Supporting materials

2D flexible metal-organic frameworks with $[Cd_2(\mu_2\text{-}X)_2]$(X = Cl or Br) units exhibiting selective fluorescence sensing for small molecules

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1. General information

All chemical reagents are commercial available, and used without further purification. The elemental analysis (C, H, N) was performed using a Vario EL III CHNOS elemental analyzer. Diffuse reflectance spectra were measured with a PerkinElmer Lambda 900 UV/VIS/NIR Spectrometer. The spectrophotometer was calibrated against BaSO4 surface for 100% reflectance over the wavelength range under consideration. The IR (KBr pellet) spectra were recorded (400–4000 cm^{-1} region) on an ABB Bomen MB102 IR spectrometer. Fluorescence measurements were carried out on a FLS920 Luminescence Spectrometer at room temperature.

Data collections of $[Cd(BCbpy)(bpdc)_{0.5}Cl]\cdot 7H_2O$ (**1**) and $[Cd(BCbpy)(bpdc)_{0.5}Br]\cdot 7H_2O$ (**2**) were performed respectively on a Rigaku Mercury CCD and Saturn 724 diffractometer by using graphite-monochromated Mo Kα (λ = 0.71073 Å). All absorption corrections were performed by using the multi-scan method (CrystalClear, Rigaku Inc., 2007) and all structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXL-97 program package. In all cases, non-hydrogen atoms are treated anisotropically. Hydrogen atoms on the BCbpy and bpdc were placed in their geometrically generated positions. Water-hydrogen atoms were located on the Fourier map and refined using the DFIX command with a fixed O-H distance of 0.85 Å and with an additional H…H restraint (1.39 Å), using the dang command in SHELX-97. After all the water-hydrogen atoms with appropriate position were determined, the DFIX and dang command were removed and the water-hydrogen atoms were refined again using the AFIX command with a appointed temperature factor data of -1.5000.

2. Synthesis

1-(4-carboxybenzyl)-4,4′-bipyridinium chloride (HBCbpyCl): This compound was synthesized according to the procedure as described previously (Published in *CrystEngComm*, 2008, 10, 1299).

$[Cd(BCbpy)(bpdc)_{0.5}Cl]\cdot 7H_2O$ (1): HBCbpyCl salt (0.5g) was dissolved in 10 mL of water with pH = 7 adjusted by 1 mol/L NaOH solution and then the solution was cooled to 5°C. Pure BCbpy deposition was obtain through filtration. After drying, 0.01 g (0.034 mmol) BCbpy and 0.008 g (0.033 mmol) H_2bpdc were dissolved in 1 mL water and the pH value was adjusted to 7 with NaOH solution (1mol/L). Subsequently, the resultant solution was carefully layered onto a mixed solution of $Cd(Ac)_2\cdot 2H_2O$(0.009 g, 0.033 mmol) and KCl (0.022g, 0.3 mmol) in

H_2O/DMSO(9:1 v:v; 1 mL) with H_2O/DMSO (10:1 v/v; 1mL) placed between the two layers. Colorless crystals were obtained in the middle of the tube after about one week. The yield is 52.1%. Elemental analysis (%): Calcd for $CdO_{11}ClN_2C_{25}H_{32}$: C, 43.87; H, 4.71; N, 4.09; Found: C, 43.80; H, 4.55; N, 4.03.

[Cd(BCbpy)(bpdc)$_{0.5}$Br]·7H$_2$O (2): Complex **2** was prepared in a process similar to that for complex 1 except that 0.022g (0.3 mmol) KCl were replaced with 0.035g (0.03 mmol) KBr. The yield is 43.5%. Elemental analysis (%); Calcd for $CdO_{11}BrN_2C_{25}H_{32}$: C, 41.19; H, 4.43; N, 3.84; Found: C, 41.31; H, 4.31; N, 3.81.

3. The crystallographic information

Crystal data for **1**: $C_{25}H_{32}CdClN_2O_{11}$, M = 684.38, orthorhombic, space group *Pbca*, a = 17.595(7), b = 17.974(7), c = 18.688(7) Å, V = 5898(4) Å^3, Z = 8, D_c = 1.541 g cm^{-3}, F_{000} = 2792, μ = 0.890 mm^{-1}, T = 293(2) K, 43985 reflections collected, 6794 unique (R_{int} = 0.0336). GOF = 1.026, R_1 = 0.0437, wR_2 = 0.1093 for 5819 reflections with $I > 2\sigma(I)$. Crystal data for **2**: $C_{25}H_{32}BrCdN_2O_{11}$, M = 728.84, orthorhombic, space group *Pbca*, a = 17.595(4), b = 18.176(5), c = 18.778(5) Å, V = 6005(3) Å^3, Z = 8, D_c = 1.612 g cm^{-3}, F_{000} = 2936, μ = 2.116 mm^{-1}, T = 293(2) K, 47069 reflections collected, 6838 unique (R_{int} = 0.0655). GOF = 1.092, R_1 = 0.0796, wR_2 = 0.1595 for 6642 reflections with $I > 2\sigma(I)$.

4. Additional Figures and Tables

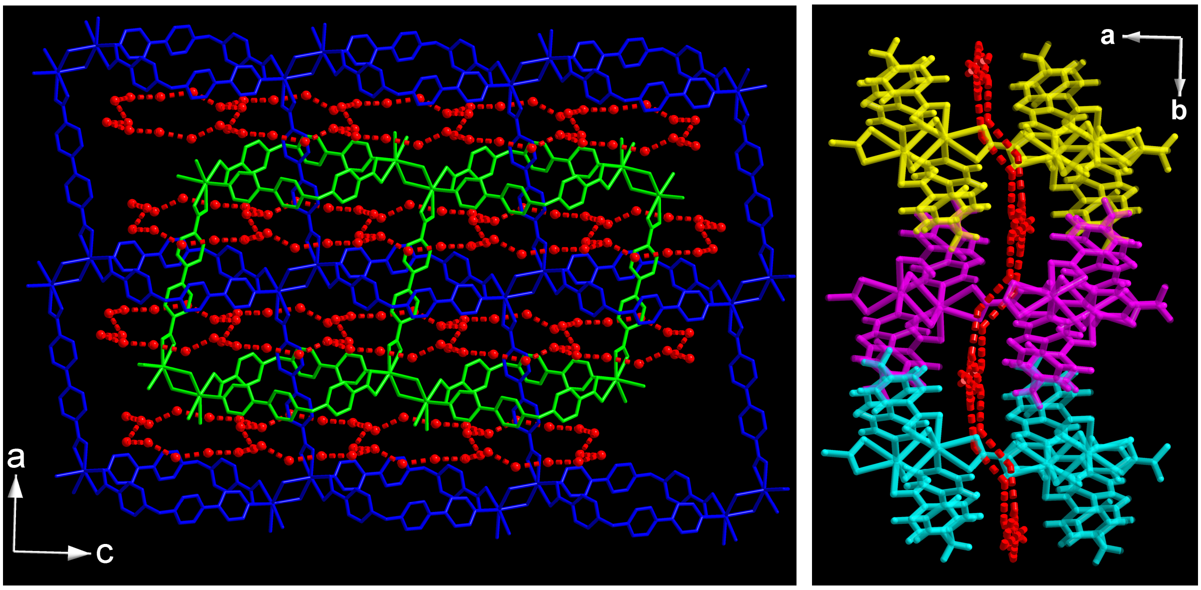

Fig.S1: Left: A view of the interpenetration of the 2D polyrotaxane-like coordination frameworks and the hydrogen-bonded water layers in the *ac* plane (the blue and green color represent the single 2D sheet in the mutually interpenetrating 2D polyrotaxane-like layer). Right: The 2D water sheet with 14-membered rings connects the 2D polyrotaxane-like coordination frameworks into a 3D network, in which the yellow, purple and turquoise colors represent different 2D interpenetrating polyrotaxane-like layers.

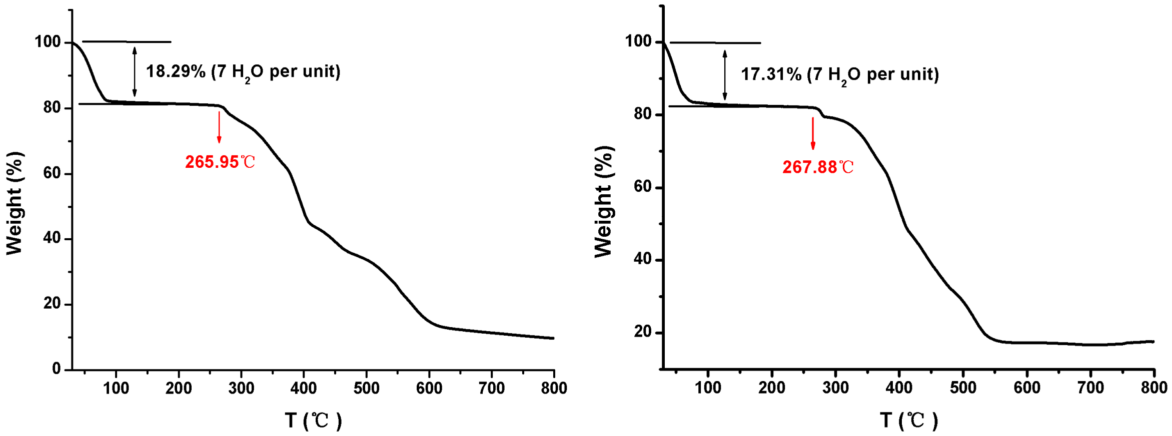

Fig.S2: Thermogravimetric analysis (TGA) curves for complexes **1** (left) and **2** (right), respectively.

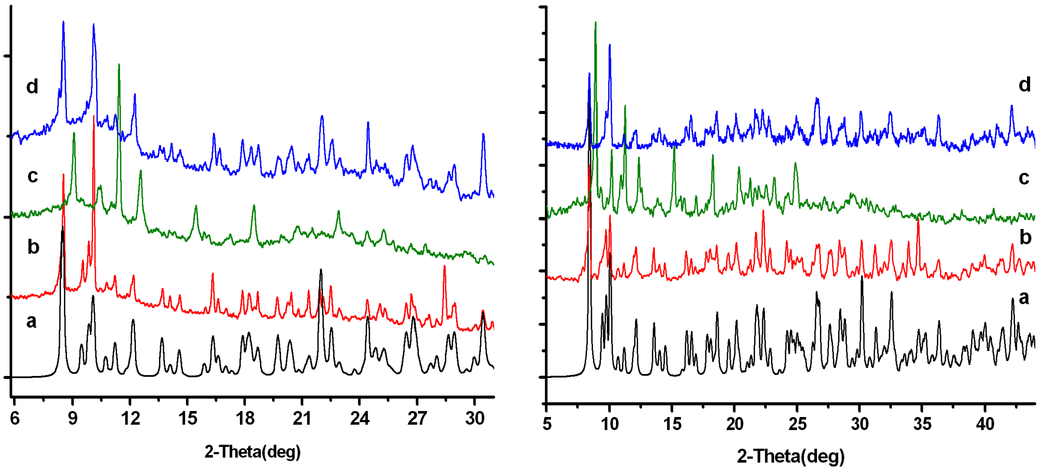

Fig.S3: The reversible structural variations for **1** (left) and **2** (right) revealed by powder X-ray diffraction. a): simulated data; b): experimental data for as-synthesized samples; c): experimental data for dehydrated samples; d): experimental data for rehydrated samples.

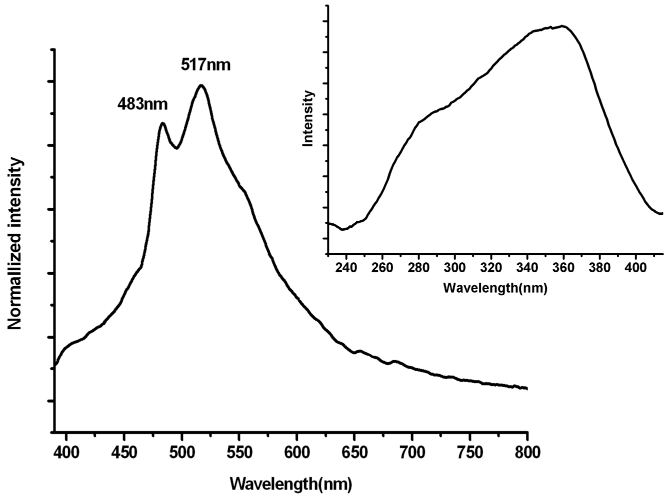

Fig. S4: The fluorescence emission spectrum of **2a** (λex = 355 nm). The inset shows its excitation spectrum.

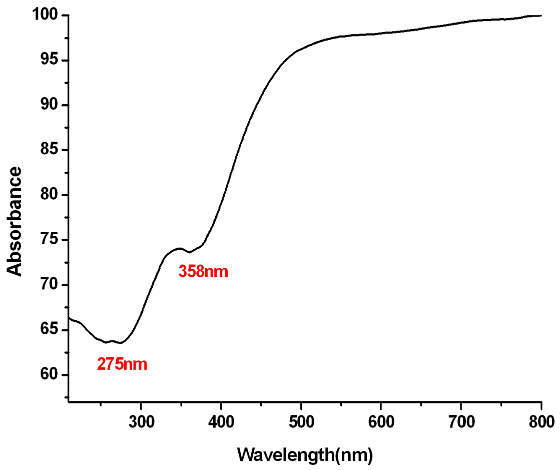

Fig. S5: UV-vis diffuse reflectance spectrum of **1**.

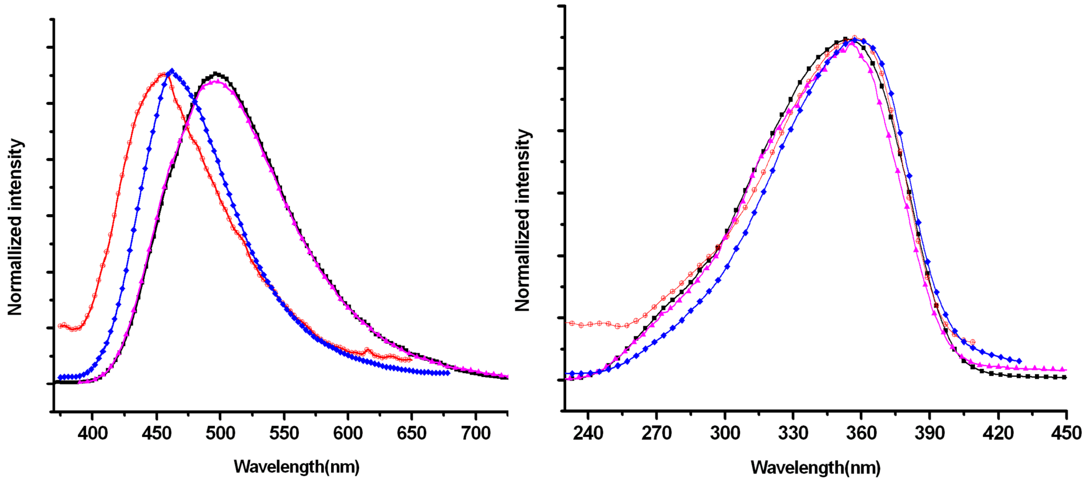

Fig. S6: The changes of the emission (left) and excitation (right) spectra for **1** upon dehydration and rehydration. Black: as-synthesized **1**; red: guest-free sample **1a**; blue: **1a** exposed to moisture slowly for 5min; purple: completely rehydrated sample.

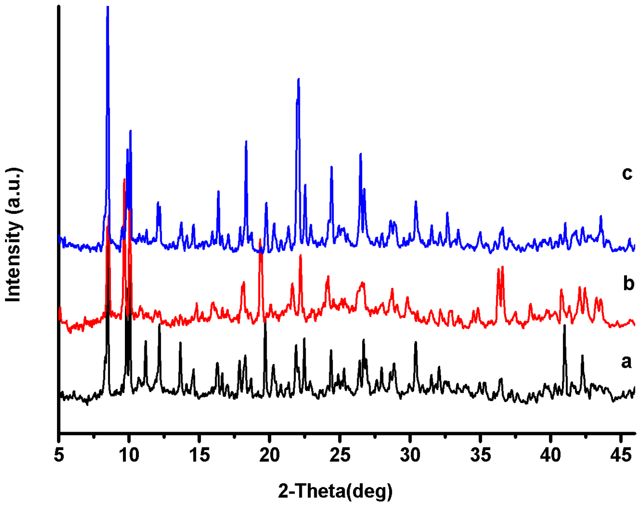

Fig.S7: The PXRD patterns for original sample **1**(a), acetonitrile-exchanged sample (b) and recovered sample (c), respectively.

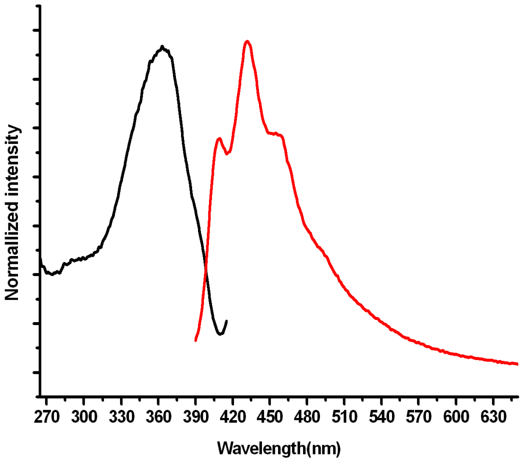

Fig. S8: The emission and excitation spectra of **2** immersed in MeCN for 30 min.

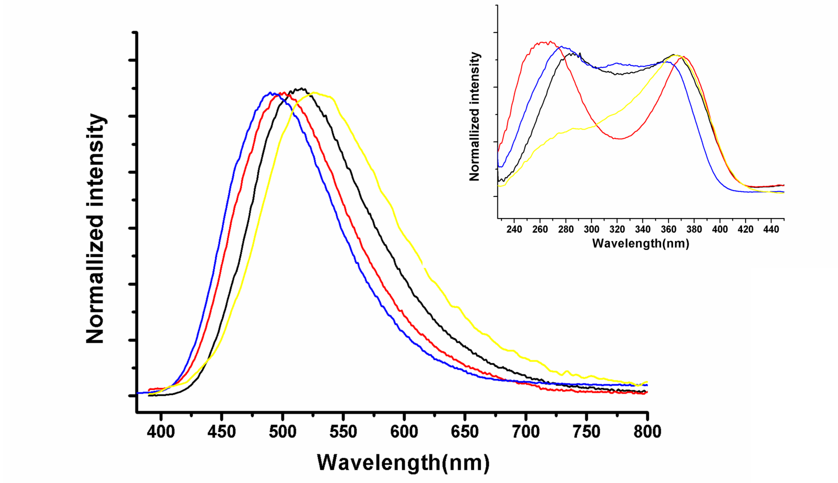

Fig. S9: The fluorescence emission spectra of **1** immersed in a mixture of THF and MeOH with different ratio. Blue: THF 100%; red: THF 66.6%; black: THF 33.3%; yellow: MeCN 100%. Insert: the excitation spectra. The emission wavelength exhibits a gradual red shift with increasing the ratio of MeCN, suggesting there is a competition between guest molecules during the exchange process.

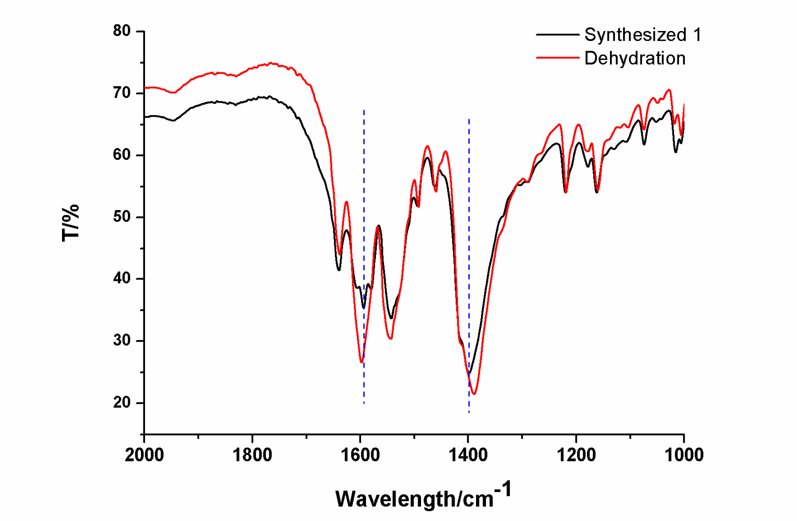

Fig. S10: The IR spectra of the synthesized and dehydrated samples of **1**. The bands centered at 1638 cm^{-1} can be assigned to the characteristic vibration of pyridinium ring, which undergoes less change after dehydration. The bands around 1603 and 1579 cm^{-1} belong to the $\nu_{as}(COO^{-})$ stretching vibration of the carboxylate groups. Due to different hydrogen bonding interactions between water molecules and two carboxylate groups, a small band split can be observed. Furthermore, the C=N and C=C characteristic vibration of terminal pyridine ring of BCbpy ligand appears at 1593 cm^{-1}. A strong band at 1397 cm^{-1} corresponds to the $\nu_s(COO^{-})$ stretching vibration of carboxylate groups. Upon dehydration, the $\nu_s(COO^{-})$ stretching vibration band moves to 1388 cm^{-1}, and the band split of the $\nu_{as}(COO^{-})$ stretching vibration disappears, a new band appears at 1598 cm^{-1}.

Table S1. Geometry Parameters for Hydrogen Bonds in 1

D-H	d(D-H)	d(H···A)	<DHA	d(D···A)	A
O(1W)-H(1C)	0.850	1.985	139.78	2.691	O(3W) #1
O(1W)-H(1D)	0.850	2.021	158.29	2.828	O3
O(2W)-H(2D)	0.850	2.074	161.81	2.894	O(6W) #2
O(3W)-H(3C)	0.850	2.475	178.71	3.325	Cl(1) #1
O(3W)-H(3D)	0.850	1.948	179.41	2.798	O(6W) #2
O(4W)-H(4C)	0.850	1.871	175.27	2.718	O(2)
O(4W)-H(4D)	0.850	1.921	166.00	2.753	O(4) #3
O(5W)-H(5C)	0.850	2.030	179.12	2.880	O(1W) #4
O(5W)-H(5D)	0.850	2.212	129.35	2.828	O(7W)
O(6W)-H(6C)	0.850	1.898	173.38	2.745	O(4W) #5
O(6W)-H(6D)	0.850	2.062	168.16	2.899	O(5W)
O(7W)-H(7D)	0.850	2.135	172.07	2.979	O(2W) #7

Symmetry codes: #1 x, -y+1/2, z-1/2 ;#2 x-1/2, -y+1/2, -z+1 ;#3 -x+1, -y, -z ;#4 x+1/2, -y+1/2, -z+1;#5 -x+1, y+1/2, -z+1/2; #6 -x+3/2, -y, z+1/2 ;#7 -x+1, -y, -z+1.

Table S2. Geometry Parameters for Hydrogen Bonds in 2

D-H	d(D-H)	d(H···A)	<DHA	d(D···A)	A
O(1W)-H(1C)	0.850	1.986	143.81	2.719	O(3W) #1
O(1W)-H(1D)	0.850	2.019	163.49	2.845	O3
O(2W)-H(2D)	0.850	2.073	162.39	2.895	O(6W) #2
O(3W)-H(3C)	0.850	2.612	173.33	3.457	Br(1) #1
O(3W)-H(3D)	0.850	1.920	175.73	2.768	O(6W) #2
O(4W)-H(4C)	0.850	1.884	175.57	2.732	O(2)
O(4W)-H(4D)	0.850	1.948	166.63	2.782	O(4) #3
O(5W)-H(5C)	0.850	2.102	174.65	2.949	O(1W) #4
O(5W)-H(5D)	0.850	2.085	139.88	2.789	O(7W)
O(6W)-H(6C)	0.850	1.901	176.56	2.750	O(4W) #5
O(6W)-H(6D)	0.850	2.018	167.47	2.853	O(5W)
O(7W)-H(7D)	0.850	2.037	172.40	2.881	O(2W) #7

Symmetry codes: #1 x, -y+1/2, z-1/2 ;#2 x-1/2, -y+1/2, -z+1 ;#3 -x+1, -y, -z ;#4 x+1/2, -y+1/2, -z+1;#5 -x+1, y+1/2, -z+1/2; #6 -x+3/2, -y, z+1/2 ;#7 -x+1, -y, -z+1.

Table S3. Interatomic distances (Å) and angles (°) for the [$Cd_2(\mu_2\text{-}Cl)_2$] unit in 1

Interatomic distances (Å)		Angles (°)	
Cd(1)-N(2) #1	**2.355(3)**	**O(1)-Cd(1)-Cl(1)**	**96.19(9)**
Cd(1)-O(1)	**2.370(3)**	**O(2)-Cd(1)-Cl(1)**	**91.60(7)**
Cd(1)-O(4)	**2.397(3)**	**O(3)-Cd(1)-Cl(1)**	**105.53(9)**
Cd(1)-O(2)	**2.459(3)**	**O(4)-Cd(1)-Cl(1)**	**95.18(8)**
Cd(1)-O(3)	**2.473(3)**	**Cl(1)-Cd(1)-Cl(1)#2**	**83.30(3)**
Cd(1)-Cl(1)	**2.5678(1)**	**Cd(1)-Cl(1)-Cd(1)#2**	**96.70(3)**
Cd(1)-Cl(1)#2	**2.7285(1)**		

Symmetry codes: #1 -x+1,-y,-z+1 ; #2 -x+1,-y,-z

Table S3. Interatomic distances (Å) and angles (°) for the [$Cd_2(\mu_2\text{-}Br)_2$] unit in 2

Interatomic distances (Å)		Angles (°)	
Cd(1)-N(2) #1	**2.358(6)**	**O(1)-Cd(1)-Br(1)**	**95.03(1)**
Cd(1)-O(1)	**2.380(5)**	**O(2)-Cd(1)-Br(1)**	**89.53(12)**
Cd(1)-O(4)	**2.404(5)**	**O(3)-Cd(1)-Br(1)**	**104.38(17)**
Cd(1)-O(2)	**2.479(5)**	**O(4)-Cd(1)-Br(1)**	**96.48(14)**
Cd(1)-O(3)	**2.474(6)**	**Br(1)-Cd(1)-Br(1)#2**	**85.05(3)**
Cd(1)-Br(1)	**2.6927(1)**	**Cd(1)-Br(1)-Cd(1)#2**	**94.95(3)**
Cd(1)-Br(1)#2	**2.8870(1)**		

Symmetry codes: #1 -x+1,-y,-z+1 ; #2 -x+1,-y,-z