.9154(3)	0.0489(3)	0.0523(8)
O4	0.3638(3)	0.9166(4)	0.4425(3)	0.0612(10)
O5	-0.1142(3)	0.9852(3)	0.1554(3)	0.0545(8)
O6	0.0486(2)	1.0869(2)	0.2354(2)	0.0389(7)
O7	0.0441(2)	0.8796(2)	0.2365(3)	0.0400(7)
O8	0.1983(2)	0.9793(3)	0.1379(2)	0.0405(7)
O9	0.3542(2)	0.8985(3)	0.2453(3)	0.0497(8)
O10	0.1917(2)	0.9804(2)	0.3445(2)	0.0374(6)
C1	0.3452(6)	0.3230(5)	0.5198(6)	0.0782(18)
C2	0.1363(7)	0.4008(6)	0.6453(7)	0.096(2)
C3	0.1285(8)	0.6598(11)	0.6513(11)	0.166(6)
C4	0.1250(6)	0.7714(4)	0.6469(9)	0.174(6)
C5	0.2205(4)	0.4688(4)	0.5943(4)	0.0825(19)
C6	0.3798(4)	0.5400(4)	0.5052(4)	0.092(2)
C7	0.3174(6)	0.6236(7)	0.5399(8)	0.098(2)
N1	0.3084(5)	0.4371(5)	0.5465(5)	0.0850(16)
N2	0.2130(4)	0.5882(4)	0.6010(4)	0.0665(12)

Table S2 Selected bond length (Å) and angle(°) for [Emmim]·$[B_5O_6(OH)_4]$(296K).

B1—O7	1.353(5)	B3—O7	1.486(5)
B1—O1	1.366(6)	B3—O8	1.493(5)
B1—O5	1.369(6)	B4—O8	1.350(5)
B2—O6	1.353(5)	B4—O3	1.363(5)
B2—O2	1.354(5)	B4—O9	1.370(6)
B2—O5	1.383(5)	B5—O4	1.340(5)
B3—O6	1.456(5)	B5—O10	1.354(5)
B3—O10	1.457(5)	B5—O9	1.393(6)

O7—B1—O1	122.6(4)	O6—B3—O7	110.3(3)
O7—B1—O5	121.6(4)	O6—B3—O8	108.9(3)
O1—B1—O5	115.8(4)	O7—B3—O8	107.1(3)
O6—B2—O2	123.5(4)	O8—B4—O3	123.7(4)
O6—B2—O5	121.5(4)	O8—B4—O9	120.8(4)
O2—B2—O5	115.0(4)	O3—B4—O9	115.6(3)
O10—B3—O8	109.5(3)	O4—B5—O9	115.5(4)
O6—B3—O10	111.5(3)	O4—B5—O10	124.5(4)
O10—B3—O7	109.5(3)	O10—B5—O9	120.0(4)

Table S3 Details of Hydrogen Bonds for [Emmim]·[$B_5O_6(OH)_4$] in different temperature.

Temperature (K)	D-H	d(D–H) (A ˚)	d(H···A) (Å)	∠D—H···A (°)	d(D···A) (A ˚)
90	O1—H1···O6^{i}	0.82	1.927	169.98	2.739
	O2—H2···O7^{ii}	0.82	1.881	167.66	2.688
	O3—H3···O10^{iii}	0.82	1.942	168.55	2.750
	O4—H4···O8^{iv}	0.82	1.854	165.41	2.656
120	O1—H1···O6^{i}	0.82	1.937	170.43	2.749
	O2—H2···O7^{ii}	0.82	1.879	168.09	2.687
	O3—H3···O10^{iii}	0.82	1.942	170.10	2.754
	O4—H4···O8^{iv}	0.82	1.869	165.38	2.670
173	O1—H1···O6^{i}	0.82	1.93	170.9	2.741
	O2—H2···O7^{ii}	0.82	1.89	168.7	2.694
	O3—H3···O10^{iii}	0.82	1.95	169.2	2.761
	O4—H4···O8^{iv}	0.82	1.87	166.2	2.673
268	O1—H1···O6^{i}	0.82	1.94	170.4	2.750
	O2—H2···O7^{ii}	0.82	1.89	168.1	2.699

	O3—H3···O10^{iii}	0.82	1.97	168.2	2.775
	O4—H4···O8^{iv}	0.82	1.88	165.1	2.679
296	O1—H1···O6^{i}	0.82	1.935	167.62	2.741
	O2—H2···O7^{ii}	0.82	1.884	167.99	2.692
	O3—H3···O10^{iii}	0.82	1.983	175.05	2.801
	O4—H4···O8^{iv}	0.82	1.889	165.81	2.692
348	O1—H1···O6^{i}	0.82	1.947	163.24	2.743
	O2—H2···O7^{ii}	0.82	1.901	165.31	2.702
	O3—H3···O10^{iii}	0.82	1.989	171.52	2.803
	O4—H4···O8^{iv}	0.82	1.897	164.39	2.696

Symmetry codes: (i) -x, -0.5+y, 0.5-z; (ii) -x, 0.5+y, 0.5-z; (iii) 0.5-x, 2-y, -0.5+z; (iv) 0.5-x, 2-y, 0.5+z.

Table S4. The length of four hydrogen bond at different test temperature.

Temperature	90k	120k	173k	268k	296k	348k
O1—H1···O6/Å	1.927	1.937	1.93	1.94	1.935	1.947
O2—H2···O7/Å	1.881	1.879	1.89	1.89	1.884	1.901
O3—H3···O10/Å	1.942	1.942	1.95	1.97	1.983	1.989
O4—H4···O8/Å	1.854	1.869	1.87	1.88	1.889	1.897

Table S5. The changes of length about O···O at different test temperature.

Temperature	90k	120k	173k	268k	296k	348k
O1···O6/Å	2.739	2.749	2.741	2.750	2.741	2.743
O2···O7/Å	2.688	2.687	2.694	2.699	2.692	2.702
O3···O10/Å	2.750	2.754	2.761	2.775	2.801	2.803
O4···O8/Å	2.656	2.656	2.673	2.679	2.692	2.696

Table S6. The changes of four hydrogen bond angle at different test temperature.

Temperature	90k	120k	173k	268k	296k	348k
O1—H1···O6/°	169.98	170.43	170.9	170.4	167.62	163.24
O2—H2···O7/°	167.66	168.09	168.7	168.1	167.99	165.31
O3—H3···O10/°	168.55	170.10	169.2	168.2	175.05	171.52
O4—H4···O8/°	165.41	165.38	166.2	165.1	165.81	164.39

Table S7. Crystal data and structure refinement for [Emmim][$B_5O_6(OH)_4$] heated at 423K for an hour under .

Formula sum	$C_7H_{17}B_5N_2O_{10}$
Formula weight	343.25
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	11.2905(3)
b (Å)	11.5410(3)
c (Å)	11.6362(4)
α /°	90.00
β/°	90.00
γ/°	90.00
Cell volume (Å3)	1516.24(8)
Z	4
Temperaturere(K)	423
Measured reflections	9726
Independent reflections	2673
R_{int}	0.0227
GOF on *F2*	2.306
F(000)	615
Indices ranges	-12 =< h =< 13, -13 =< k =< 13, -11 =< l =< 13
Final R Indices [I>2σ(I)] [a]	R_1=0.0854, wR_2=0.2628

R indices (all data) [b]	R_1= 0.0905, wR_2=0.2703
Largest diff. Peak and hole (e.A^{-3}) (e.A-	1.479 and -0.490
Refinement method	full-matrix least-squares on F^2

[a] $R_1 = \_F_o - F_c / F_o$. [b] $wR_2 = [w(F_o^2 - F_c^2)^2 / w(F_o^2)^2]^{1/2}$

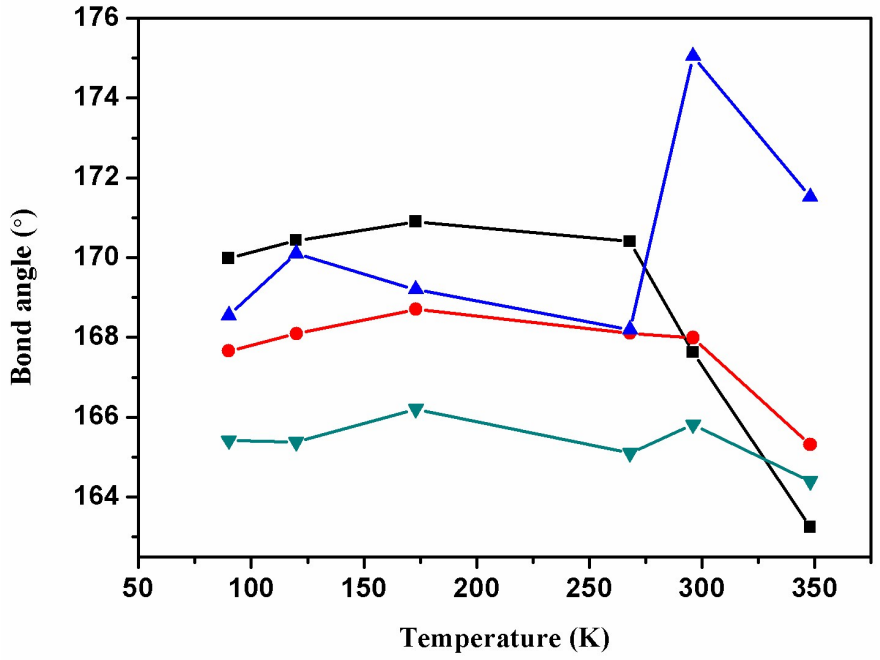

Figure S1. The change trend of four hydrogen bond angle O1—H1···O6 (black); O2—H2···O7 (red); O3—H3···O10 (blue); O4—H4···O8 (green).

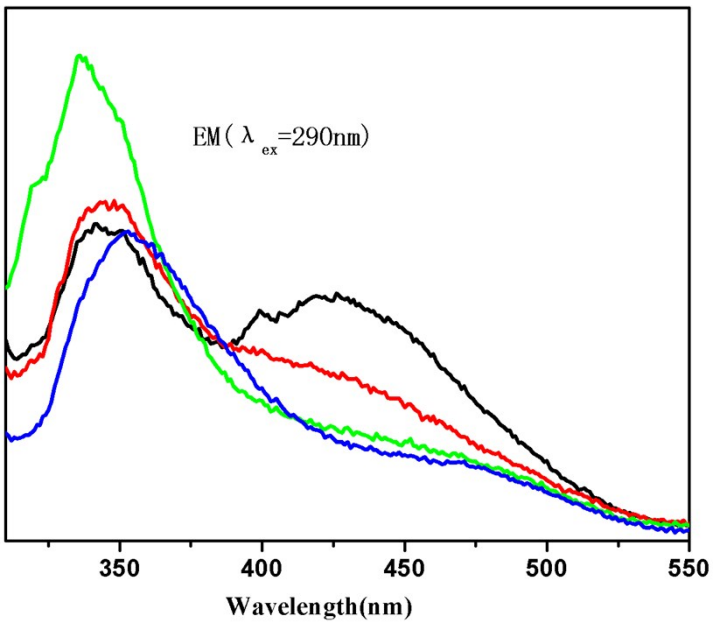

Figure S2. Emission spectra of sample A (black, no treatment), B (red, processed by 100 ℃), C (green, processed by 150 ℃), D (blue, processed by 200℃).