Photoluminescent carbon dots based on a rare 3D inorganic-organic hybrid cadmium borate crystal

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All starting materials were purchased without further purification.

Characterizations. All of the chemicals are commercially available and used without further purification. Fluorescent spectra were measured using a Shimadzu RF-5301PC spectrofluorophotometer. Elemental analyses were determined using an Elementar Vario EL elemental analyzer. The elemental analysis (C, H, and N) were carried out on a PE2400 II elemental analyzer. The Infrared spectra were recorded from the sample pelletized with KBr on a Thermo Scientific Nicolet iS10 FT-IR spectrometer in the range of 4000□400 cm^{-1}. The UV□Vis reflection spectra were measured at room temperature on a PerkinElmer Lambda 900 UV/Vis spectrophotometer equipped with an integrating sphere attachment in the wavelength region of 190~700 nm using the BaSO4 plate as the standard (100% reflectance). Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/DSC 1100 analyzer from room temperature to 1000 ℃ in flowing air atmosphere with a heating rate of 10 ℃/min. Powder X-ray diffraction data were collected on a Bruker D8 Advance XRD diffractometer with Cu Ka radiation at room temperature in the angular range of 2□ = 5°-60° with a step size of 0.02°. Electron paramagnetic resonance was recorded on a Bruker EMX spectrometer. The figures of TEM was recorded by Libra200.

Element analysis for **1**, Calcd: C 6.46 %; H 2.44 %; N 7.54%, Found: C 6.71 %; H 2.76 %; N 7.66%.

The FTIR spectrum of 1 is shown in Fig. S1. The bands at 3327, 3282 and 3162 cm^{-1} are stretching modes of NH_2 groups. The band at 1596 cm^{-1} might be due to the bending mode of N – H bonds. The sharp peaks at 2966 and 2880 cm^{-1} are characteristic of stretching vibrations of C-H bonds. The bands at 1449 and 1297 cm^{-1} are assigned as the asymmetric and symmetric stretching modes of B-O bond in BO_3 groups. The band at 1188, 1046 cm^{-1} might be the asymmetric and symmetric stretching modes of B-O in BO_4.

The PXRD pattern of title compound and simulated pattern on the basis of single crystal structure of the compound **1** was shown in Fig. S2. The experimental and simulated powder X-ray diffraction patterns corresponded well in position, indicating the phase purity of **1**.

TG-DSC analysis of the **1** was carried out in air atmosphere from 25°C to 1000 °C with a heating rate of 10 °C/min. As shown in the Fig. S3, the TG curve of **1** showed a continuous weight loss between 280 and 800 °C, corresponding to the removal of organic amine and the dehydration of hydroxyls (Found: 18.2%; Calcd:18.6%).

Crystal Structures Determination for 1. The single crystal of the title compound was carefully selected under an optical microscope and glued to thin glass fiber with epoxy resin. Diffraction data were measured on Rigaku Mercury CCD diffractometer using graphite monochromated Mo K□ (□ = 0.71073 Å) radiation at room temperature. All absorption corrections were performed using the multiscan program. The structure was solved by the direct methods and refined by full-matrix least-squares fitting on F2 by SHELX-97 and SHELX-97 programs, respectively. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. Crystallographic data and the structure determination for compound 1 were summarized in Table S1. Table S2 contains final atomic coordinates and equivalent thermal isotropic Displacement Ueq with e.sl.d's in Parentheses of 1. Table S3 contains selected bond length (Å) and angles (˚) for 1. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 1584690.

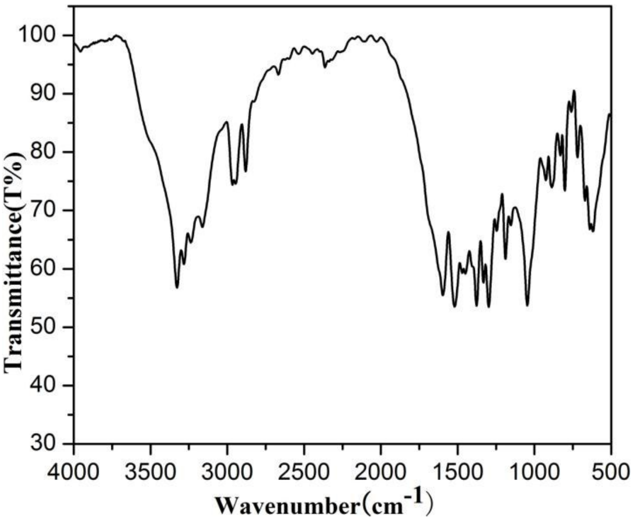

Fig. S1. FTIR spectra of compound **1**.

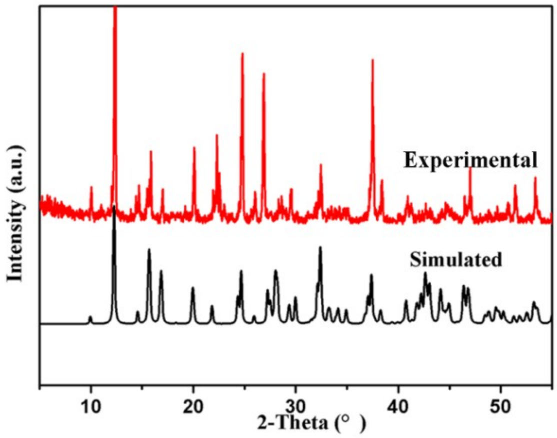

Fig. S2. PXRD patterns of compound **1**.

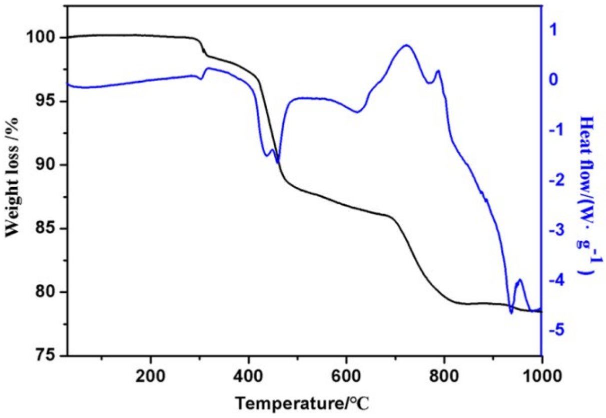

Fig. S3. TG and DSC curves of **1**.

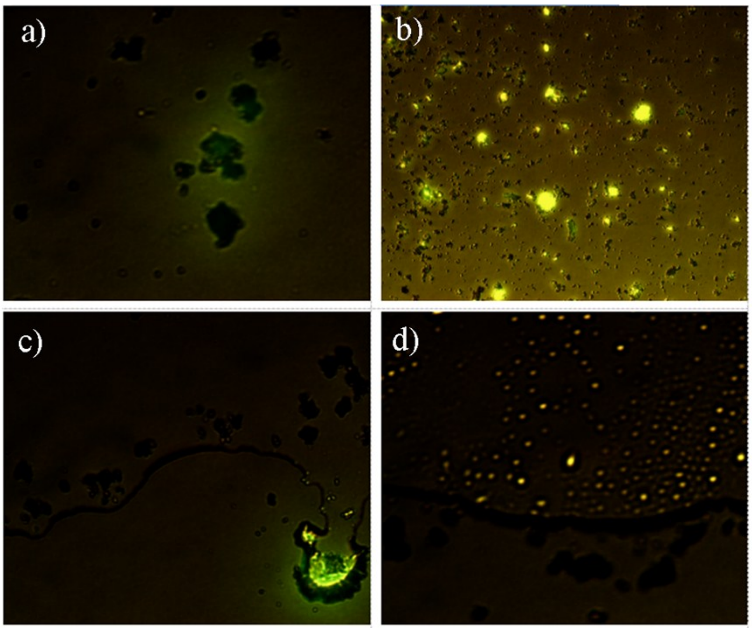

Fig. S4. The fluorescence images of 1-a, 1-b, 1-c, 1-d.

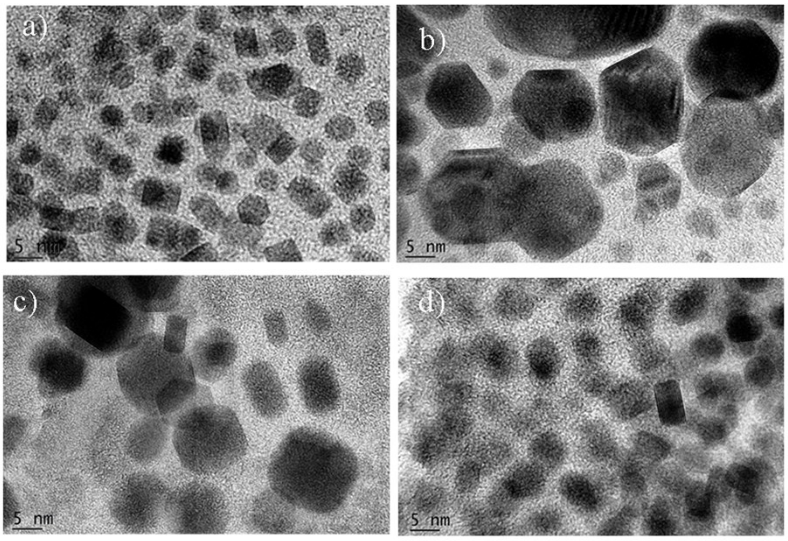

Fig. S5. The TEM images of 1-a, 1-b, 1-c, 1-d.

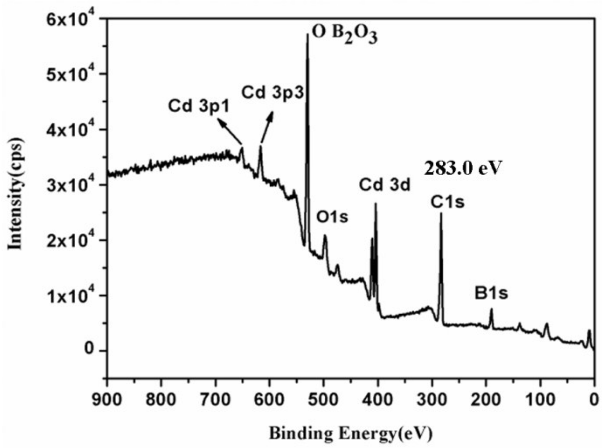

Fig. S6. XPS of 1-d sample.

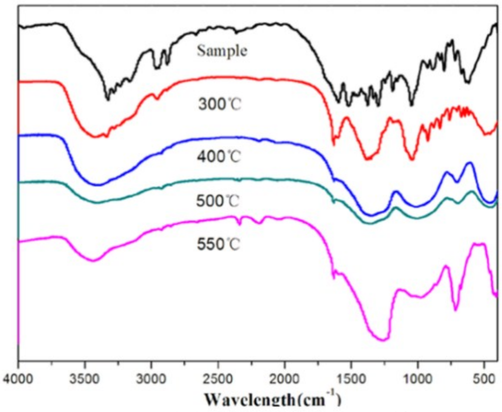

Fig. S7. The IR spectrums of 1-a, 1-b, 1-c, 1-d.

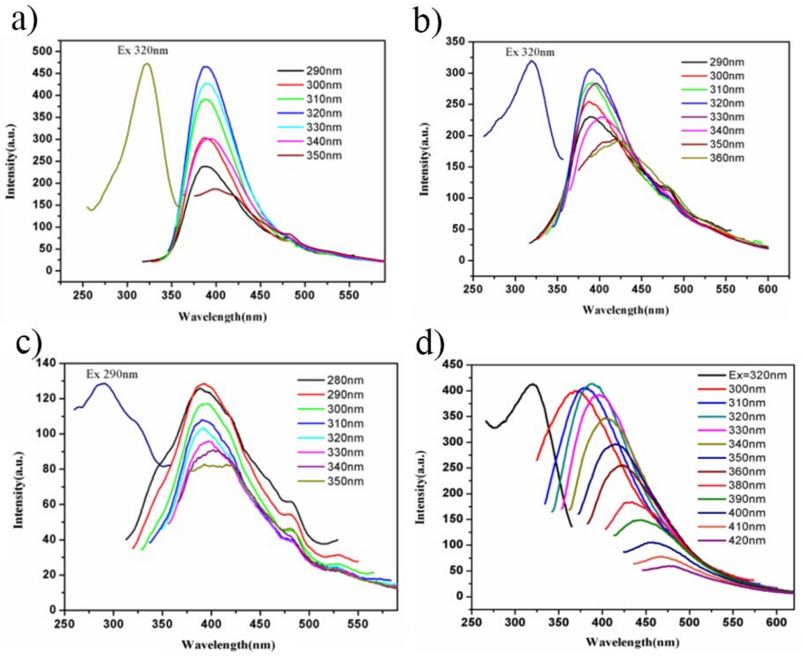

Fig. S8. Fluorescence excitation and emission spectras of 1-a, 1-b, 1-c, 1-d in different excitation.

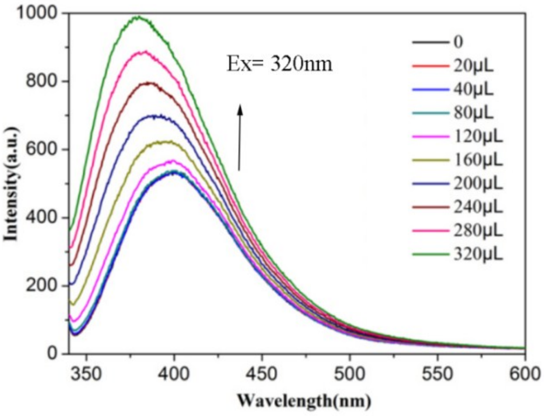

Fig. S9. The influence of HCl to a sample.

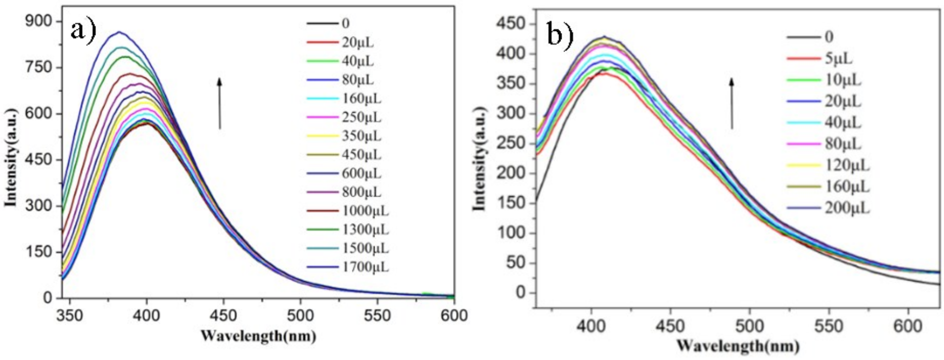

Fig. S10. Luminescence changes of 1-a (a) and 1-d (b) by gradual addition of ethanol solutions of Cs^+ ion ($C=1\times10^{-3}$mol/L and Ex=320nm).

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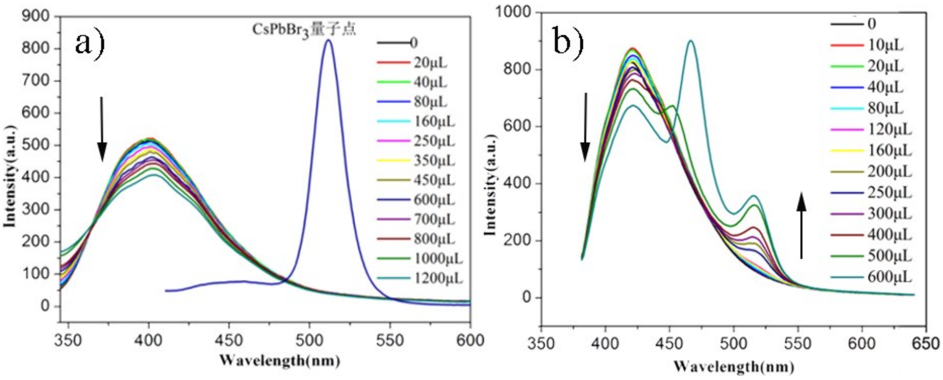


Fig. S11. Luminescence changes of 1-a (a) and 1-d (b) by gradual addition of ethanol solutions of $CsPbBr_3$ quantum dot ($C= 5\times10^{-3}$mg/Ml and Ex=320nm).

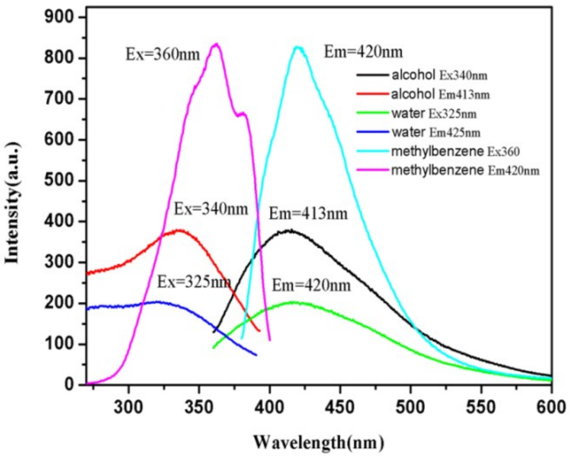
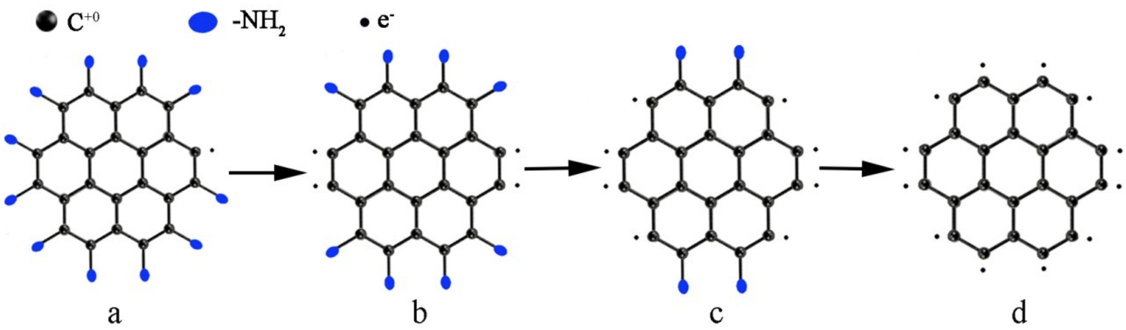


Fig. S12. Fluorescence excitation and emission spectras of 1-d.



Scheme 1. The possible formation process during calcining treatment from 1- a to 1-d.

Table S1. Crystal data and structure refinement for [Cden][B_5O_8(OH)].

Formula sum	$C_2H_9B_5N_2O_9Cd$
Formula weight	371.57
Crystal system	Monoclinic
Space group	*P2(1)/n*
a (Å)	6.5342(3)
b (Å)	14.4355(8)
c (Å)	11.2808(7)
α /°	90.00
β/°	90.659(5)
γ/°	90.00
Cell volume (Å^3)	1063.98(10)
Z	4
Measured reflections	6347
Independent reflections	1890
R_{int}	0.0630
GOF on F^2	1.064
F(000)	720
Indices ranges	$-7 \leq h \leq 7$, $-16 \leq k \leq 17$, $-13 \leq l \leq 13$,
Final R Indices [I>2σ(I)] [a]	R_1= 0.0572, wR_2= 0.1015
R indices (all data) [b]	R_1= 0.0428, wR_2= 0.0932
Largest diff. Peak and hole (e.A^{-3})	1.246/-0.596
Refinement method	full-matrix least-squares on F^2

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

Table S2 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) of [Cden]B_5O_8(OH).

Atoms	x	y	z	Ueq
Cd1	0.14153(7)	0.73674(3)	0.71806(5)	0.01658(19)
B1	-0.2612(11)	0.5481(6)	0.5888(7)	0.0191(18)
B2	-0.3908(10)	0.6919(6)	0.6747(7)	0.0155(17)

B3	-0.1518(10)	0.7018(6)	0.5170(7)	0.0170(17)
B4	0.1433(10)	0.7608(5)	0.3890(7)	0.0115(15)
B5	0.4937(10)	0.7440(5)	0.4767(7)	0.0134(16)
O1	-0.2468(8)	0.4535(3)	0.5948(5)	0.0423(16)
O2	-0.3846(6)	0.5900(3)	0.6711(4)	0.0183(10)
O3	-0.1953(6)	0.7302(3)	0.6371(4)	0.0122(10)
O4	-0.1509(6)	0.5976(3)	0.5084(4)	0196(11)
O5	0.0503(6)	0.7345(3)	0.4903(4)	0.0176(11)
O6	0.0369(6)	0.7768(3)	0.2890(4)	0.0150(10)
O7	0.3535(6)	0.7747(3)	0.3917(4)	0154(10)
O8	0.6870(6)	0.7373(3)	0.4340(4)	0.0145(10)
O9	0.4442(6)	0.7247(3)	0.5893(4)	0.0151(10)
C1	0.2960(16)	0.9367(6)	0.6484(9)	0.060(2)
C2	0.2975(16)	1.0413(6)	0.6488(8)	0.055(2)
N1	0.1558(10)	0.8912(4)	0.7211(6)	0.0400(16)
N2	0.3225(9)	1.0830(4)	0.7660(6)	0.0280(14)

Table S3 Selected bond length (Å) and angle (°) for [Cden]$B_5O_8(OH)$.

Cd1—N1	2.231(6)	B2—O9^{iii}	1.513(8)
Cd1—N2^{i}	2.239(6)	B3—O5	1.438(8)
Cd1—O3	2.375(4)	B3—O3	1.447(9)
Cd1—O9	2.474(4)	B3—O8^{iii}	1.492(8)
Cd1—O8^{ii}	2.479(4)	B3—O4	1.507(9)
Cd1—O5	2.631(4)	B4—O6	1.339(8)

B1—O4	1.367(9)	B4—O5	1.354(8)
B1—O1	1.370(9)	B4—O7	1.388(8)
B1—O2	1.376(8)	B5—O9	1.344(9)
B2—O6^{ii}	1.451(9)	B5—O8	1.360(8)
B2—O3	1.460(8)	B5—O7	1.391(8)
B2—O2	1.472(9)		
N1—Cd1—N2^{i}	170.0(3)	O6^{ii}—B2—O3	115.8(6)
N1—Cd1—O3	94.8(2)	O6^{ii}—B2—O2	110.2(5)
N2^{i}—Cd1—O3	95.00(19)	O3—B2—O2	110.3(5)
N1—Cd1—O9	92.63(19)	O6^{ii}—B2—O9^{iii}	103.4(5)
N2^{i}—Cd1—O9	83.88(18)	O3—B2—O9^{iii}	108.4(5)
O3—Cd1—O9	121.00(14)	O2—B2—O9^{iii}	108.4(5)
N1—Cd1—O8^{ii}	80.2(2)	O5—B3—O3	107.1(5)
N2^{i}—Cd1—O8^{ii}	93.4(2)	O5—B3—O8^{iii}	113.5(6)
O3—Cd1—O8^{ii}	118.95(13)	O3—B3—O8^{iii}	110.2(5)
O9—Cd1—O8^{ii}	120.00(13)	O5—B3—O4	108.1(5)
N1—Cd1—O5	92.1(2)	O3—B3—O4	110.1(6)
N2^{i}—Cd1—O5	95.1(2)	O8^{iii}—B3—O4	107.8(5)
O3—Cd1—O5	54.93(13)	O6—B4—O5	121.7(6)
O9—Cd1—O5	66.39(13)	O6—B4—O7	119.8(6)
O8^{ii}—Cd1—O5	169.92(14)	O5—B4—O7	118.4(6)
O4—B1—O1	121.1(6)	O9—B5—O8	123.6(6)
O4—B1—O2	122.4(6)	O9—B5—O7	123.7(6)
O1—B1—O2	116.4(6)	O8—B5—O7	112.7(6)

Symmetry codes: (i) 0.5-x, -0.5+y, 1.5-z; (ii) -0.5+x, 1.5-y, 0.5+z; (iii) -1+x, y, z; (iv) 0.5+x, 1.5-y, -0.5+z; (v) 1+x, y, z; (vi) 0.5-x, 0.5+y, 1.5-z.

Table S4 Details of Hydrogen Bonds for [Cden]B_5O_8(OH).

D-H	d(D–H) (A ˚)	d(H···A) (Å)	∠D–H···A (°)	d(D···A) (A ˚)
O1–H···O4^{i}	0.82	2.134	176.37	2.953
O1–H···O5^{ii}	0.82	2.621	124.32	3.157
N1–H···O4^{iii}	0.90	2.619	157.70	3.469
N2–H···O4^{iv}	0.90	2.636	133.06	3.316
N2–H···O2^{v}	0.90	2.188	143.13	2.958

Symmetry codes: (i) -x, -y+1, -z+1, 1.5-z; (ii) -x, -y+1, -z+1; (iii) x+1/2, -y+3/2, z+1/2; (iv) -x+1/2, y+1/2, -z+3/2; (v) -x-1/2, y+1/2, -z+3/2.