Supplementary Information

Bright Blue Emissions with Temperature-Dependent Quantum Yields from Microporous Metal-Organic Frameworks

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Materials and Methods:

All reagents and solvents used were received from commercial suppliers without further purification. Elemental analyses (C, H, and N) were performed with a Vario MICRO CHNOS elemental analyzer. The infrared spectra with KBr pellet were recorded in the range of 4000–400 cm^{-1} on a Perkin-Elmer Spectrum One FT-IR spectrometer. Thermal analyses were performed on a NETZSCH STA 449C instrument from room temperature to 800 °C with a heating rate of 10 °C min^{-1} under nitrogen flow. ^1H NMR was done on a Bruker AVANCE III spectrometer at 400 MHz. The ESI-MS spectrum was obtained from DECAX-30000 LCQ Deca XP mass spectrometer. The solid-state luminescence emission/excitation spectra were recorded on a FLS920 fluorescence spectrophotometer equipped with a continuous Xe-900 xenon lamp and a μF900 microsecond flash lamp. For low-temperature measurements, microcrystal samples were mounted on a closed cycle helium cryostat. Powder X-ray diffraction (PXRD) data were collected on a DMAX-2500 diffractometer with Cu K_α. The calculated patterns were generated with PowderCell.

Synthesis:

The ligand N,N',N"-1,3,5-triazine-2,4,6-triyltris(4-aminomethylbenzoic acid) (H_3TTAA) was synthesized according to the method described in the literature.[1]

N,N',N"-1,3,5-triazine-2,4,6-triyltris(4-aminomethylbenzoic acid) (H_3TTAA). A solution of 4-aminomethylbenzoic acid (9.82 g, 65 mm) and sodium hydroxide (5.60 g, 140 mm) in 100 ml water was added dropwise into cyanuric chloride (3.69 g, 20mm) in 100ml water at 0-5 °C under stirring. After 3 h, the mixture was warmed to room temperature and reacted under stirring for 3 h. And then the mixture was allowed to reflux at 105 °C for another 6 hours. After cooling, the pH value was adjusted to about 3 using concentrated HCl. The white solid was collected by filtration, washed with alcohol and water and dried under vacuum at 60 °C in 86% yield. ^1H NMR (400 MHz, DMSO): δ 3.40 (s, 3H), 4.41 (p, 6H), 7.34 (p, 6H), 7.85(p, 6H). Elemental analysis calcd for H_3TTAA ($C_{27}H_{24}N_6O_6$): C 61.36, H 4.58, N 15.90;

found: C 60.81, H 4.46, N 15.50. ESI-MS: *m/z* 527.6 ($[M-H]^+$, 100%, calcd 527.5). The IR spectrum of H_3TTAA is shown in **Fig S9**.

{(H_2NMe_2)[Cd(TTAA)]}·$2H_2O$ (**1**). A mixture of H_3TTAA (106 mg, 0.20 mmol) and $Cd(NO_3)\cdot 4H_2O$ (123 mg, 0.40 mmol) in 12 ml DMF, ethanol and water (v/v/v = 6:1:1) was sealed in a 23 ml Teflonlined autoclave and heated at 120 °C for 3 d, then cooled to room temperature at a rate of 5 °C/h. The resultant colorless block crystals were separated by filtration, washed with DMF to give the pure sample. (yield: ca. 86% based on H_3TTAA). Anal. Calcd for $CdC_{29}H_{33}N_7O_8$: C, 48.38; H, 4.62; N, 13.62; found: C, 48.49; H, 4.94, N, 14.14 %. The IR spectrum of **1** is shown in **Fig S9**.

{(H_2NMe_2)[Cd(TTAA)]}·H_2O (**2**). A mixture of H_3TTAA (106 mg, 0.20 mmol), $Cd(NO_3)\cdot 4H_2O$ (123 mg, 0.40 mmol) and 4,4'-bipy (39 mg, 0.25 mmol) in 12 ml DMF, ethanol and water (v/v/v = 6:1:1) was sealed in a 23 ml Teflonlined autoclave and heated at 120 °C for 3 d, then cooled to room temperature at a rate of 5 °C/h. The resultant colorless octahedral crystals were separated by filtration, washed with DMF to give the pure sample. (yield: ca. 74% based on H_3TTAA). Anal. Calcd for $CdC_{29}H_{31}N_7O_7$: C, 49.62; H, 4.45; N, 13.97; found: C, 49.52; H, 4.66, N, 13.68%. The IR spectrum of **2** is shown in **Fig S9**.

Crystallographic Analyses:

The structural determination of single crystal was performed on Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at room temperature. The structures were solved by direct methods and refined by the full-matrix leasts-squares technique on F^2 using the SHELXTL-97 program.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of hydrogen atoms attached to carbon and nitrogen atoms were generated geometrically (C-H bond fixed at 0.97 Å). Crystallographic data and structure determination summaries are listed in Table S1. And the selected bond lengths and angles of the complexes are listed in Table S2-S3.

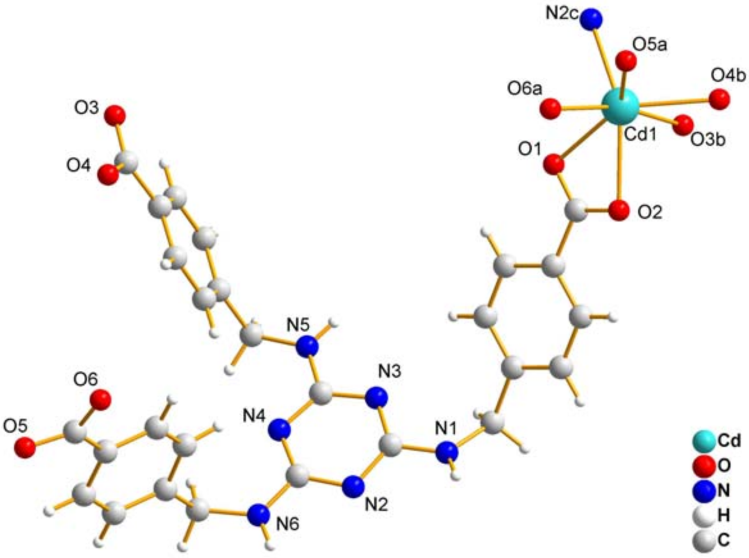


Fig. S1 Coordination environment of the Cd(II) ion in framework **1**. Symmetry codes for the generate atoms: a, 1-x, -y, -z; b, x, 0.5-y, -0.5+z; c, x, 1+y, z.

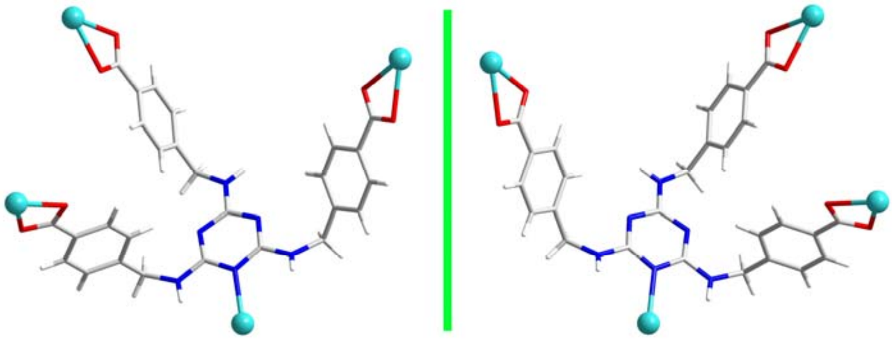


Fig. S2 An enantiometric pair of ligands are formed in framework **1**.

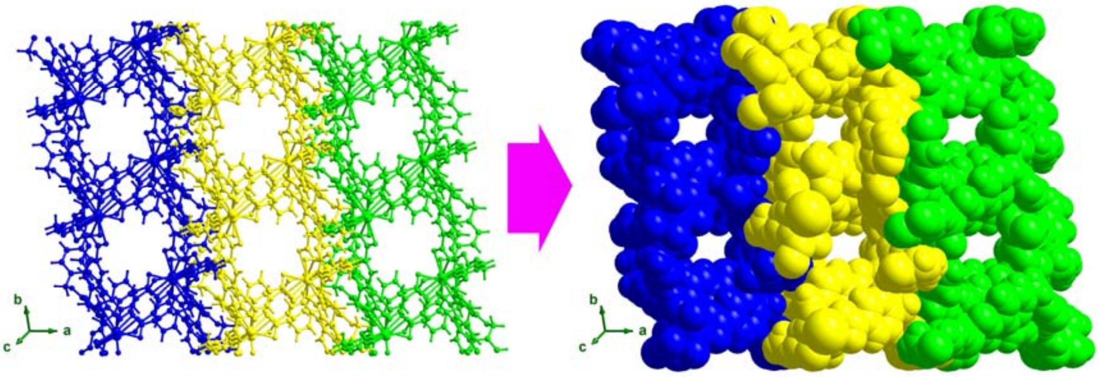


Fig. S3 Ball-and-stick and space-filling representations of selected three layers in framework **1** with inter-immersion arrangement.

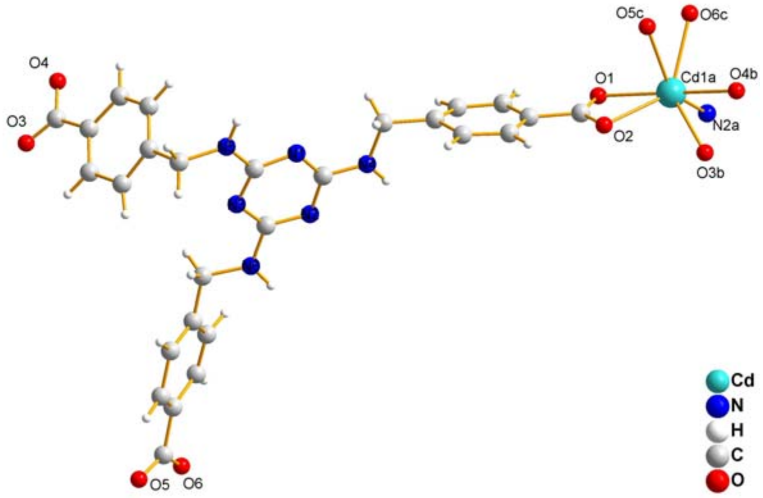


Fig. S4 Coordination environment of the Cd(II) ion in framework **2**. Symmetry codes for the generate atoms: a, -x, 1-y, -z; b, -0.5+x, -0.5+y, -1+z; c, -0.5+x, 0.5+y, -1+z.

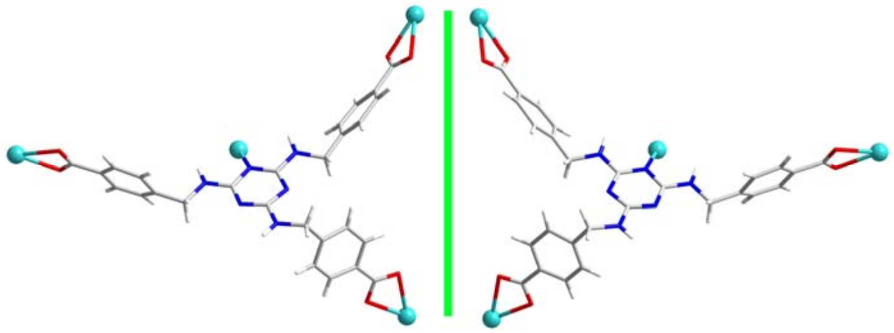


Fig. S5 An enantiometric pair of ligands are formed in framework **2**.

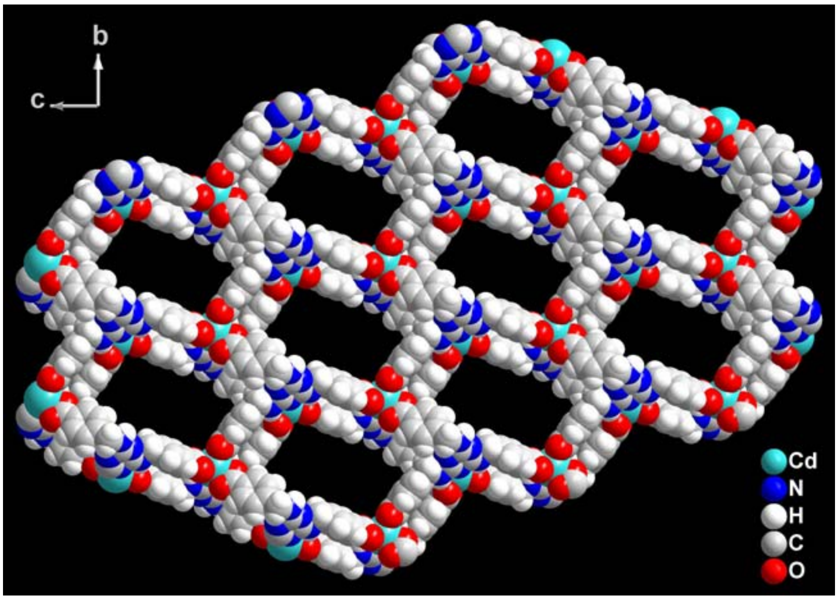


Fig. S6 Space-filling representation of single layer with large cavities in framework **2**.

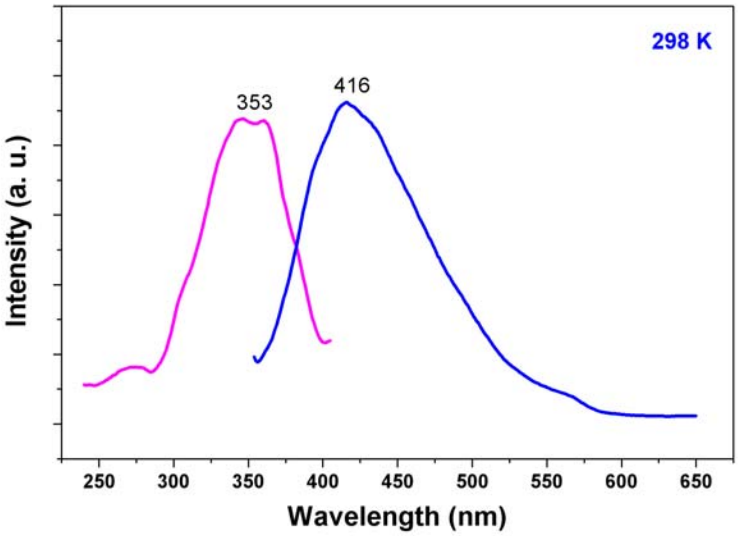
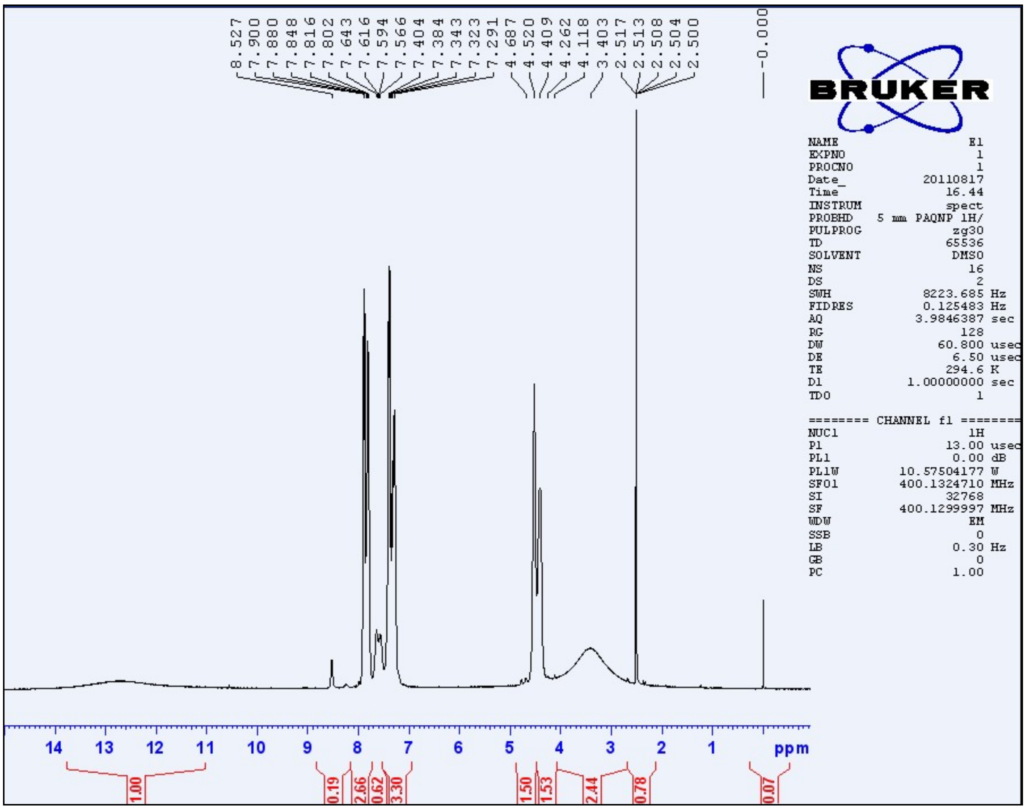


Fig. S7 Excitation and emission spectra of H_3TTAA in the solid state at room temperature.



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TD0                    1

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Fig. S8 ^{1}HMR spectrum of H_3TTAA in DMSO.

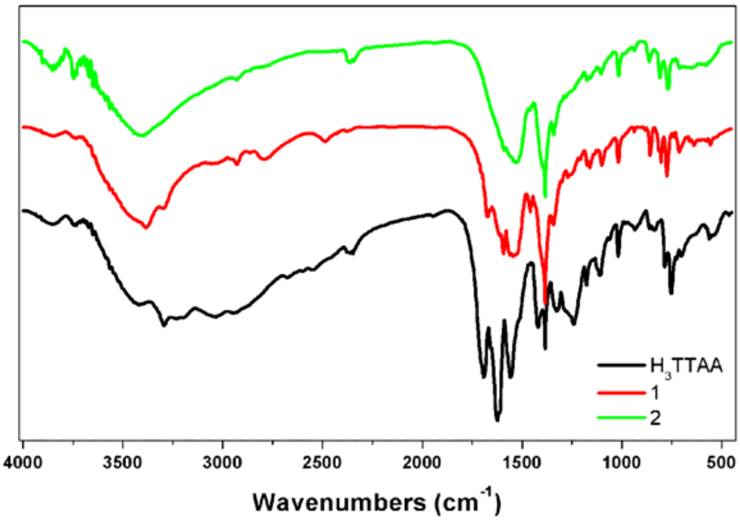

Fig. S9 IR spectra of H_3TTAA, **1** and **2**.

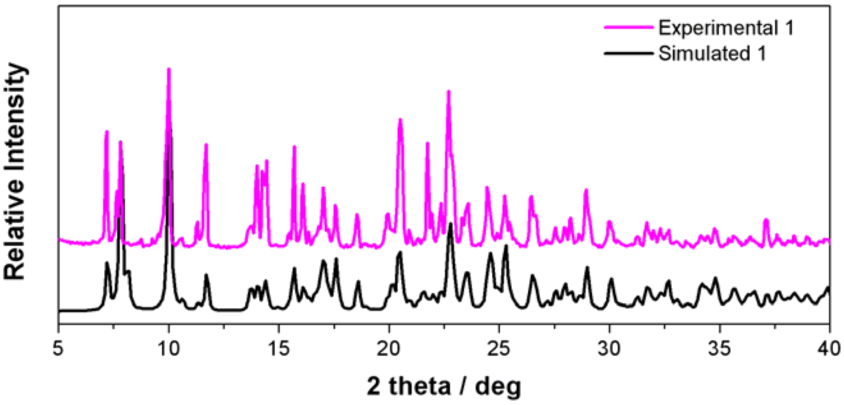

Fig. S10 Powder X-ray diffractions for simulated and experimental **1.**

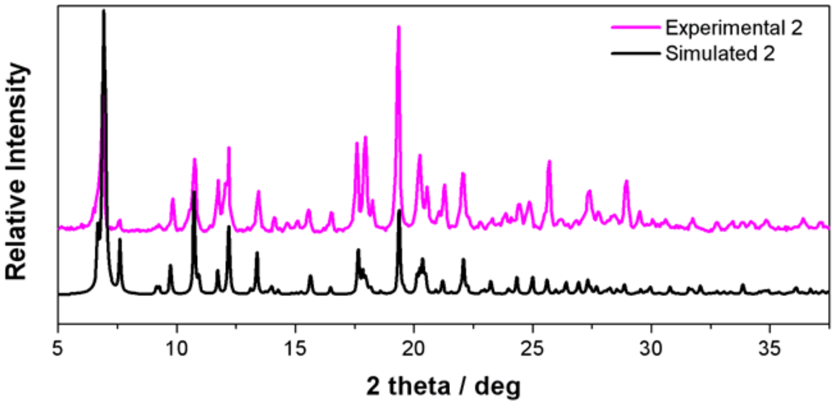

Fig. S11 Powder X-ray diffractions for simulated and experimental **2.**

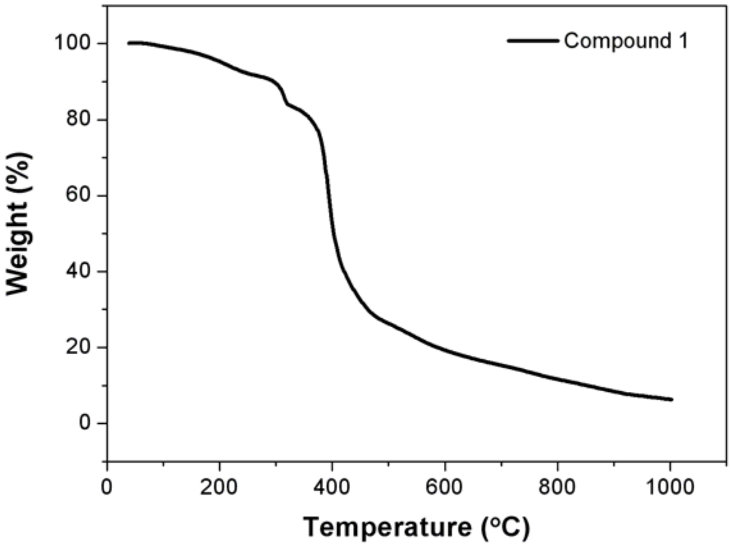

Fig. S12 TGA curve of compound **1.**

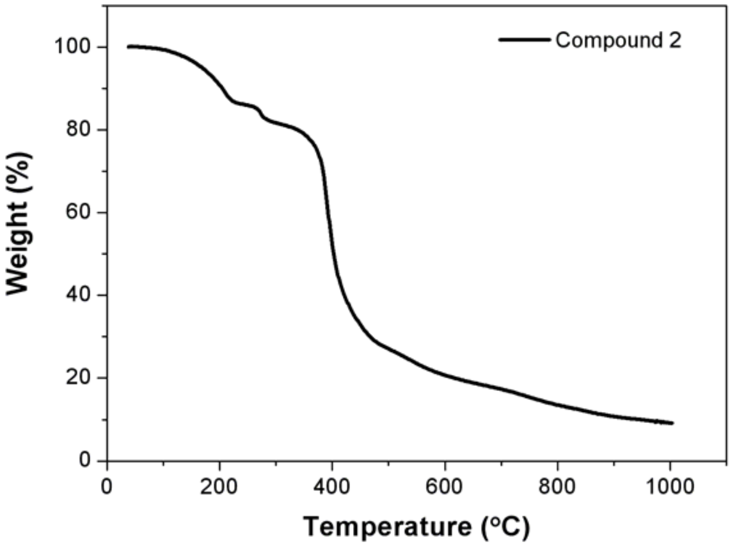

Fig. S13 TGA curve of compound **2.**

Table S1. Crystal Data and Structure Refinements for **1**and **2**

Compound	**1**	**2**
Formula	$CdC_{29}H_{33}N_7O_8$	$CdC_{29}H_{31}N_7O_7$
FW	719.77	702.01
Temperature	293 K	293 K
Cryst syst	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	12.943(4)	29.28(2)
b (Å)	12.329(3)	14.524(10)
c (Å)	23.867(5)	20.084(15)
α (deg)	90	90
β (deg)	108.881(12)	115.414(11)
γ (deg)	90	90
V (Å^3)	3603.6(16)	7714(10)
Z	4	8
D_c (g cm^{-3})	1.327	1.209
μ (mm^{-1})	0.658	0.612
Reflns collcd	27237	25354
Unique reflns (R_{int})	7817 (0.0346)	8737 (0.0666)
S on F^2	0.975	1.104
R1,[a] wR2[b] [$I>2\sigma(I)$]	0.0522, 0.1645	0.0758, 0.2071
R1,[a] wR2[b] (all data)	0.0587, 0.1723	0.1219, 0.3054

[a] $R1 = \Sigma(||F_o| - |F_c||) / \Sigma |F_o|$. [b] $wR2 = \{\Sigma w [(F^2_o - F^2_c)] / \Sigma w [(F^2_o)^2]\}^{0.5}$.

Table S2. Selected Bond Lengths [Å] and Angles [°] for Compound **1**[a]

Cd1-N2c	2.320(3)	Cd1-O1	2.336(3)	Cd1-O2	2.436(3)
Cd1-O4b	2.320(3)	Cd1-O6a	2.345(3)	Cd1-O3b	2.467(4)
Cd1-O5a	2.488(4)				
N2c-Cd1-O4b	103.37(11)	O4b-Cd1-O2	94.85(11)	O2-Cd1-O3b	81.97(11)
N2c-Cd1-O1	97.73(10)	O1-Cd1-O2	55.24(10)	N2c-Cd1-O5a	88.97(13)
O4b-Cd1-O1	134.74(11)	O6a-Cd1-O2	86.47(12)	O4b-Cd1-O5a	85.39(11)
N2c-Cd1-O6a	94.96(13)	N2c-Cd1-O3b	92.04(11)	O1-Cd1-O5a	134.97(12)
O4b-Cd1-O6a	134.36(13)	O4b-Cd1-O3b	54.36(10)	O6a-Cd1-O5a	53.16(13)
O1-Cd1-O6a	81.86(13)	O1-Cd1-O3b	85.65(11)	O2-Cd1-O5a	113.11(13)
N2c-Cd1-O2	152.54(10)	O6a-Cd1-O3b	166.39(11)	O3b-Cd1-O5a	138.81(11)

[a]Symmetry codes: (a) -x+1,-y,-z; (b) x,-y+1/2,z-1/2; (c) x,y+1,z.

Table S3. Selected Bond Lengths [Å] and Angles [°] for Compound **2**[a]

Cd1-N2	2.319(5)	Cd1-O1a	2.355(5)	Cd1-O5b	2.435(6)
Cd1-O4c	2.324(6)	Cd1-O2a	2.426(6)	Cd1-O6b	2.450(5)
Cd1-O3c	2.476(7)				
N2-Cd1-O4c	95.8(2)	O4c-Cd1-O5b	85.1(2)	O5b-Cd1-O6b	53.56(17)
N2-Cd1-O1a	92.56(18)	O1a-Cd1-O5b	90.06(19)	N2-Cd1-O3c	96.2(2)
O4c-Cd1-O1a	171.2(2)	O2a-Cd1-O5b	81.0(2)	O4c-Cd1-O3c	51.6(2)
N2-Cd1-O2a	129.6(2)	N2-Cd1-O6b	89.13(18)	O1a-Cd1-O3c	124.6 (2)
O4c-Cd1-O2a	117.1(3)	O4c-Cd1-O6b	83.3(2)	O2a-Cd1-O3c	79.0(2)
O1a-Cd1-O2a	54.65(18)	O1a-Cd1-O6b	99.77(17)	O5b-Cd1-O3c	112.8(2)
N2-Cd1-O5b	142.43(19)	O2a-Cd1-O6b	129.4(2)	O6b-Cd1-O3c	134.86(17)

[a] Symmetry codes: (a) -x,-y+1,-z; (b) -x+1/2,-y+1/2,-z+1; (c) -x+1/2,-y+3/2,-z+1.

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[1] Q.-L. Zhu, T.-L. Sheng, R.-B. Fu, S.-M. Hu, J.-S. Chen, S.-C. Xiang, C.-J. Shen and X.-T. Wu, *Cryst. Growth Des.*, 2009, **9**, 5128.

[2] *SHELXTL*, version 5.10; Siemens Analytical X-ray Instruments Inc.: Madison, WI, **1994**.