Three Self-penetrated, interlocked, and polycatanated supramolecular isomers via one-pot synthesis and crystallization

Jin-Song Hu, Ling Qin, Ming-Dao Zhang, Xiao-Qiang Yao, Yi-Zhi Li, Zi-Jian Guo, He-Gen Zheng, Zi-Ling Xue

State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, P. R. China. Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996-1600

Materials and Methods. Reagents and solvents employed were commercially available and used as received. Ligand TPOM was prepared by the literature methods.[1] IR absorption spectra of the complexes were recorded in the range of 400–4000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation (0.15418 nm), in which the X-ray tube was operated at 40 kV and 40 mA. Luminescent spectra were recorded with a SHIMAZU VF–320 X-ray fluorescence spectrophotometer at room temperature. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K using a heating rate of 10 K min^{-1} under N_2 atmosphere.

Syntheses of 1, 2, and 3: A mixture of $Cd(NO_3)_2·4H_2O$ (30 mg, 0.1 mmol), H_2hfipbb (39 mg, 0.1 mmol) and TPOM (22 mg, 0.1 mmol) was dissolved in 10 mL of DMF and H_2O (1:1, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) and heated at 100 °C for 4d. Large quantities of colorless-block crystals **1**, **2**, and **3** were obtained and crystals were filtered off, washed with mother liquid, and dried under ambient conditions. The crystals were separated by hand picking and yield of the reaction were ca. 40% in **1**, 20% in **2**, 20% in **3** based on TPOM.

IR (KBr, cm^{-1}): **1**: 3410m, 3061w, 2929w, 1663m, 1602s, 1543s, 1505m, 1400s, 1249s, 1210s, 1169s, 1023m, 851m; **2**: 3406m, 3068w, 2927w, 1661m, 1603s, 1545s, 1501m, 1395s, 1250s, 1212s, 1168s, 1021m, 852m; **3**: 3409m, 3072w, 2937w, 1663m, 11604s, 1542s, 1505m, 1401s, 1291s, 1253s, 1211s, 1169s, 1020m, 854m.

The distribution of peaks in the channels of **1-3** was chemically featureless to refine, using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining solvent molecules were removed by the SQUEEZE routine in PLATON.[2]

The thermogravimetric analysis (TGA) was performed in N_2 atmosphere on polycrystalline samples of compounds **1-3** (Fig. S11). For complex **1**, the weight loss of 10.15% is observed from 20 to 200 °C corresponds to the departure of the lattice water and DMF, and the structure was then decomposed starting at 380 °C. For **2**, the weight loss of 11.18% in the region of 20–135 °C corresponds to the loss of water molecules, and the framework begins to collapse at 370 °C. Complex **3** lost water and DMF molecules (10.35%) before 195 °C, and the framework begins to decompose at 370 °C.

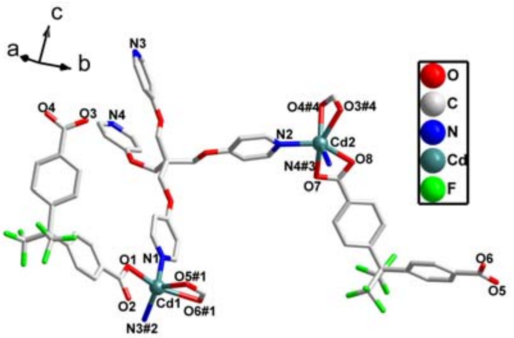


Fig. S1. Coordination environment of the Cd(II) ion in **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = -x, 2-y, 1-z; #2 = x, 0.5-y, -0.5+z; #3 = x, 1+y, z; #4 = 1-x, 0.5+y, 1.5-z.

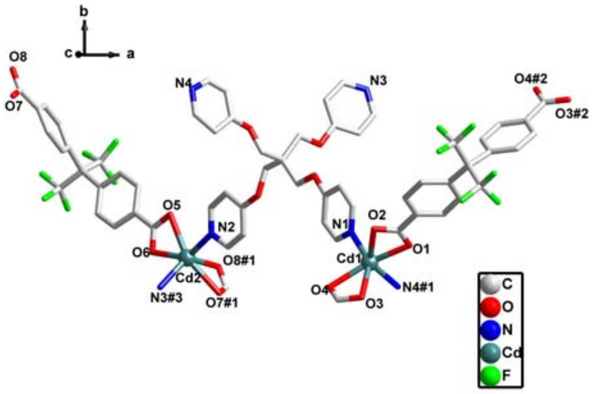


Fig. S2. Coordination environment of the Cd(II) ion in **2**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = 0.5+x, -0.5+y, z; #2 = 0.5+x, 0.5+y, z; #3 = -0.5+x, -0.5+y, z.

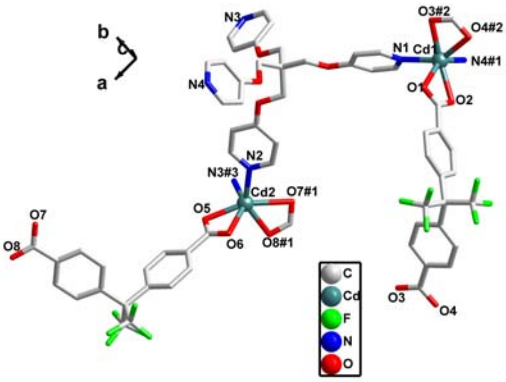


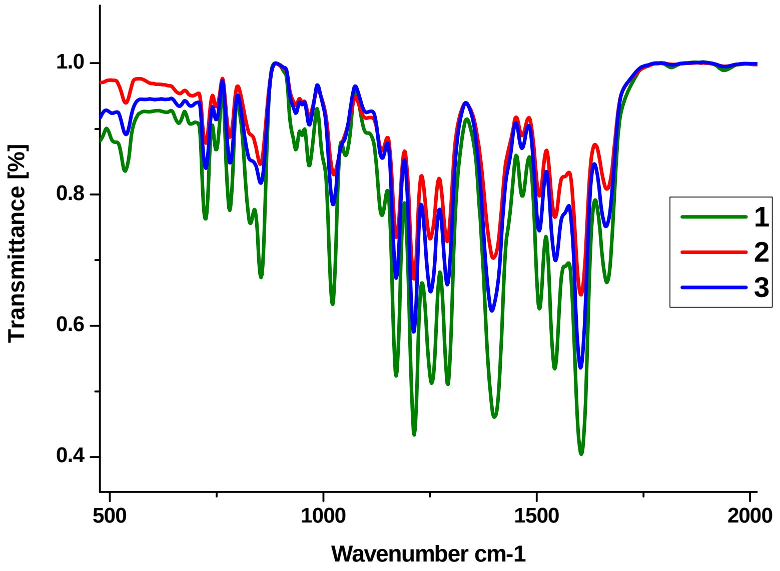
Fig. S3. Coordination environment of the Cd(II) ion in **3**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = -0.5+x, -0.5+y, z; #2 = -0.5+x, 0.5+y, z; #3 =1.5-x, 1.5-y, 1.0-z.

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

Complex **1**			
N3#2-Cd1	2.221(5)	N4#3-Cd2	2.283(5)
O3#4-Cd2	2.349(4)	O4#4-Cd2	2.339(4)
O5#1-Cd1	2.221(4)	O6#1-Cd1	2.488(4)
Cd2-N2	2.263(5)	Cd2-O8	2.344(5)
Cd2-O7	2.368(5)	Cd1-O1	2.193(4)
Cd1-N1	2.261(4)	O8-Cd2-O3	100.19(17)
O1-Cd1-N3#2	112.06(19)	O1-Cd1-O5#1	105.41(18)
N3#2-Cd1-O5#1	129.94(18)	O1-Cd1-N1	87.45(17)
N3#2-Cd1-N1	107.45(18)	O5#1-Cd1-N1	106.16(18)
O1-Cd1-O6#1	157.81(17)	N3#2-Cd1-O6#1	89.69(17)
O5#1-Cd1-O6#1	54.29(15)	N1-Cd1-O6#1	90.16(16)
O7-Cd2-O3	153.69(18)	N2-Cd2-N4#3	100.2(2)
N2-Cd2-O4	94.22(17)	N4#3-Cd2-O4	143.56(18)
N2-Cd2-O8	139.50(18)	N4#3-Cd2-O8	91.21(19)
O4-Cd2-O8	99.21(16)	N2-Cd2-O7	84.69(17)
N4#3-Cd2-O7	99.16(19)	O4-Cd2-O7	115.47(17)
O8-Cd2-O7	55.04(15)	N2-Cd2-O3	118.54(19)
N4#3-Cd2-O3	89.18(18)	O4-Cd2-O3	54.70(16)
Complex **2**			
Cd1-N4#1	2.24(2)	Cd1-N1	2.252(3)
Cd1-O1	2.290(3)	Cd1-O4#2	2.337(3)
Cd1-O2	2.411(3)	Cd2-N2	2.272(4)
Cd2-O6	2.274(3)	Cd2-N3#3	2.326(4)
Cd2-O8#1	2.353(3)	Cd2-O7#1	2.372(3)

Cd2-O5	2.464(3)	Cd1-O3#2	2.342(4)
N4#1-Cd1-N1	105.6(6)	N4#1-Cd1-O1	81.2(9)
N1-Cd1-O1	108.79(13)	N4#1-Cd1-O4	105.7(9)
N1-Cd1-O4	92.11(13)	O1-Cd1-O4	155.63(14)
N4#1-Cd1-O3	93.2(7)	N1-Cd1-O3	146.35(12)
O1-Cd1-O3	101.35(13)	O4-Cd1-O3	55.54(12)
N4#1-Cd1-O2	136.1(9)	N1-Cd1-O2	91.82(13)
O1-Cd1-O2	54.90(12)	O4-Cd1-O2	113.79(13)
O3-Cd1-O2	93.48(12)	N2-Cd2-O6	140.15(13)
N2-Cd2-N3#3	106.69(13)	O6-Cd2-N3#3	89.05(14)
N2-Cd2-O8#1	102.83(14)	O6-Cd2-O8#1	93.33(14)
N3-Cd2-O8#1	129.98(14)	N2-Cd2-O7#1	91.94(13)
O8#1-Cd2-O7#1	53.84(11)	N2-Cd2-O5	87.14(13)
O6-Cd2-O7#1	126.29(14)	N3-Cd2-O7#1	85.47(14)
O6-Cd2-O5	54.38(12)	N3#3-Cd2-O5	122.82(14)
O8#1-Cd2-O5	97.83(12)	O7#1-Cd2-O5	150.68(12)
Complex **3**			
Cd1-N4#1	2.282(4)	Cd1-N1	2.286(4)
Cd1-O2	2.299(3)	Cd1-O4#2	2.322(4)
Cd1-O3#2	2.355(3)	Cd1-O1	2.394(3)
Cd2-O8#1	2.222(3)	Cd2-N2	2.258(4)
Cd2-O5	2.263(3)	Cd2-N3#3	2.279(4)
Cd2-O7#1	2.458(4)	Cd2-O6	2.468(3)
O8#1-Cd2-N2	139.12(14)	O8#1-Cd2-O5	105.64(13)
N2-Cd2-O5	112.02(14)	O8#1-Cd2-N3#3	101.81(14)
N2-Cd2-N3#3	94.38(13)	O5-Cd2-N3#3	88.88(13)

O8-Cd2-O7#1	54.61(12)	N2-Cd2-O7#1	86.46(14)
O5-Cd2-O7#1	160.10(13)	N3#3-Cd2-O7#1	97.30(14)
O8#1-Cd2-O6	89.64(12)	N2-Cd2-O6	99.30(12)
O5-Cd2-O6	54.53(12)	N3-Cd2-O6	143.41(13)
O7-Cd2-O6	117.19(13)	N4#1-Cd1-N1	96.79(15)
N4#1-Cd1-O2	88.35(14)	N1-Cd1-O2	108.90(14)
N4#1-Cd1-O4#2	95.99(14)	N1-Cd1-O4#2	144.76(13)
O2-Cd1-O4#2	104.16(13)	N4#1-Cd1-O3#2	117.05(15)
N1-Cd1-O3#2	89.79(14)	O2-Cd1-O3#2	146.93(13)
O4#2-Cd1-O3#2	55.25(12)	N4#1-Cd1-O1	143.13(14)
N1-Cd1-O1	90.54(13)	O2-Cd1-O1	55.27(11)
O4#2-Cd1-O1	98.53(12)	O3#2-Cd1-O1	98.99(13)



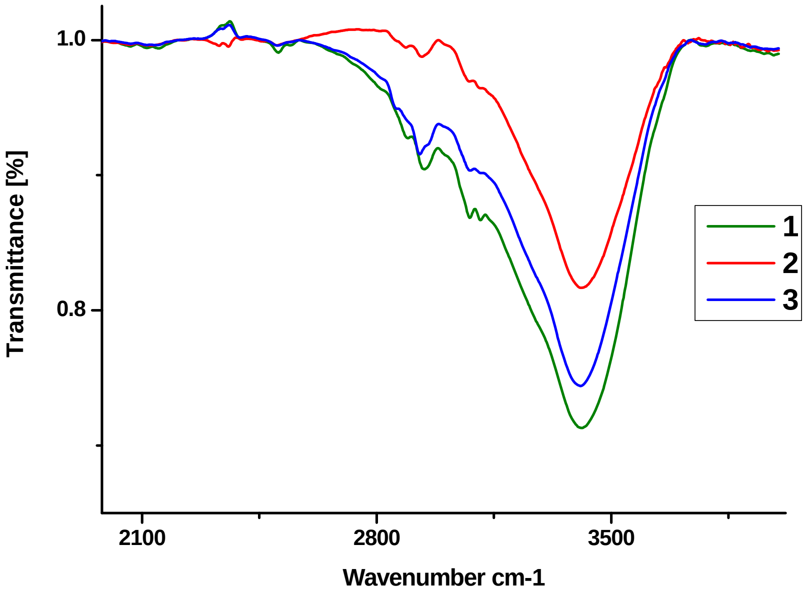


Fig. S4. IR spectra of **1**, **2**, and **3** at room temperature.

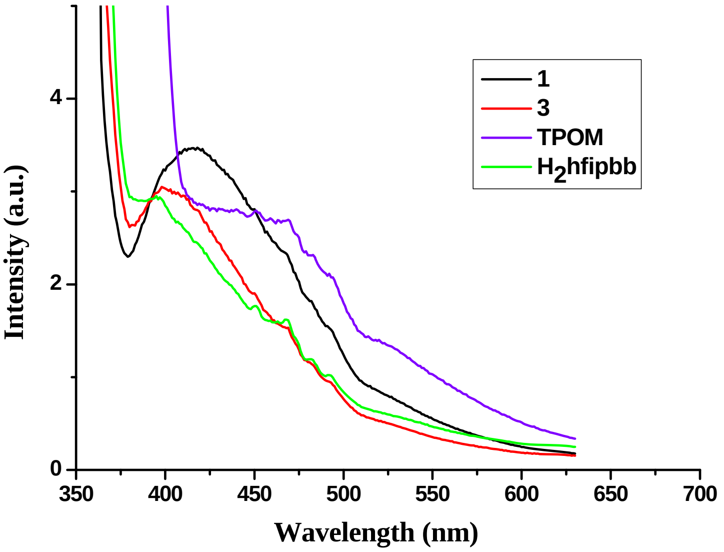


Fig. S5. Solid-state photoluminescent spectra of **1**, and **3**, TPOM, H_2hfipbb at room temperature.

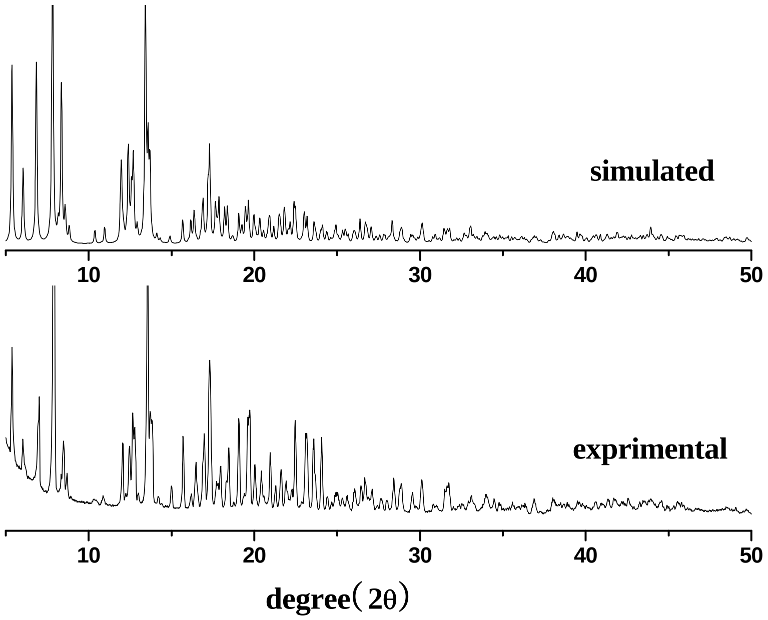


Fig. S6. Powder X-ray diffraction patterns of complex **1**

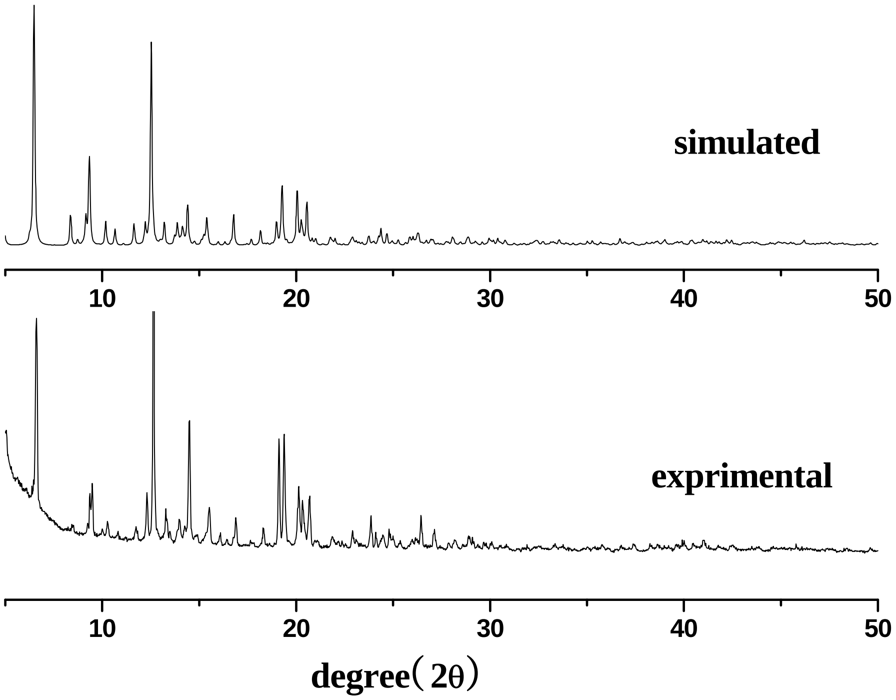


Fig. S7. Powder X-ray diffraction patterns of complex **2**

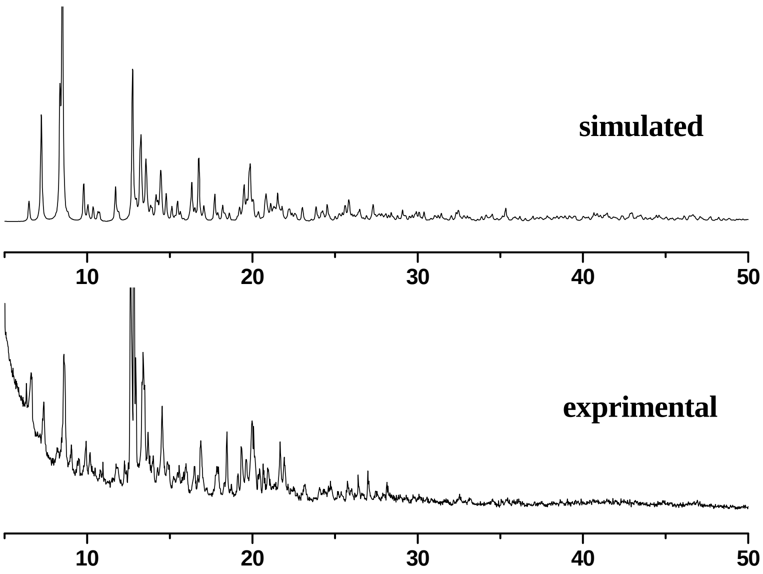


Fig. S8. Powder X-ray diffraction patterns of complex **3**

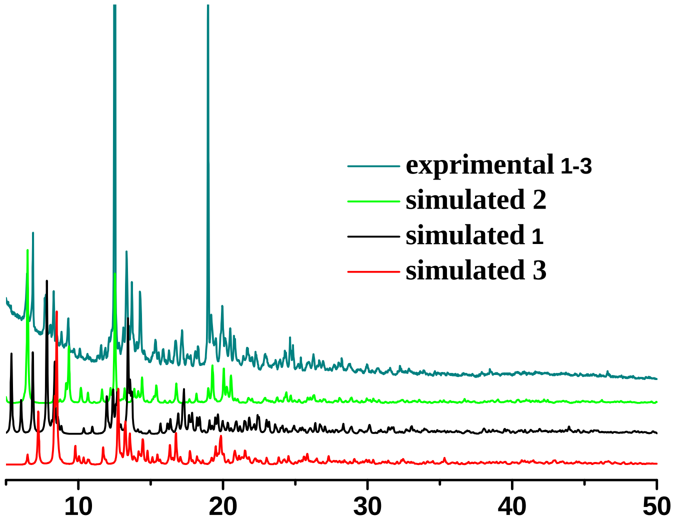


Fig. S9. Powder X-ray diffraction patterns of complexes **1-3**

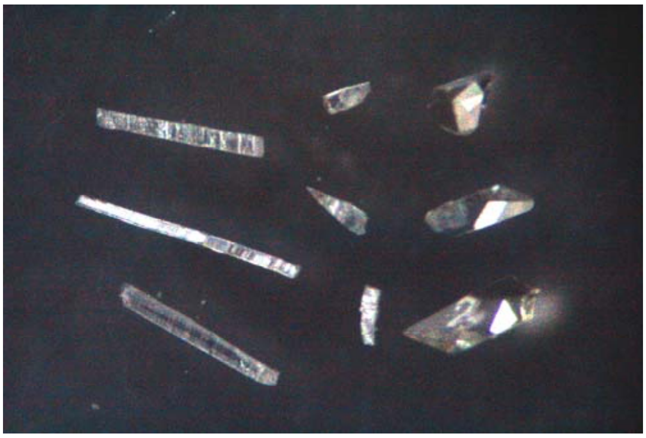


Fig. S10. The photograph of complexes **1-3**. Compound **1** is needle-shaped, **2** is rice-shaped and **3** is block.

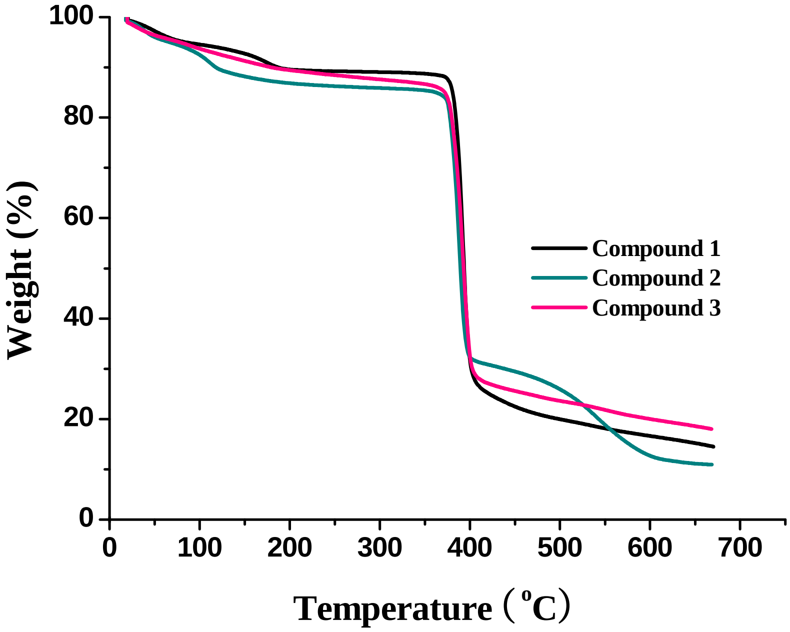


Figure S11. TG plots of compounds **1-3**.

Table S2. Summary of the product isolated at different conditions

Ratio Temp.(Solv.)	**3/1**	**2/1**	**1/1**	**1/2**	**1\3**	**CdX$_2$**
80°C (DMF/H$_2$O)	**1**	**1**	**1**	**1**	No	Cd(NO$_3$)$_2$
90°C (DMF/H$_2$O)	**1**	**1**	**1**	**1**	**1**	Cd(NO$_3$)$_2$
100°C (DMF/H$_2$O)	**1**	**1**+**2**(trace)+**3**(trace)	**1**+**2**+**3**	**1**+**2**(trace)+**3**(trace)	**1**	Cd(NO$_3$)$_2$
110°C (DMF/H$_2$O)	**1**	**1**	**1**	**1**	**1**	Cd(NO$_3$)$_2$
120°C (DMF/H$_2$O)	**1**	**1**	**1**	**1**	**1**	Cd(NO$_3$)$_2$
90°C (DMA/H$_2$O)	**1**	**1**	**1**	**1**	**1**	Cd(NO$_3$)$_2$
100°C (DMA/H$_2$O)	**1**	**1**	**1**	**1**	**1**	Cd(NO$_3$)$_2$
110°C (DMA/H$_2$O)	**1**	**1**	**1**	**1**	**1**	Cd(NO$_3$)$_2$
100°C (DMF/H$_2$O)	**1**	**1**	**1**	**1**	**1**	Cd(ClO$_4$)$_2$
100°C (DMF/H$_2$O)	No	No	No	No	No	CdCl$_2$
100°C (DMF/H$_2$O)	No	No	No	No	No	CdSO$_4$
100°C (DMF/H$_2$O)	**1**	**1**	**1**	No	No	Cd(AcO)$_2$
120°C (H$_2$O,PH=7)	No	No	No	No	No	Cd(NO$_3$)$_2$
140°C (H$_2$O,PH=7)	No	No	No	No	No	Cd(NO$_3$)$_2$

Table S3. Summary of the product isolated at different times (100 °C, H_2O/DMF: 1/1).

Time (h)	**products**
6	**1**
12	**1**
18	**1**
24	**1**
30	**1**+**2**(trace)
36	**1**+**2**(trace)
42	**1**+**2**(trace)
48	**1**+**2**(trace)+**3**(trace)
54	**1**+**2**(trace)+**3**(trace)
60	**1**+**2**(trace)+**3**(trace)
66	**1**+**2**(trace)+**3**(trace)
72	**1**+**2**(trace)+**3**(trace)

1. P. Metrangolo, F. Meyer, T. Pilati, D. M. Proserpio and G. Resnati, *Chem. Eur. J.*, 2007, **13**, 5765.
2. A. L. Spek, *Acta Crystallogr., Sect. A: Found Crystallogr*. 1990, **46**, 194.