Electronic Supplementary Information (ESI)

Single-crystal to single-crystal transformation of 1D coordination polymer *via* photochemical [2+2] cycloaddition reaction

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Experimental Section

General procedure. All chemicals and reagents were obtained from commercial sources and used as received. The IR spectra were recorded on a Varian 1000 FT–IR spectrometer as KBr disks (4000-400 cm^{-1}). The elemental analyses for C, H, and N were performed on an EA1110 CHNS elemental analyzer. ^{1}H NMR spectra were recorded at ambient temperature on a Varian UNITYplus-400 spectrometer. ^{1}H NMR chemical shifts were referenced to the solvent signal in d_6-DMSO. Powder XRD patterns were obtained using a PANalytical X'Pert PRO MPD system (PW3040/60). Thermal analysis was performed with a Perkin_Elmer TGA-7 thermogravimetric analyser at a heating rate of 10 °C/min and a flow rate of 100 cm^3/min (N_2).

Preparation of [Cd(bpe)(CBA)$_2$]$_n$ (1). To a 10 mL Pyrex glass tube was loaded $CdCl_2 \cdot 2.5H_2O$ (23 mg, 0.1 mmol), CBA (31 mg, 0.2 mmol), bpe (18 mg, 0.1 mmol) and H_2O (3 mL). The tube was sealed and heated in an oven to 150°C for 3 d, and then cooled to ambient temperature at the rate of 5°C h^{-1} to form colorless crystals of **1**, which were washed with water/ethanol and dried in air. Yield: 47 mg (78% yield based on Cd). Anal. calcd. for $C_{26}H_{18}CdCl_2N_2O_4$: C, 63.30; H, 3.68; N, 5.68. Found: C, 63.54; H, 3.49; N, 5.72. IR (KBr, cm^{-1}): 3441m, 3056m, 1605s, 1593s, 1538s, 1505s, 1404s, 1383s, 1295m, 1222w, 1176m, 1129m, 1093s, 1015s, 979m, 933w, 854s, 831s, 684m, 550s, 474m. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K, TMS): δ = 8.61 (s, 4H, Py–H), 7.94 (d, 4H, Ph–H), 7.63 (d, 4H, Py–H), 7.54 (s, 2H, CH=CH), 7.47 (d, 4H, Ph–H).

Preparation of [Cd(*rctt*-tpcb)$_{0.5}$(CBA)$_2$]$_n$ (2). Single crystals of **1** were irradiated by Hg lamp (400 W) for about 5 hours to form crystals of **2** in 100% yield based on **1**. Anal. calcd. for $C_{26}H_{18}CdCl_2N_2O_4$: C, 63.30; H, 3.68; N, 5.68. Found: C, 63.36; H, 3.51; N, 5.58. IR (KBr, cm^{-1}): 3437m, 3068m, 1608s, 1595s, 1539s, 1506s, 1404s, 1383s, 1282m, 1222w, 1167m, 1093s, 1016s, 929m, 854s, 829s, 685m, 539s, 474m. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K, TMS): δ = 8.34 (s, 4H, Py–H), 7.93 (d, 4H, Ph–H), 7.47 (d, 4H, Ph–H), 7.24 (d, 4H, Py–H), 4.66 (s, 2H, CH–CH).

Preparation of {[Cd(*rtct*-tpcb)Cl$_2$]·2H$_2$O}$_n$ (3). To a Pyrex tube (10 mL) was added **2** (30 mg, 0.05 mmol) and 3 mL of H_2O. After the pH value was adjusted to about 1.0 by addition of HCl (6 M, 0.06 mL), the tube was sealed and heated in an oven to 150°C for 3 d, and then cooled to ambient temperature at a rate of 5°C h^{-1} to form colorless blocks of **3**, which were washed with water/ethanol and dried in air. Yield: 11 mg (75% yield based on **2**). Anal. calcd. for $C_{24}H_{24}CdCl_2N_4O_2$: C, 49.38; H, 4.14; N, 9.60. Found: C, 49.65; H, 3.99; N, 9.68. IR (KBr, cm^{-1}): 3448m, 3052w, 1609s, 1556m, 1501w, 1427s, 1384m, 1294w, 1228m, 1070s, 1013s, 993w, 832s, 653m, 617m, 595w, 542s, 472w.

X-ray diffraction crystallography: single-crystal X-ray diffraction data for **1-3** were collected on a Rigaku Mercury CCD diffractometer by using graphite monochromated Mo-Kα (λ = 0.71073 Å). Cell parameters were refined by using the program *CrystalClear* (Rigaku and MSC, version 1.3, 2001). The collected data were reduced by using the program *CrystalClear*, and an absorption correction (multiscan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The crystal structures of **1-3** were solved by direct methods and refined on F^2 by full-matrix least-squares methods with the *SHELXL-97* program.[1] All non-hydrogen atoms refined anisotropically. The H atoms of the water solvent molecule in **3** were located from the Fourier map. All other H atoms were introduced at the calculated positions and included in the structure-factor calculations. All the calculations were performed on a Dell workstation using the CrystalStructure crystallographic software package (Rigaku and MSC, Ver.3.60, 2004).

[1] Sheldrick, G. M. *SHELXS-97and SHELXL-97. Program for the refinement of crystal structures*, University of Göttingen, Germany. **1997**.

Table S1. Selected Bond Lengths (Å) and Angles (º) for **1-3**

		Compound **1**	
Cd(1)-N(2A)	2.3181(19)	Cd(1)-N(1)	2.3237(19)
Cd(1)-O(4)	2.3338(18)	Cd(1)-O(3B)	2.3576(18)
Cd(1)-O(1)	2.3878(19)	Cd(1)-O(2)	2.3924(19)
N(2A)-Cd(1)-N(1)	172.75(6)	N(2A)-Cd(1)-O(4)	93.77(7)
N(1)-Cd(1)-O(4)	91.01(7)	O(1)-Cd(1)-O(2)	54.91(6)
N(2A)-Cd(1)-O(1)	88.34(7)	N(1)-Cd(1)-O(1)	91.56(7)
O(4)-Cd(1)-O(1)	139.52(6)	N(2A)-Cd(1)-O(2)	97.60(7)
N(1)-Cd(1)-O(2)	88.25(7)	O(4)-Cd(1)-O(2)	84.81(7)
O(3B)-Cd(1)-O(2)	145.29(6)		
		Compound **2**	
Cd(1)-O(1)	2.294(2)	Cd(1)-N(1)	2.321(2)

Cd(1)-N(2A)	2.331(2)	Cd(1)-O(2B)	2.364(2)
Cd(1)-O(3)	2.375(2)	Cd(1)-O(4)	2.405(2)
O(1)-Cd(1)-N(1)	91.04(9)	O(1)-Cd(1)-N(2A)	1.23(9)
N(1)-Cd(1)-N(2A)	176.08(8)	O(1)-Cd(1)-O(3)	145.51(8)
N(1)-Cd(1)-O(3)	91.72(9)	N(2A)-Cd(1)-O(3)	88.22(9)
O(2B)-Cd(1)-O(3)	90.29(8)	O(1)-Cd(1)-O(4)	90.96(8)
N(1)-Cd(1)-O(4)	87.88(8)	N(2A)-Cd(1)-O(4)	95.27(8)
O(2B)-Cd(1)-O(4)	144.39(8)	O(3)-Cd(1)-O(4)	54.82(7)
Compound **3**			
Cd(1)-N(2A)	2.359(3)	Cd(1)-N(2B)	2.359(3)
Cd(1)-N(1C)	2.384(3)	Cd(1)-N(1)	2.384(3)
Cd(1)-Cl(1)	2.6215(10)	N(2A)-Cd(1)-N(2B)	103.61(13)
N(2A)-Cd(1)-N(1C)	86.18(9)	N(2B)-Cd(1)-N(1C)	167.54(9)
N(2A)-Cd(1)-N(1)	167.54(9)	N(2B)-Cd(1)-N(1)	86.18(9)
N(1C)-Cd(1)-N(1)	85.27(13)	N(2A)-Cd(1)-Cl(1)	84.46(8)
N(2B)-Cd(1)-Cl(1)	91.42(8)	N(1C)-Cd(1)-Cl(1)	97.26(7)
N(1)-Cd(1)-Cl(1)	87.66(7)	N(2A)-Cd(1)-Cl(1C)	91.42(8)
N(2B)-Cd(1)-Cl(1C)	84.46(8)	N(1C)-Cd(1)-Cl(1C)	87.66(7)
N(1)-Cd(1)-Cl(1C)	97.26(7)	Cl(1)-Cd(1)-Cl(1C)	173.34(5)

Symmetry codes: for **1**: A: $x + 1$, $y - 1$, z; B: $-x$, $-y$, $-z + 1$; for **2**: A: $x + 1$, $y - 1$, z; B: $-x$, $-y + 1$, $-z$; for **3**: A: $-x + 3/2$, $y - 1$, $z - 1/2$; B: x, $-y + 1$, $z - 1/2$; C: $-x + 3/2$, $-y$, z.

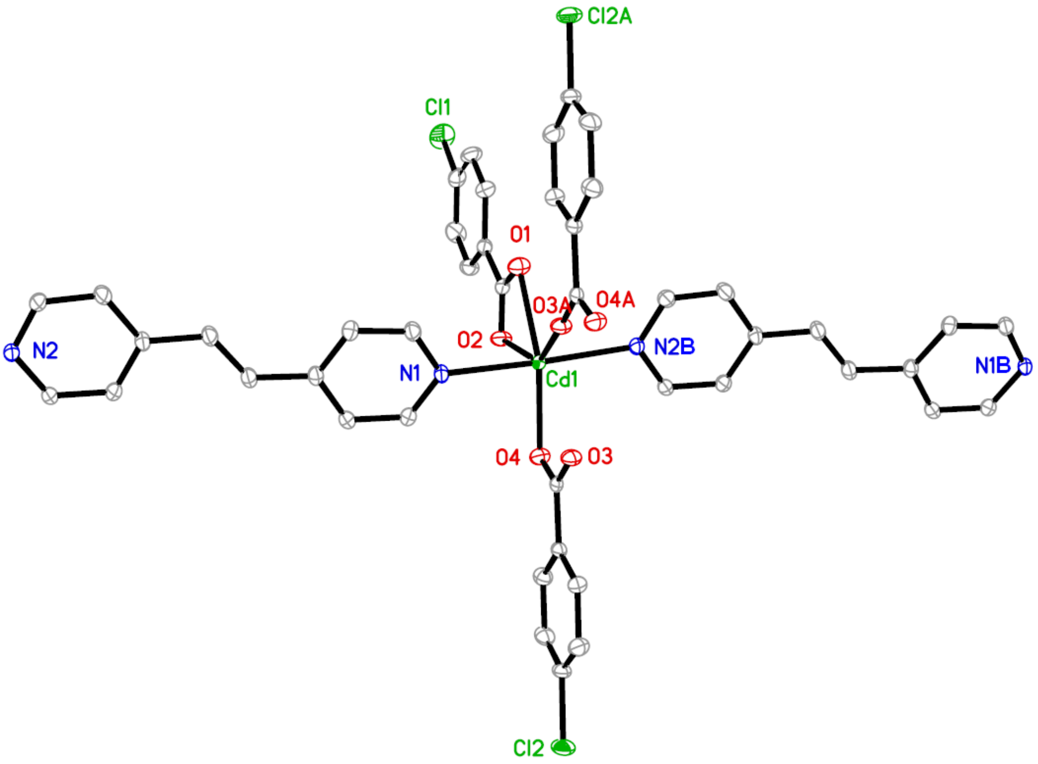


Fig. S1 View of the coordination environment of Cd center in **1** with labeling scheme. Symmetry codes: (A) - *x* + 1, - *y*, - *z* + 1; (B) *x* + 1, *y* - 1, *z*.

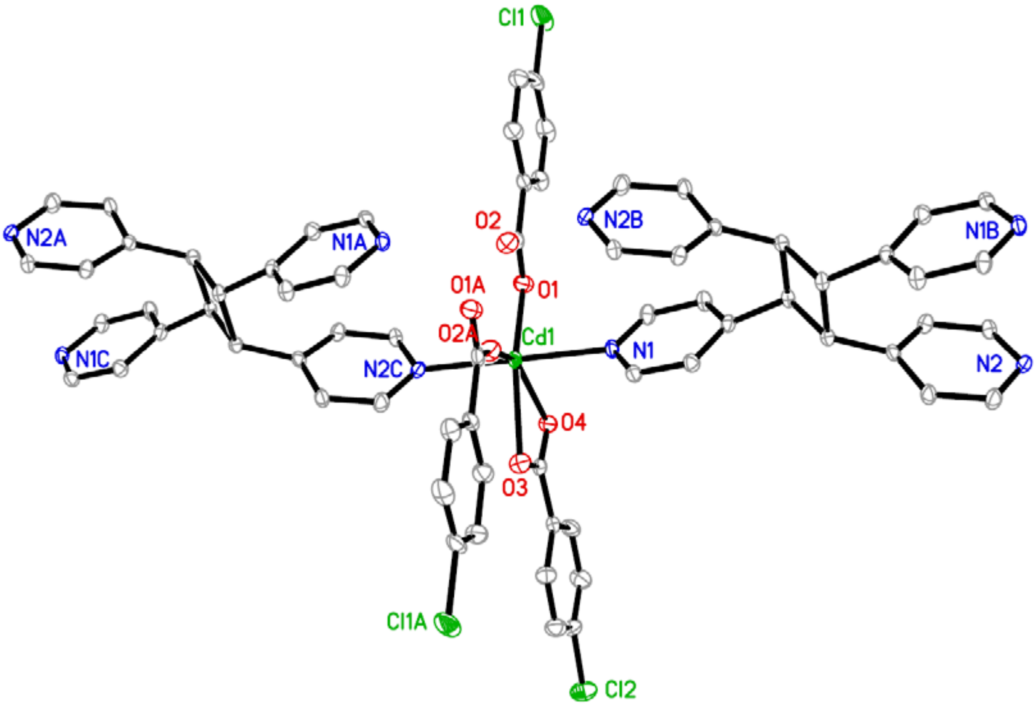


Fig. S2 View of the coordination environment of the Cd atom in **2** with a labeling scheme. Symmetry codes: (A) - *x*, - *y* + 1, - *z*; (B) - *x* + 1, - *y* + 2, - *z*; (C) *x* + 1, *y* - 1, *z*.

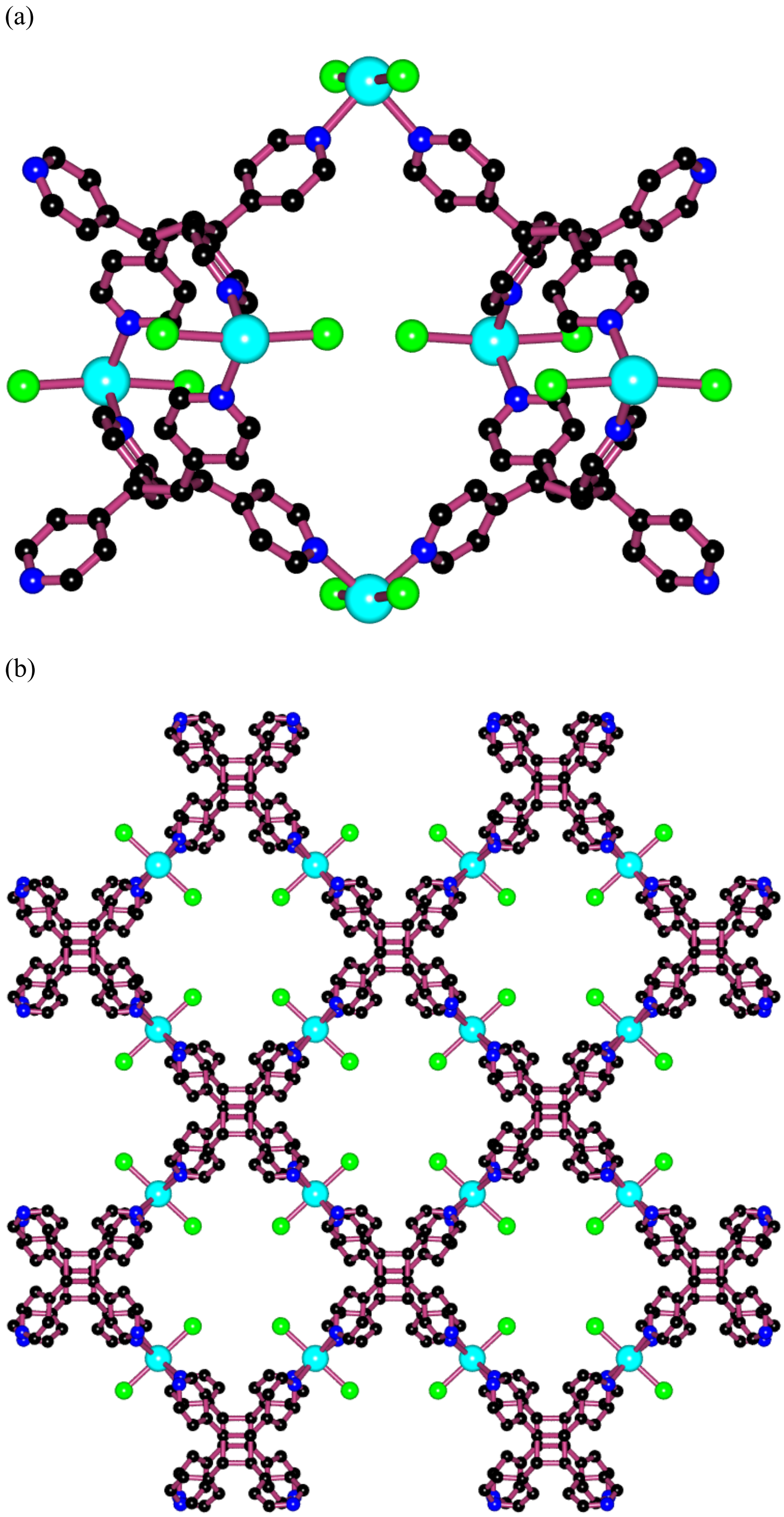


Fig. S3 (a) The single cage in **3**. (b) The 3D network of **3**. All hydrogen atoms are omitted for clarity. The black, red, blue, green and cyan balls represent carbon, oxygen, nitrogen, chlorine and cadmium atoms, respectively.

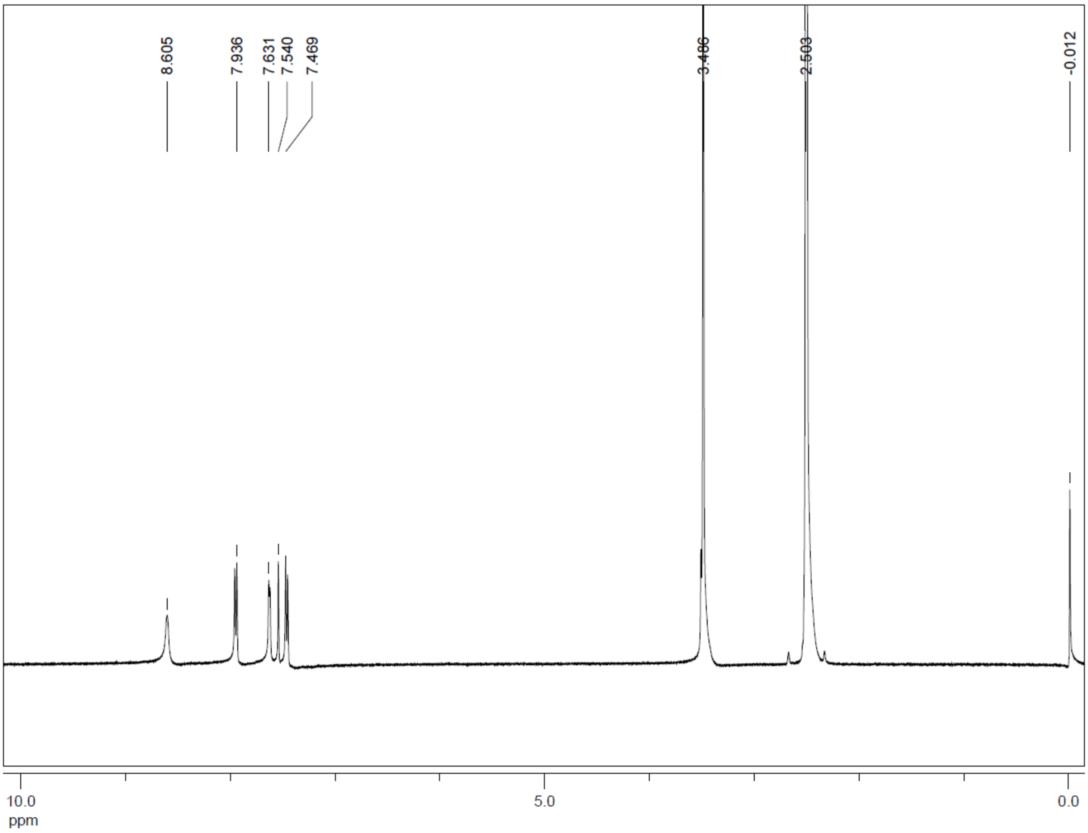


Fig. S4a The ^{1}H NMR spectrum of **1** in *d*$_6$-DMSO at ambient temperature.

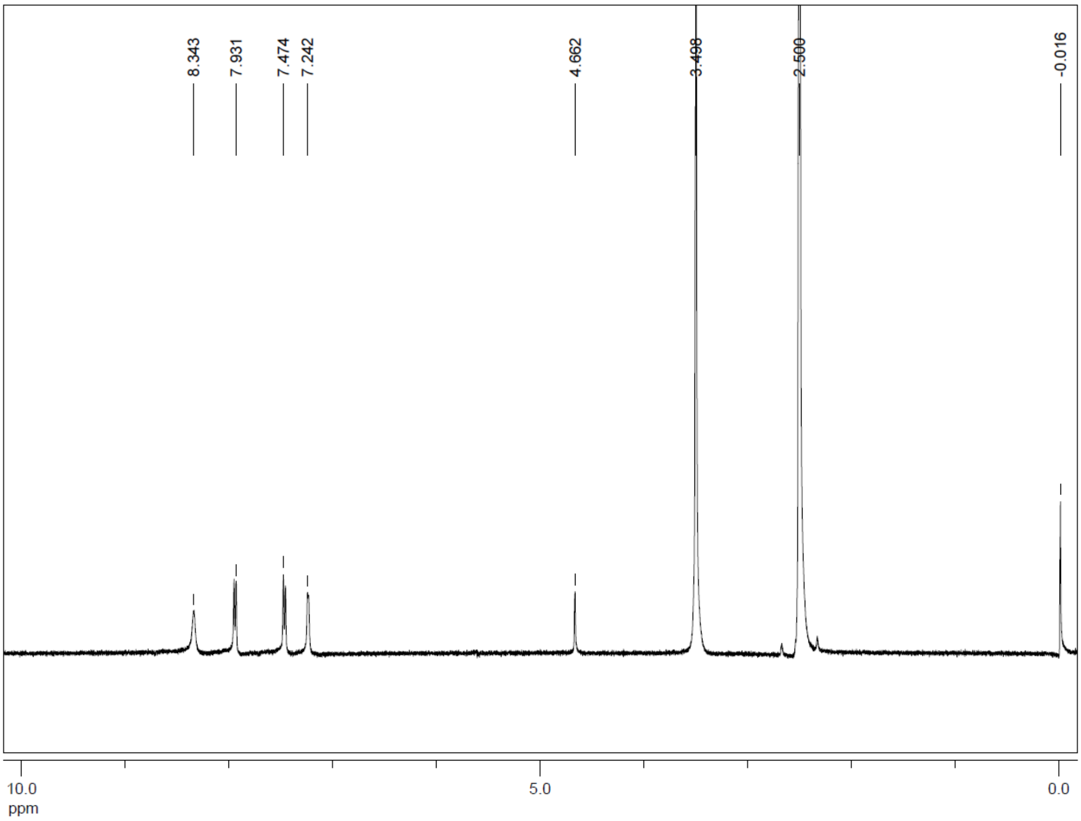
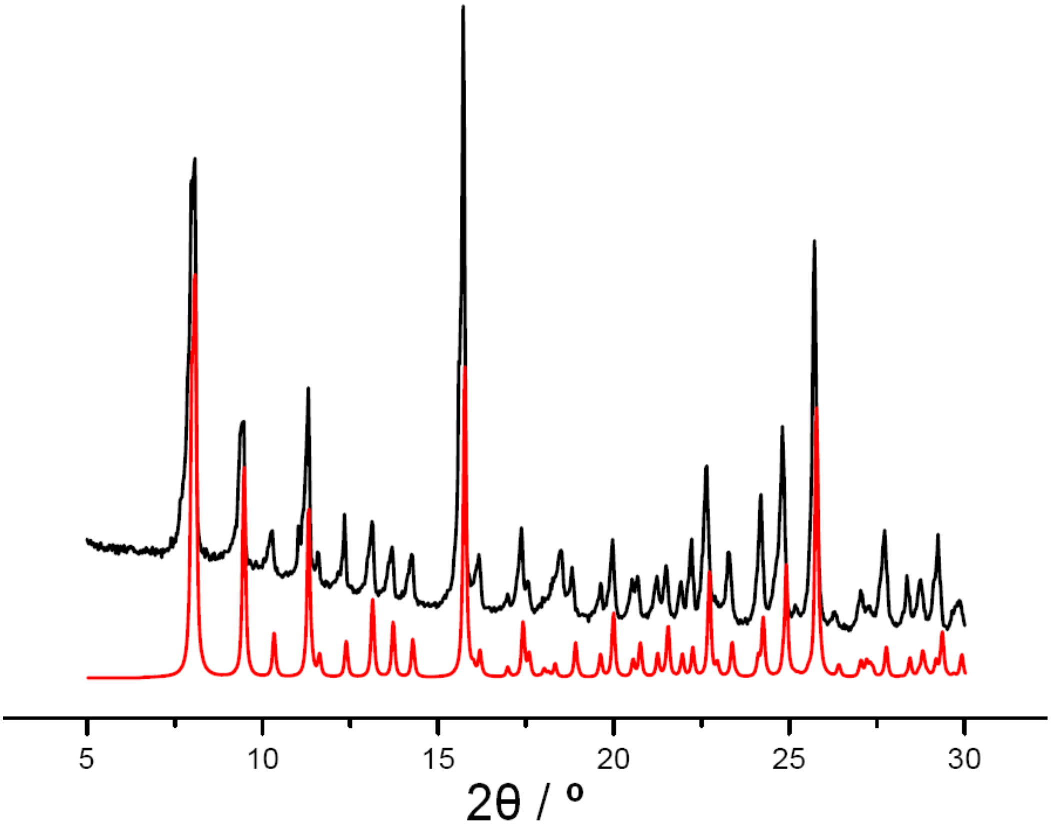
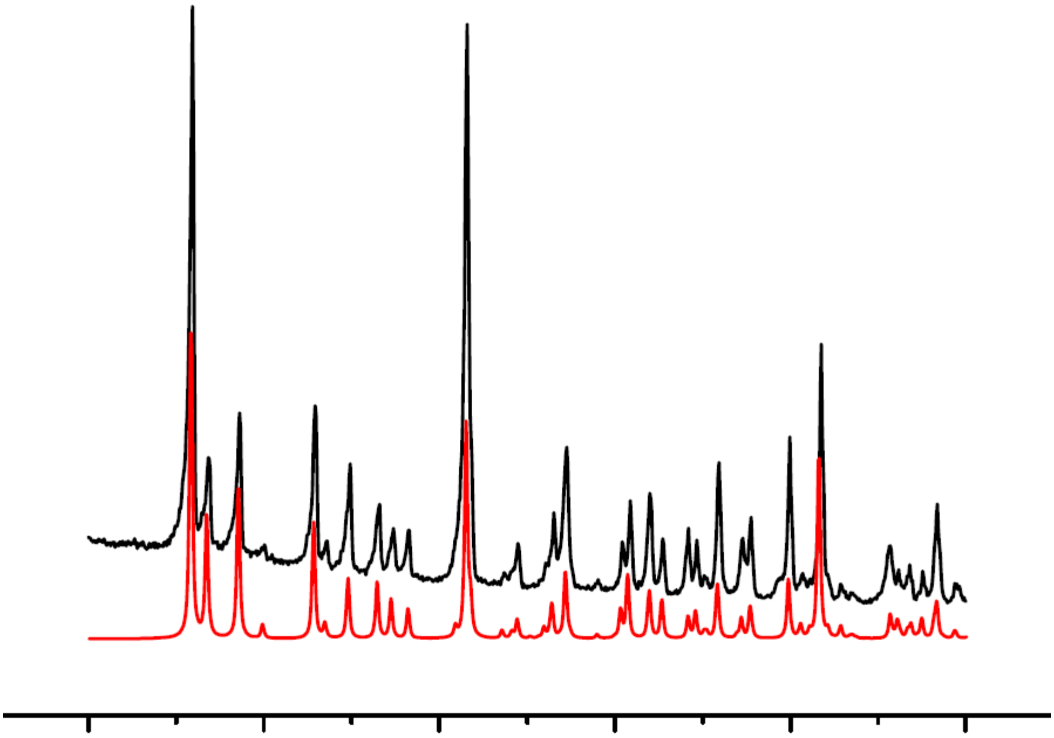


Fig. S4b The ^{1}H NMR spectrum of **2** in *d*$_6$-DMSO at ambient temperature.

(a)



(b)



(c)

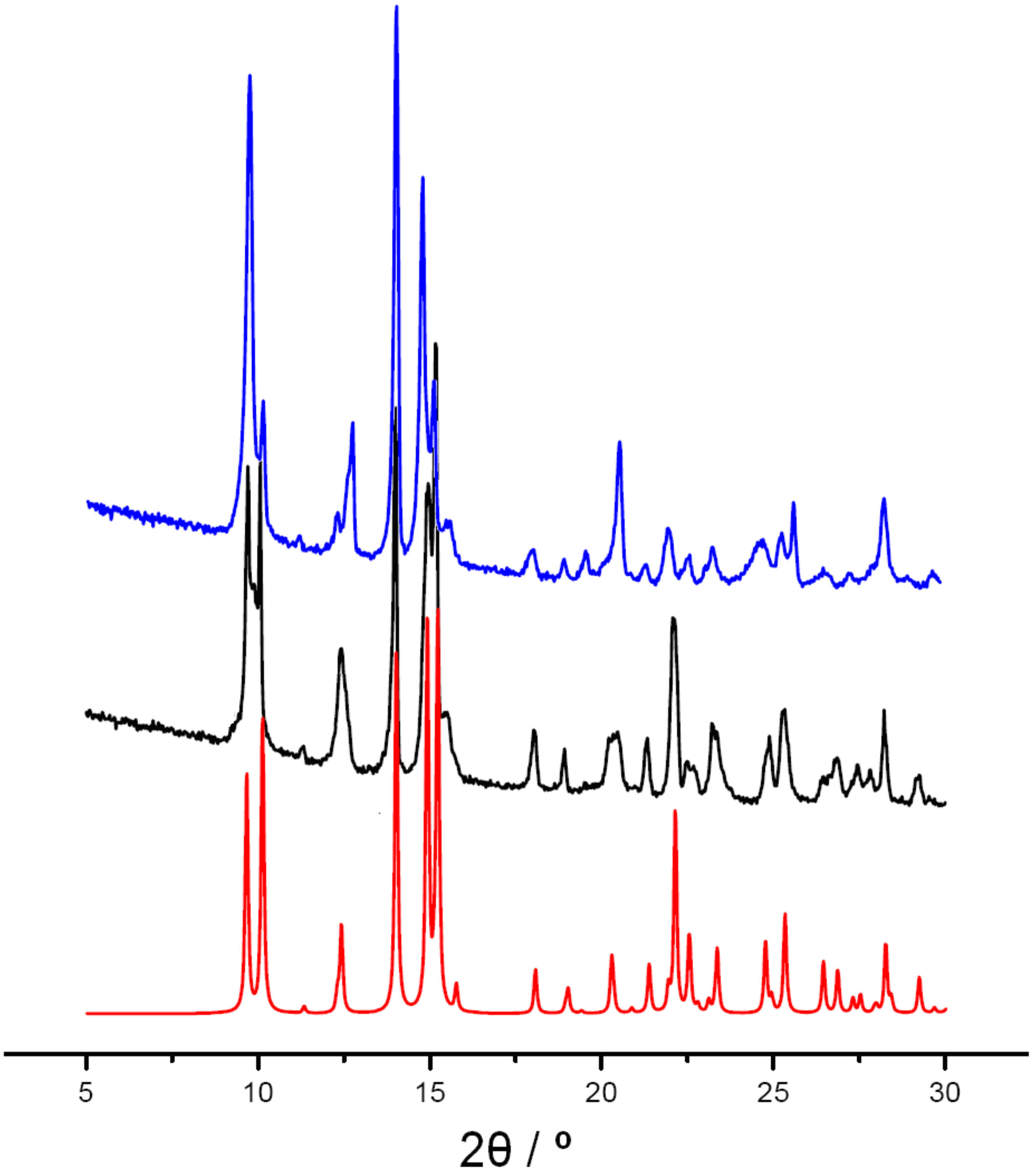


Fig. S5 (a) PXRD patterns of **1** (simulated pattern form single crystal: red; experimental pattern form grinding crystals: black). (b) PXRD patterns of **2** (simulated pattern form single crystal: red; experimental pattern form grinding crystals: black). (c) PXRD patterns of **3** (simulated pattern form single crystal: red; experimental pattern form grinding crystals: black; experimental pattern form the precipitates which produced by the reaction of $CdCl_2·2.5H_2O$ and tpcb: blue).

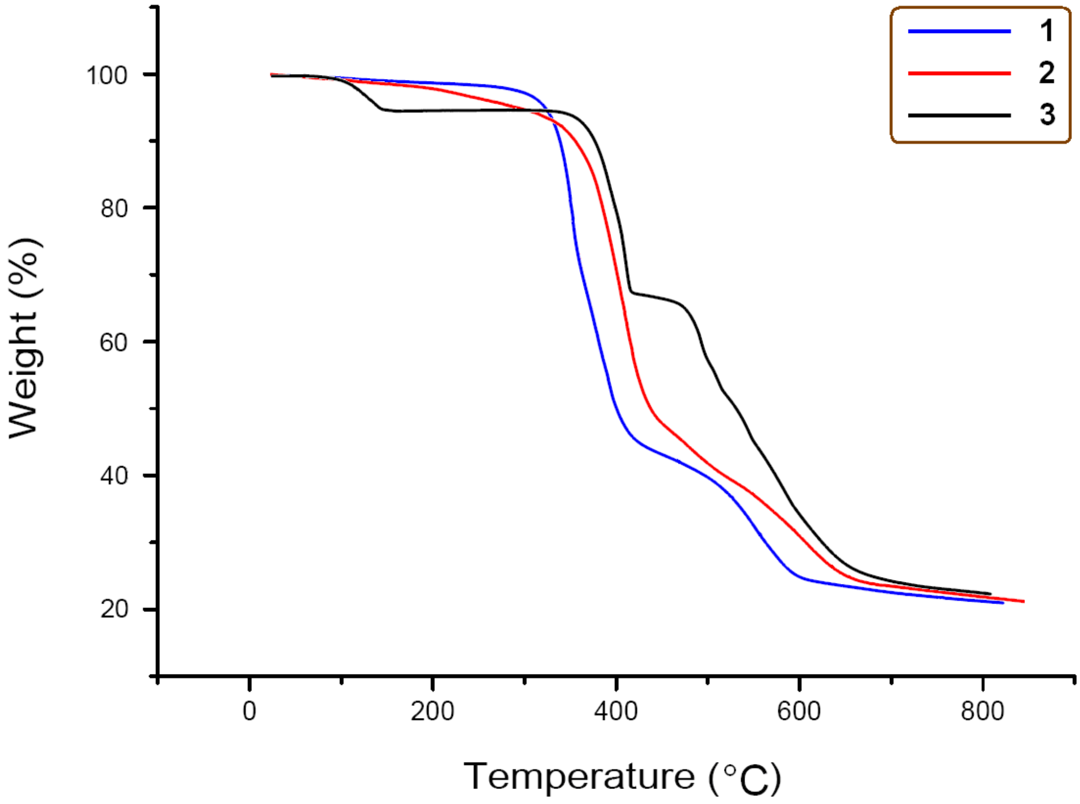


Fig. S6 The TG curves for the three compounds **1**-**3**. Compound **1** was stable up to about 300 °C, above which decomposition started. The final residue (20.76%) was assumed to be CdO (ca. 21.20%). For **2**, the whole structure remained contact until about 200 °C. The weight loss above 200 °C indicates the decomposition of the coordination worked. The final residue (20.95%) was also assumed to be CdO (ca. 21.20%). Compound **3** showed a first weight loss of 5.78% in the range of 70-145 °C, which corresponds to two H_2O molecules per formula unit and is consistent with the formula of $\{[Cd(\textit{rtct}\text{-tpcb})Cl_2]\cdot 2H_2O\}_n$ (ca. 6.17%). After about 340 °C, the ligands in compound **3** started to decompose and the weight of the final residue (22.13%) was assumed to be CdO (ca. 22.00%).