Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Caption:

Section 1: Experimental Section:

Compound **1** can be prepared by means of the boric acid reflux method. Typically, a mixture of H_3BO_3, $Na_2B_4O_7{\cdot}10H_2O$, $Na_2HPO_4{\cdot}12H_2O$, CH_3COOK and $Cd(CH_3COO)_2{\cdot}2H_2O$ with the molar composition of 20: 1.5: 1 :2: 1.6 was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 6 days. After the mixture was slowly cooled to RT, colourless columnar crystals were isolated. The crystals were washed with deionized water (50 °C) until the residual H_3BO_3 was completely removed, purified ultrasonically, and dried in air. The yield of **1** is about 68% based on $Cd(CH_3COO)_2{\cdot}2H_2O$. In addition, we tried to prepare compound **1** without adding $Na_2B_4O_7{\cdot}10H_2O$ during the synthesis process, unfortunately, **1** could not be synthesized by using the same synthesis method, we only obtained the known colorless prism crystals $NaCd(H_2O)_2[BP_2O_8]{\cdot}0.8H_2O$ with the B/P ratio of 1/2 which was previously reported by kniep *et. al*. in 2003.

Section 2: Structure determination:

The suitable single crystal (0.24 × 0.22 × 0.15 mm) was selected for single-crystal X-ray diffraction. The data were collected on a Bruker APEX-II CCD diffractometer (Mo-Kα, λ =0.71073 Å) at 293(2) K. A total of 8754 reflections were collected, of which 1113 reflections were unique (R_{int} = 0.0477). The structure was solved by the direct method and refined by the full-matrix least-squares on F^2 using the *SHELXTL* crystallographic software package. The Cd, B, P, O, Na and K atoms could be located from a difference Fourier map. The H atoms bonded to protonated O(7) have been added, the H atoms attached to O(1W) and O(2W) were not added due to their disorders. The non-hydrogen atoms were refined anisotropically. Crystal data: $B_9Cd_3H_7KNa_5O_{38}P_6$, Hexagonal, space group $P6_3/m$ (no. 176), a = 12.071(3) Å, b = 12.071(3) Å, c = 12.118(2) Å, V = 1529.1(6) Å^3, Z = 2, D_c = 3.009 g·cm^{-1}, μ = 2.737 mm^{-1}, F(000) = 1320, GOF = 1.071, R_1 = 0.0919 and wR_2 = 0.2092 ($I > 2\sigma(I)$). The selected bond lengths and angles of **1** are provided in Table S1.

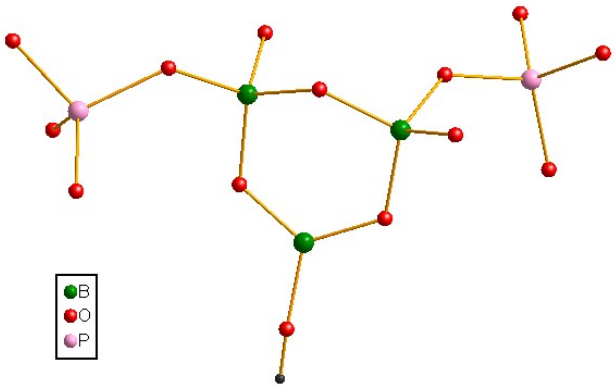

Figure S1. The structure for the FBU of the borophosphate anion.

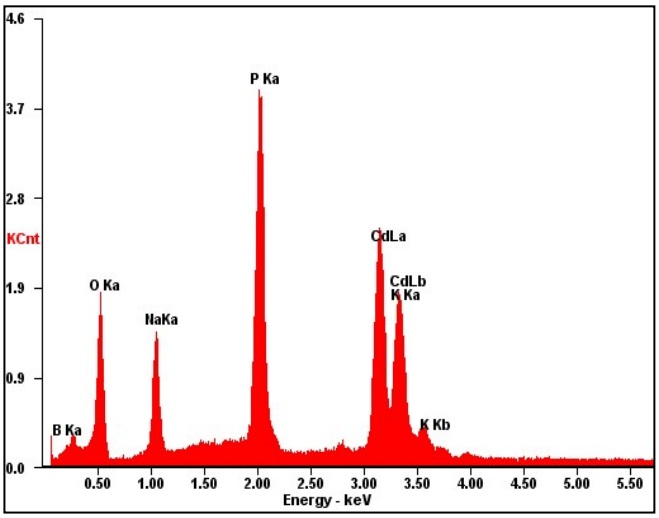

Figure S2. The EDS spectrum for **1**.

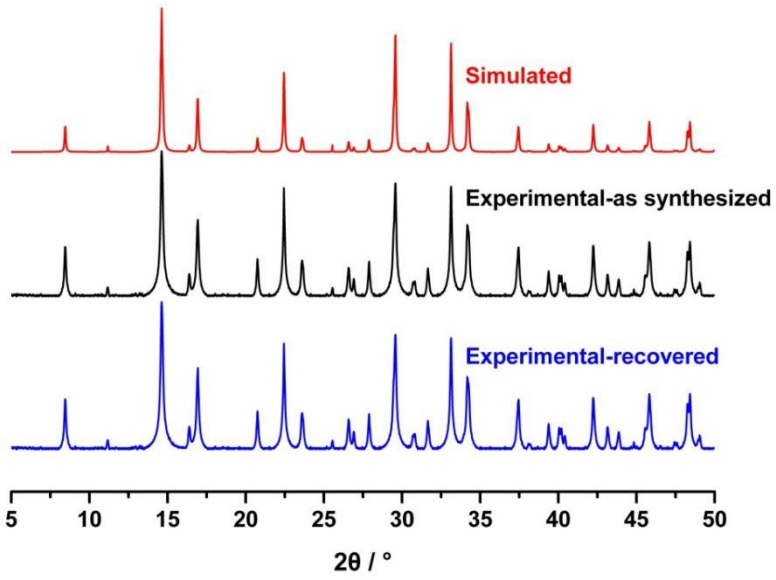

Figure S3. The simulated, experimental (as-synthesized, **1**) and experimental after performing ion exchange (recovered) powder XRD patterns.

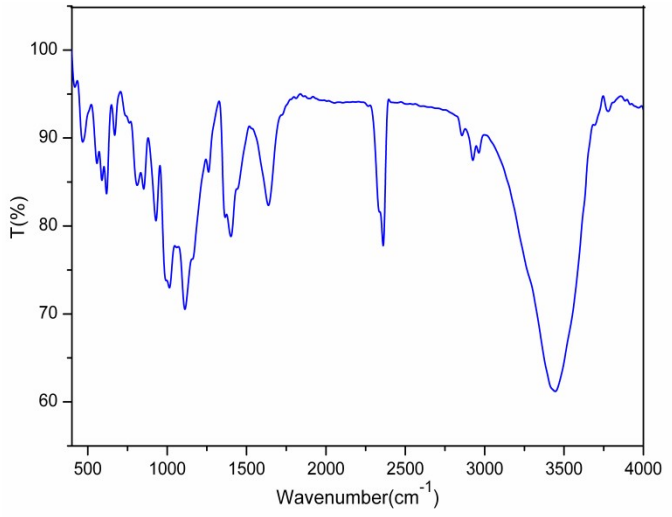

Figure S4. The IR spectrum for **1**.

Figure S5. The luminescence spectra (a: emission curve; b: excitation curve) for **1**.

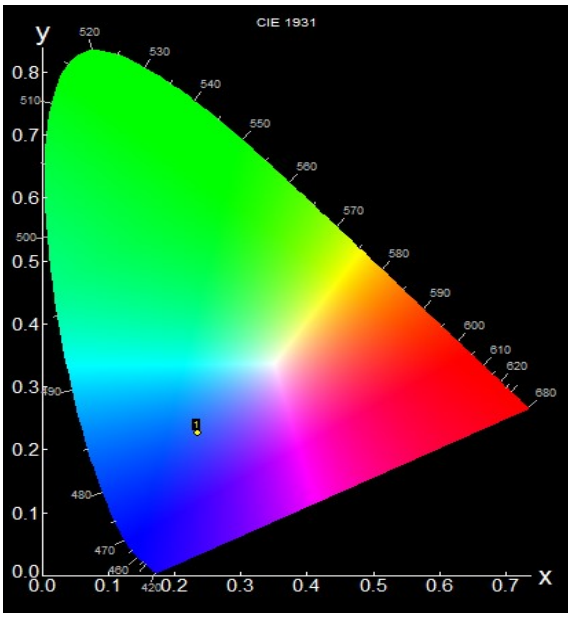

Figure S6. The CIE (1931) chromaticity diagram for **1**.

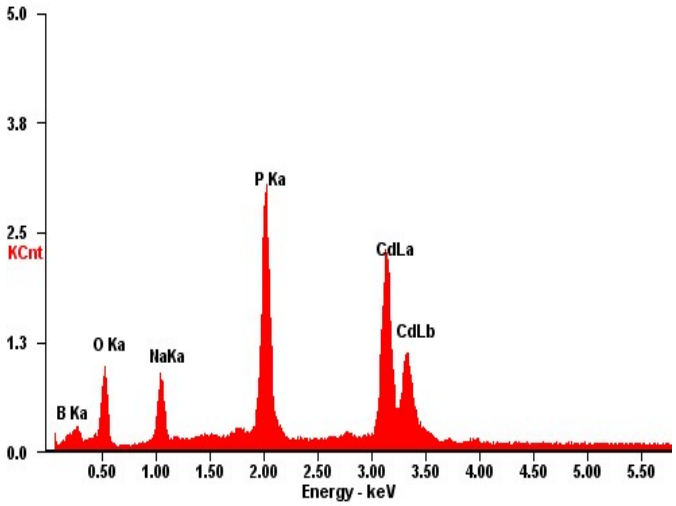

Figure S7. The EDS spectrum for ion-exchanged **1** with Na^+ cations.

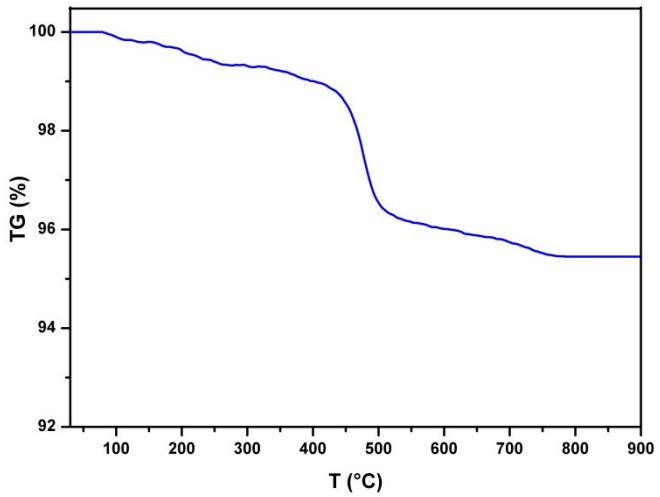

Figure S8. The TG curve for **1**.

Table S1. Selected bond lengths (Å) and bond angles (°) for **1**.

Bond	***Bond lengths***	***Bond***	***Bond lengths***
Cd1-O4	2.222(10)	B1-O6	1.498(18)
Cd1-O4#1	2.222(10)	B2-O6	1.346(14)
Cd1-O5#2	2.223(9)	B2-O6#4	1.346(14)
Cd1-O5#3	2.223(9)	B2-O7	1.37(3)
Cd1-O6	2.370(9)	P1-O2	1.552(9)
Cd1-O6#1	2.370(9)	P1-O3	1.543(10)
B1-O1#4	1.438(17)	P1-O4	1.508(10)
B1-O2	1.507(17)	P1-O5	1.503(9)
B1-O3#5	1.443(18)		
Angle	**Degree(°)**	**Angle**	**Degree(°)**
O4-Cd1-O4#6	180.0(7)	O1-B1-O2	108.0(11)
O4-Cd1-O5#6	90.2(4)	O1-B1-O3#10	109.7(12)
O4-Cd1-O5#7	89.8(4)	O1-B1-O6#10	110.2(12)
O4-Cd1-O5#8	89.8(4)	O3-B1-O2#10	109.0(12)
O4-Cd1-O5#7	90.2(4)	O3-B1-O6#10	111.2(11)
O4-Cd1-O6#8	87.8(4)	O6-B1-O2#10	108.6(11)
O4-Cd1-O6#7	87.8(4)	O6-B2-O6#11	122.4(18)
O4-Cd1-O6#9	92.2(4)	O6-B2-O7#11	118.8(9)
O4-Cd1-O6#7	92.2(4)	O6-B2-O7	118.8(9)
O5-Cd1-O5#7	180.0(4)	O2-P1-O3	105.5(6)
O5-Cd1-O6#7	98.4(3)	O2-P1-O4	112.4(7)
O5-Cd1-O6#7	98.4(3)	O2-P1-O5	104.7(6)
O5-Cd1-O6	81.6(3)	O3-P1-O4	109.7(7)
O5-Cd1-O6#7	81.6(3)	O3-P1-O5	111.7(6)
O6-Cd1-O6#7	180.000(2)	O4-P1-O5	112.6(6)

Symmetry transformations used to generate equivalent atoms:

#1: -*x*, 1-*y*, -*z*; #2: *x*-*y*, *x*, -*z*; #3: -*x*+*y*, 1-*x*, *z*; #4: *x*, *y,* 1/2 -*z*;

#5: *y*, -*x*+ *y,* -*z*; #6:1+*x*-*y*, *x*, 1/2+z; #7: 2-*x*, 1-*y*, 1-*z*; #8: 2-*x*+*y*, 1-*x*, 3/2-*z*;

#9: 1+*x*-*y*, *x*, 1/2+*z*; #10: *y*, -*x*+*y*, 1-*z*; #11: *x*, *y*, 3/2-*z*.

Table S2. The BVS values for Cd(1), B(1), B(2) and P(1) sites in **1**.

Bond	Bond lengths (Å)	BVS values	Sum
Cd1-O4	2.222(10)	0.423	2.254
Cd1-O4#1	2.222(10)	0.423	
Cd1-O5#2	2.223(9)	0.421	
Cd1-O5#3	2.223(9)	0.421	
Cd1-O6	2.370(9)	0.283	
Cd1-O6#1	2.370(9)	0.283	
B1-O1#4	1.438(17)	0.834	3.058
B1-O2	1.507(17)	0.692	
B1-O3#5	1.443(18)	0.823	
B1-O6	1.498(18)	0.709	
B2-O6	1.346(14)	1.070	3.135
B2-O6#4	1.346(14)	1.070	
B2-O7	1.37(3)	0.995	
P1-O2	1.552(9)	1.148	4.933
P1-O3	1.543(10)	1.179	
P1-O4	1.508(10)	1.296	
P1-O5	1.503(9)	1.310	

Symmetry transformations used to generate equivalent atoms:

#1: -*x*, 1-*y*, -*z*; #2: *x*-*y*, *x*, -*z*; #3: -*x*+*y*, 1-*x*, *z*; #4: *x*, *y*, 1/2 -*z*; #5: *y*, -*x*+ *y*, -*z*.