

## Electronic Supplementary Information (ESI)

### Stepwise ligand transformations through [2+2] photodimerization and hydrothermal in situ oxidation reactions

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## Experimental Section

**General procedures.** All chemicals and reagents were purchased from TCI Co., Ltd., and Sigma-Aldrich Co. All the chemicals were of reagent grade and used without any further purification. Infrared (IR) samples were prepared as KBr pellets, and spectrum was obtained in the 4000–400  $\text{cm}^{-1}$  range using a Nicolet Avatar 360 FT-IR spectrophotometer. The elemental analyses for C, H, and N were performed on an EA1110 CHNS elemental analyzer. 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  $^{\circ}\text{C}/\text{min}$  and a flow rate of 100  $\text{cm}^3/\text{min}$  ( $\text{N}_2$ ).  $^1\text{H}$  NMR spectra were recorded at ambient temperature on a Bruker Avance-III 400 MHz NMR spectrometer.  $^1\text{H}$  NMR chemical shifts were referenced to the solvent signal in  $d_6$ -DMSO.

**Preparation of  $[\text{Cd}(\mathbf{1,3\text{-bdc}})(\mathbf{4\text{-spy}})_2]_n$  (**1**).** To a 50 mL Teflon-lined autoclave was loaded  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  (0.228 g, 1 mmol), 1,3- $\text{H}_2\text{bdc}$  (0.166 g, 1 mmol), 4-spy (0.362 g, 2 mmol), NaOH (0.080 g, 2 mmol) and  $\text{H}_2\text{O}$  (25 mL). The Teflon-lined autoclave was sealed and heated in an oven to 165 $^{\circ}\text{C}$  for 50 hours, and then cooled to ambient temperature at a rate of 5 $^{\circ}\text{C h}^{-1}$  to form yellow blocks of **1**, which were washed with ethanol and dried in air. Yield: 0.466 g (73% yield based on Cd).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  = 8.55 (d, 4H, Py-H, 4-spy), 8.51 (s, 1H, Ph-H, 1,3-bdc), 8.15 (d, 2H, Ph-H, 1,3-bdc), 7.66 (s, 1H, Ph-H, 1,3-bdc), 7.56 (d, 4H, CH=CH, 4-spy), 7.52–7.23 (m, 14H, Ph-H and Py-H of 4-spy). Anal. calcd. for  $\text{C}_{34}\text{H}_{26}\text{CdN}_2\text{O}_4$ : C, 63.91; H, 4.10; N, 4.38. Found: C, 64.12; H, 4.08; N, 4.15. IR (KBr,  $\text{cm}^{-1}$ ): 3422m, 3024w, 1607s, 1556s, 1499m, 1437m, 1427m, 1385s, 1308m, 1224m, 1100m, 1071w, 1017m, 962s, 867m, 832s, 743s, 720s, 649m, 539s, 421w.

**Preparation of [Cd(1,3-bdc)(4-spy)(HT-ppcb)<sub>0.5</sub>]<sub>n</sub> (2).** Single crystals of **1** (1.278 g, 2 mmol, combined product from three Teflon-lined autoclaves) were irradiated by Hg lamp (250 W) for about 10 hours to form crystals of **2** in an almost quantitative yield (based on **1**). <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO): δ = 8.62 (d, 2H, Py-H, 4-spy), 8.56 (s, 1H, Ph-H, 1,3-bdc), 8.32 (d, 2H, Py-H, HT-ppcb), 8.07 (d, 2H, Ph-H, 1,3-bdc), 7.65 (s, 1H, Ph-H, 1,3-bdc), 7.58 (d, 2H, CH=CH, 4-spy), 7.52–7.03 (m, 14H, Py-H and Ph-H of 4-spy and HT-ppcb), 4.57 (d, 2H, C-H, HT-ppcb). Anal. calcd. for C<sub>34</sub>H<sub>26</sub>CdN<sub>2</sub>O<sub>4</sub>: C, 63.91; H, 4.10; N, 4.38. Found: C, 63.74; H, 3.96; N, 4.22. IR (KBr, cm<sup>-1</sup>): 3424m, 3026w, 1608s, 1558s, 1506m, 1439m, 1420m, 1386s, 1309m, 1226m, 1101m, 1074w, 1018m, 963s, 869m, 833s, 744s, 720s, 650m, 538s, 422w.

**Isolation of HT-ppcb.** A mixture of Na<sub>2</sub>(H<sub>2</sub>edta)·2H<sub>2</sub>O (3.722 g, 10 mmol), NaOH (0.800g, 20 mmol), **2** (1.278 g, 2 mmol), H<sub>2</sub>O (50 mL) and CH<sub>2</sub>Cl<sub>2</sub> (30 mL) were placed in a 150 mL flask and stirred for 20 hours. The organic phase was separated from the reaction mixture and the aqueous layers were extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 30 mL). The combined organic phase was concentrated to dryness *in vacuo*. The powder was then washed thoroughly with NaOH solution and H<sub>2</sub>O, and finally dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> to give yellow powder (4-spy and HT-ppcb). HT-ppcb was further isolated from the aforementioned yellow powder by column chromatography. Yield: 0.264 g (73% based on **2**). <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO): δ = 8.30 (d, 4H, Py-H), 7.22–7.05 (m, 14H, Py-H, Ph-H), 4.59 (s, 4H, CH-CH). Anal. Calcd. for C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>: C 86.15, H 6.12, N 7.73; found: C 85.97, H 6.39, N 8.04. IR (KBr, cm<sup>-1</sup>): 3435m, 3023m, 1598s, 1552s, 1494s, 1448m, 1414s, 1220m, 1141m, 1074m, 993m, 820s, 575m, 545s, 425w.

**Preparation of {[Cd(H<sub>2</sub>O)(1,3-bdc)(bpbpf)]·H<sub>2</sub>O}<sub>n</sub> (3).** To a 50 mL Teflon-lined autoclave was loaded CdCl<sub>2</sub>·2.5H<sub>2</sub>O (0.114 g, 0.5 mmol), 1,3-H<sub>2</sub>bdc (0.083 g, 0.5 mmol), HT-ppcb (0.181 g, 0.5

mmol), H<sub>2</sub>O<sub>2</sub> (3%, 1.2 mL) and H<sub>2</sub>O (25 mL). The Teflon-lined autoclave was sealed and heated in an oven to 165°C for 20 hours. The mixture was then cooled to ambient temperature at a rate of 5 °C h<sup>-1</sup> to form yellow rhombic crystals of **3**, which were washed with ethanol and dried in air. Yield: 0.141g (41% yield based on Cd). <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO): δ = 8.61 (s, 1H, Ph-H, 1,3-bdc), 8.52 (d, 2H, Py-H, bpbpf), 8.38 (s, 1H, Py-H, bpbpf), 8.14 (s, 1H, Py-H, bpbpf), 7.95 (d, 2H, Ph-H, 1,3-bdc), 7.65 (s, 1H, Ph-H, 1,3-bdc), 7.56–6.97 (m, 14H, Ph-H and Py-H of bpbpf). Anal. calcd. for C<sub>34</sub>H<sub>26</sub>CdN<sub>2</sub>O<sub>7</sub>: C, 59.44; H, 3.81; N, 4.08. Found: C, 59.27; H, 4.11; N, 4.29. IR (KBr, cm<sup>-1</sup>): 3398s, 3062m, 2959w, 1606s, 1548s, 1520s, 1475m, 1439m, 1383s, 1269m, 1224m, 1068m, 1016s, 966m, 832s, 772m, 743m, 723s, 629m, 557s, 420w.

**Isolation of bpbpf.** Na<sub>2</sub>(H<sub>2</sub>edta)·2H<sub>2</sub>O (0.372 g, 1 mmol), NaOH (0.080 g, 2 mmol), **2** (0.137 g, 0.2 mmol), H<sub>2</sub>O (20 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) were placed in a 100 mL flask and stirred for 20 hours. The organic phase was separated from the reaction mixture and the aqueous layers were extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL). The combined organic phase was concentrated to dryness in vacuo. The powder was then washed thoroughly with NaOH solution and H<sub>2</sub>O, and finally dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> to give bpbpf as a yellow powder. Yield: 52mg (69%). <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO): δ = 8.50 (d, 2H, Py-H), 8.37 (s, 1H, Py-H), 8.14 (s, 1H, Py-H), 7.63–6.97 (m, 14H, Ph-H and Py-H). Anal. Calcd. for C<sub>26</sub>H<sub>18</sub>N<sub>2</sub>O: C 83.40, H 4.85, N 7.48; found: C 83.01, H 4.63, N 7.12. IR (KBr, cm<sup>-1</sup>): 3413m, 3029m, 1596s, 1542s, 1498m, 1484m, 1409s, 1260m, 1219m, 1069m, 990m, 831s, 822s, 790m, 710s, 573m, 551s, 421w.

**Single-crystal X-ray diffraction crystallography.** All measurements were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated Mo K $\alpha$  ( $\lambda = 0.071073$  nm). Single crystals of **1–3** suitable for X-ray analysis were obtained directly from the above preparations. These crystals were mounted on glass fibers and cooled at 223 K in a liquid nitrogen stream. Cell parameters were refined on all observed reflections by using the program *Crystalclear* (Rigaku and MSc, Ver. 1.3, 2001). The collected data were reduced by the program *CrystalClear*, and an absorption correction (multiscan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The structures were solved by direct methods, and nonhydrogen atoms were refined anisotropically by least-squares on  $F^2$  using the *SHELXTL-97* program.<sup>[1]</sup> All non-hydrogen atoms were refined anisotropically. The H atoms of the water molecules 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.

[1] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction for Area Detector Data; University of Göttingen: Göttingen, Germany, **2000**.

*Crystal data* for **1**: C<sub>34</sub>H<sub>26</sub>CdN<sub>2</sub>O<sub>4</sub>,  $M_r = 638.98$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.258(2)$ ,  $b = 10.714(2)$ ,  $c = 14.328(3)$  Å,  $\alpha = 106.41(3)$ ,  $\beta = 93.68(3)$ ,  $\gamma = 108.85(3)^\circ$ ,  $V = 1408.4(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.507\text{g/cm}^3$ ,  $R_1 = 0.0450$  ( $I > 2\sigma$ ),  $wR_2 = 0.1144$ ,  $GOF = 1.020$ . *Crystal data* for **2**: C<sub>34</sub>H<sub>26</sub>CdN<sub>2</sub>O<sub>4</sub>,  $M_r = 638.98$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.298(2)$ ,  $b = 10.631(2)$ ,  $c = 14.608(3)$  Å,  $\alpha = 107.72(3)$ ,  $\beta = 93.61(3)$ ,  $\gamma = 108.14(3)^\circ$ ,  $V = 1425.5(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.489\text{g/cm}^3$ ,  $R_1 = 0.0993$  ( $I > 2\sigma$ ),  $wR_2 = 0.2133$ ,  $GOF = 1.185$ . *Crystal data* for **3**: C<sub>34</sub>H<sub>26</sub>CdN<sub>2</sub>O<sub>7</sub>,  $M_r = 686.98$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.300(2)$ ,  $b = 11.960(2)$ ,  $c = 14.114(3)$  Å,  $\alpha = 70.96(3)$ ,  $\beta = 70.79(3)$ ,  $\gamma = 66.70(3)^\circ$ ,  $V = 1468.9(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.553\text{g/cm}^3$ ,  $R_1 = 0.0282$  ( $I > 2\sigma$ ),  $wR_2 = 0.0633$ ,  $GOF = 1.038$ .

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

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Compound 1			
Cd(1)-N(1)	2.298(4)	Cd(1)-O(2A)	2.310(3)
Cd(1)-O(1)	2.311(3)	Cd(1)-N(2)	2.312(4)
Cd(1)-O(3B)	2.385(3)	Cd(1)-O(4B)	2.392(3)
N(1)-Cd(1)-O(2A)	88.57(13)	N(1)-Cd(1)-O(1)	93.81(13)
O(2A)-Cd(1)-O(1)	125.65(11)	N(1)-Cd(1)-N(2)	175.08(12)
O(2A)-Cd(1)-N(2)	86.74(12)	O(1)-Cd(1)-N(2)	87.72(12)
N(1)-Cd(1)-O(3B)	93.80(12)	O(2B)-Cd(1)-O(3B)	95.32(10)
O(1)-Cd(1)-O(3B)	138.45(10)	N(2)-Cd(1)-O(3B)	88.12(12)
N(1)-Cd(1)-O(4B)	93.62(13)	O(2A)-Cd(1)-O(4B)	150.23(10)
O(1)-Cd(1)-O(4B)	83.87(10)	N(2)-Cd(1)-O(4B)	91.19(13)
O(3B)-Cd(1)-O(4B)	54.91(9)		
Compound 2			
Cd(1)-N(1)	2.282(9)	Cd(1)-N(2)	2.297(10)
Cd(1)-O(3A)	2.313(6)	Cd(1)-O(4B)	2.313(8)
Cd(1)-O(1)	2.378(7)	Cd(1)-O(2)	2.404(6)
N(1)-Cd(1)-N(2)	174.1(3)	N(1)-Cd(1)-O(3A)	94.2(3)
N(2)-Cd(1)-O(3A)	87.4(3)	N(1)-Cd(1)-O(4B)	88.6(3)
N(2)-Cd(1)-O(4B)	85.9(3)	O(3A)-Cd(1)-O(4B)	126.5(2)
N(1)-Cd(1)-O(1)	96.1(3)	N(2)-Cd(1)-O(1)	89.6(3)
O(3A)-Cd(1)-O(1)	84.8(2)	O(4B)-Cd(1)-O(1)	148.0(2)

N(1)-Cd(1)-O(2)	93.6(3)	N(2)-Cd(1)-O(2)	88.8(3)
O(3A)-Cd(1)-O(2)	138.9(2)	O(4B)-Cd(1)-O(2)	94.0(2)
O(1)-Cd(1)-O(2)	54.2(2)		

Compound **3**

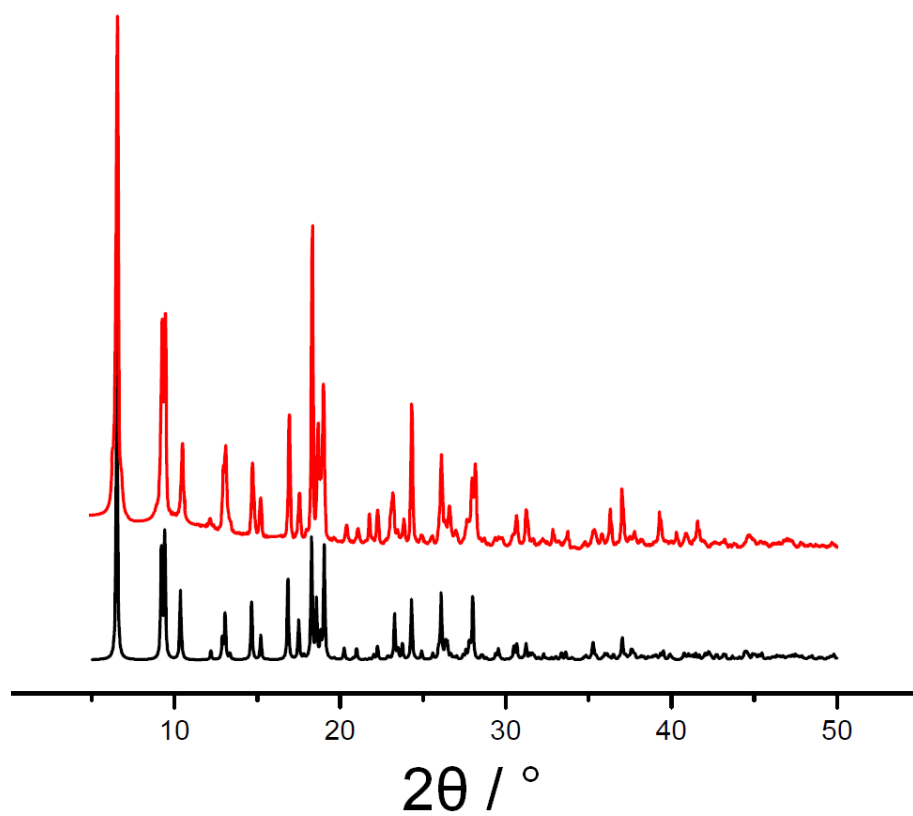
Cd(1)-O(4A)	2.2492(16)	Cd(1)-N(2B)	2.322(2)
Cd(1)-N(1)	2.331(2)	Cd(1)-O(1)	2.353(2)
Cd(1)-O(6)	2.3562(19)	Cd(1)-O(2)	2.4384(16)
Cd(1)-O(3A)	2.8482(19)		
O(4A)-Cd(1)-N(2B)	101.33(7)	O(4A)-Cd(1)-N(1)	87.35(7)
N(2B)-Cd(1)-N(1)	166.08(7)	O(4A)-Cd(1)-O(1)	88.08(6)
N(2B)-Cd(1)-O(1)	95.42(8)	N(1)-Cd(1)-O(1)	95.73(7)
O(4A)-Cd(1)-O(6)	128.45(6)	N(2B)-Cd(1)-O(6)	85.10(7)
N(1)-Cd(1)-O(6)	80.98(7)	O(1)-Cd(1)-O(6)	142.77(6)
O(4A)-Cd(1)-O(2)	141.98(6)	N(2B)-Cd(1)-O(2)	90.57(7)
N(1)-Cd(1)-O(2)	89.10(7)	O(1)-Cd(1)-O(2)	54.66(6)
O(6)-Cd(1)-O(2)	88.14(7)	O(4A)-Cd(1)-O(3A)	49.55(6)
N(2B)-Cd(1)-O(3A)	83.68(7)	N(1)-Cd(1)-O(3A)	94.04(7)
O(1)-Cd(1)-O(3A)	135.89(6)	O(6)-Cd(1)-O(3A)	81.26(6)
O(2)-Cd(1)-O(3A)	168.32(5)		

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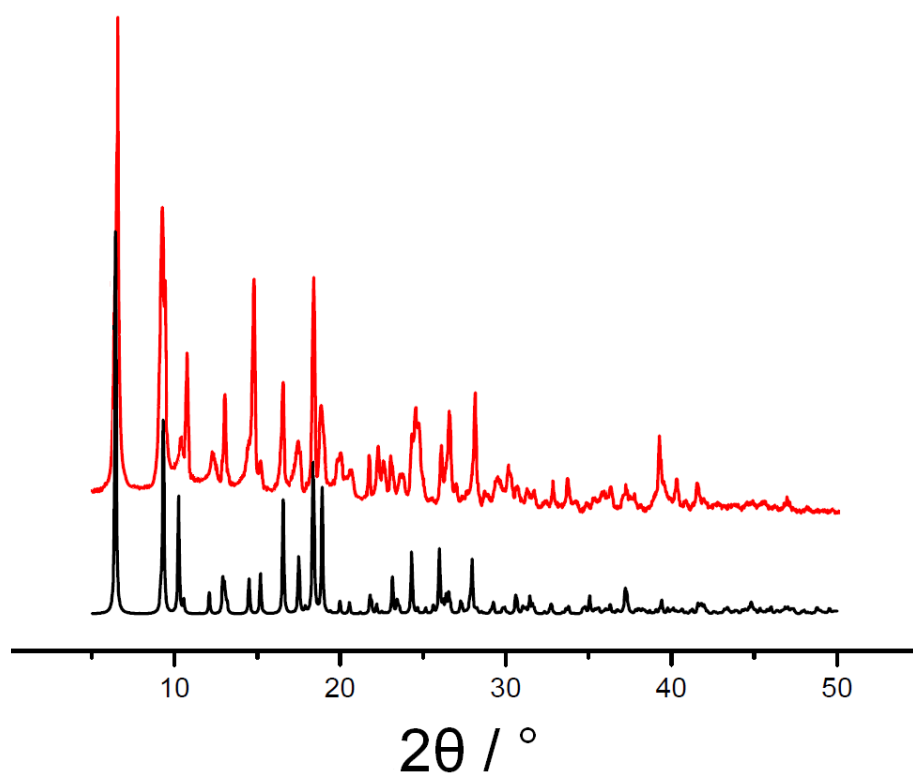
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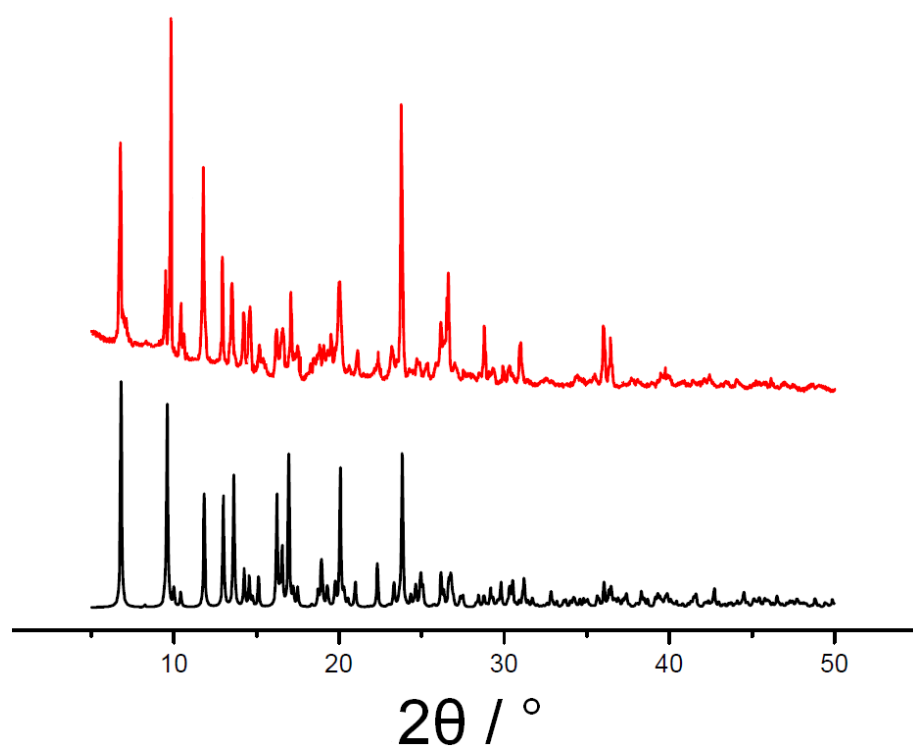
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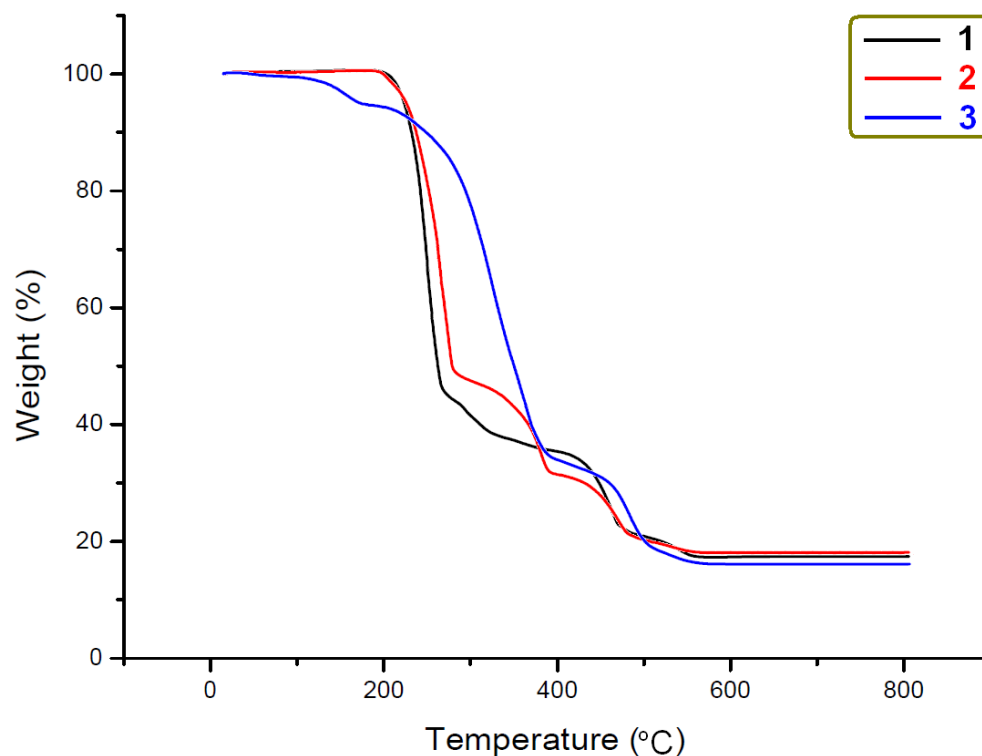
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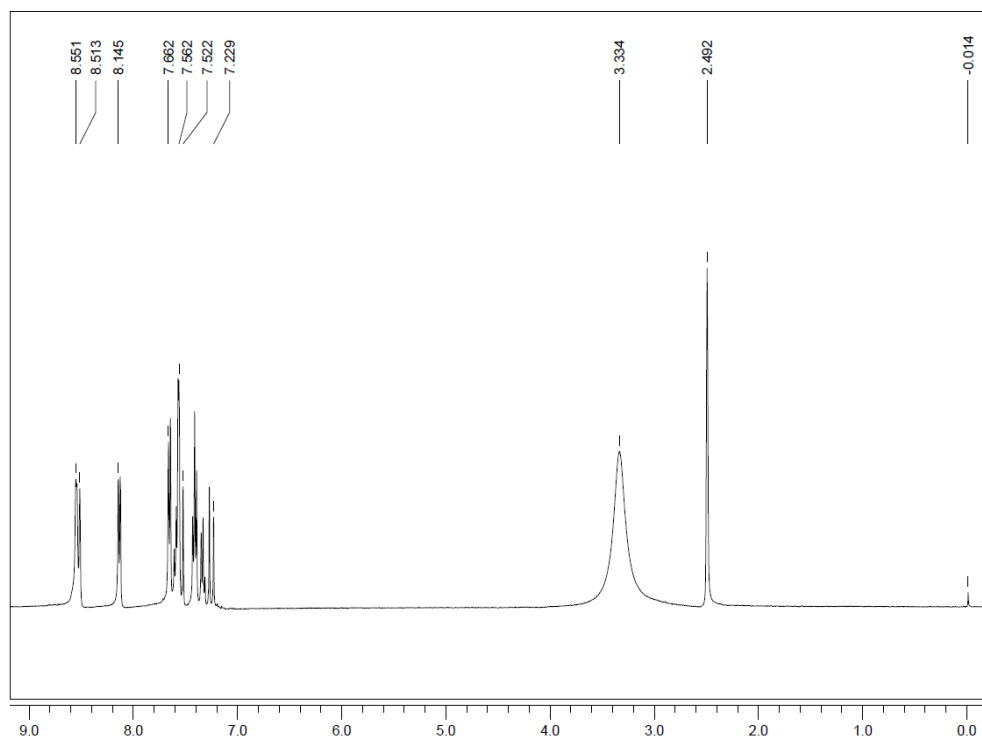


**Fig. S1.** Experimental (red) and simulated (black) PXR D patterns for **1** (a); **2** (b) and **3** (c).

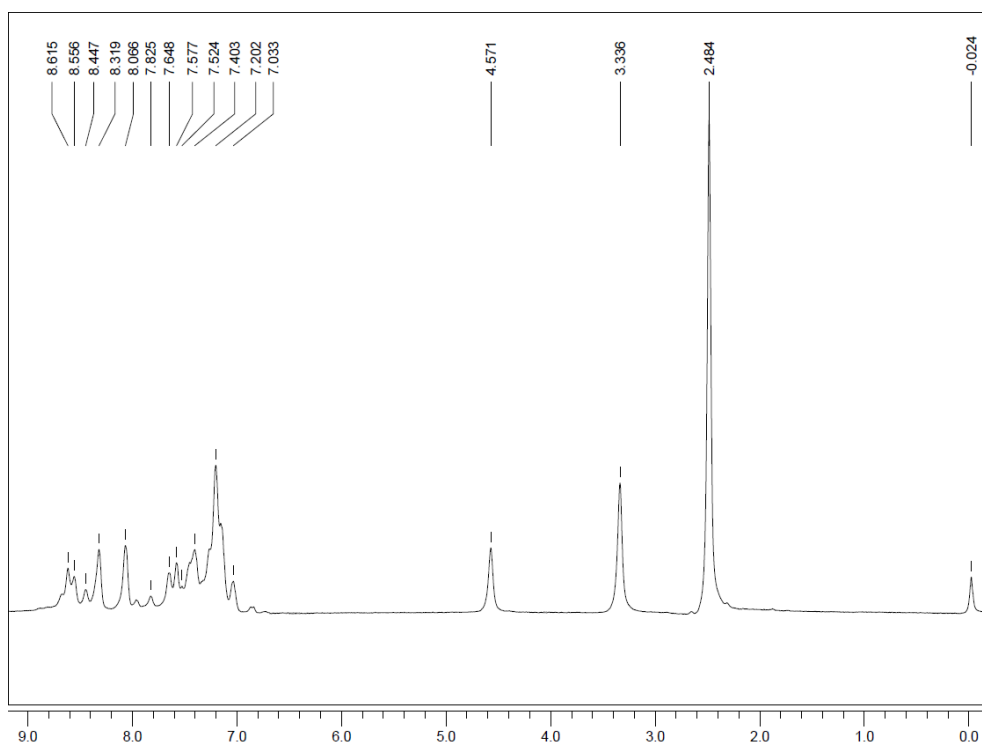


**Fig. S2.** The TGA curves for **1-3**. Compound **1** is stable up to about 200°C, and then becomes continuous decomposition. The TGA curve of **2** is almost the same as **1**. The final residues were assumed to be Cd (ca. 17.59%), which is corresponding to the experimental weight of residues (17.39% for **1** and 17.72% for **2**). Compound **3** showed a first weight loss of 5.66% in the range of 50-175°C, which corresponds to the removal of two water molecules per formula unit (ca. 5.24%). When the temperature rises, a series of decomposition steps commence. The weight of the final residue (16.04%) was assumed to be Cd (ca. 16.36%).

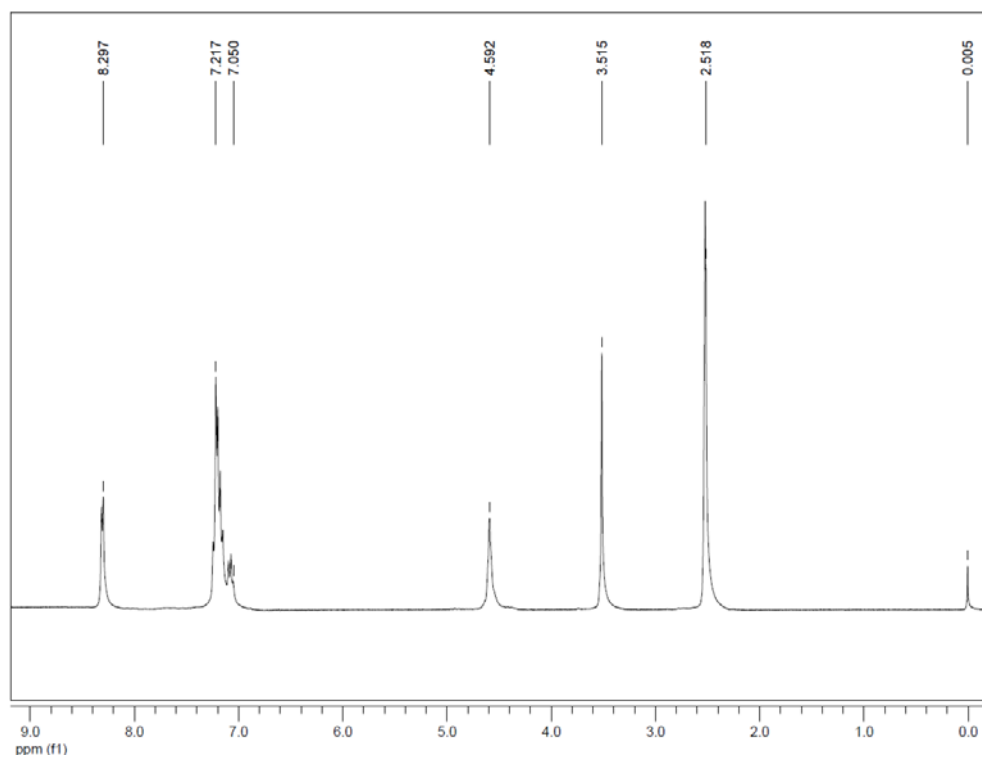
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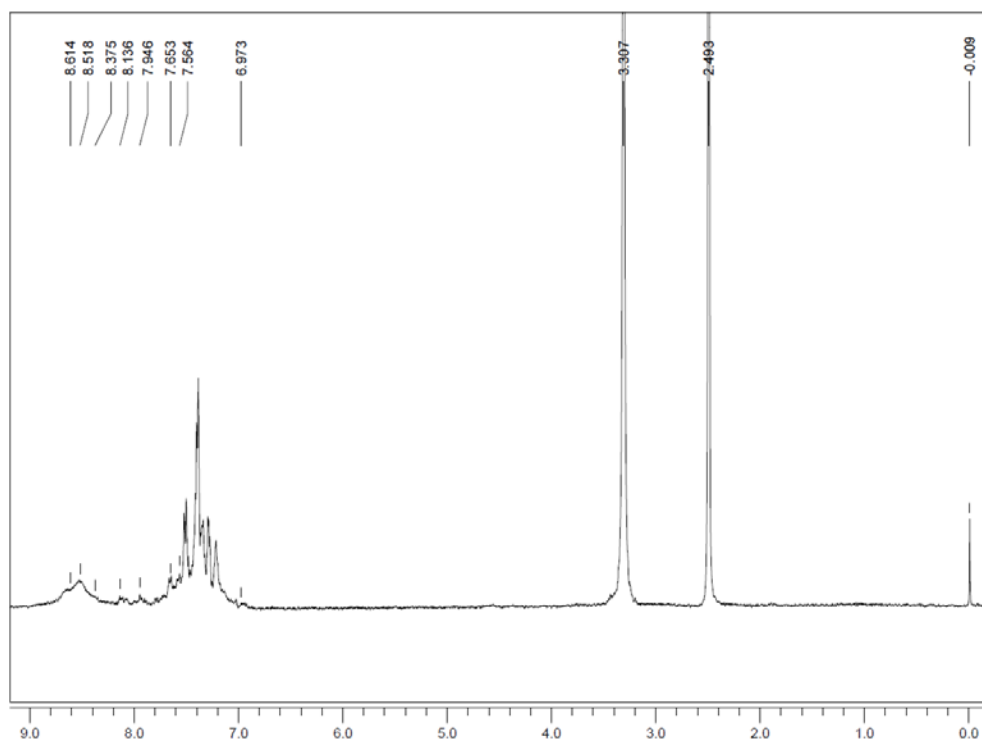
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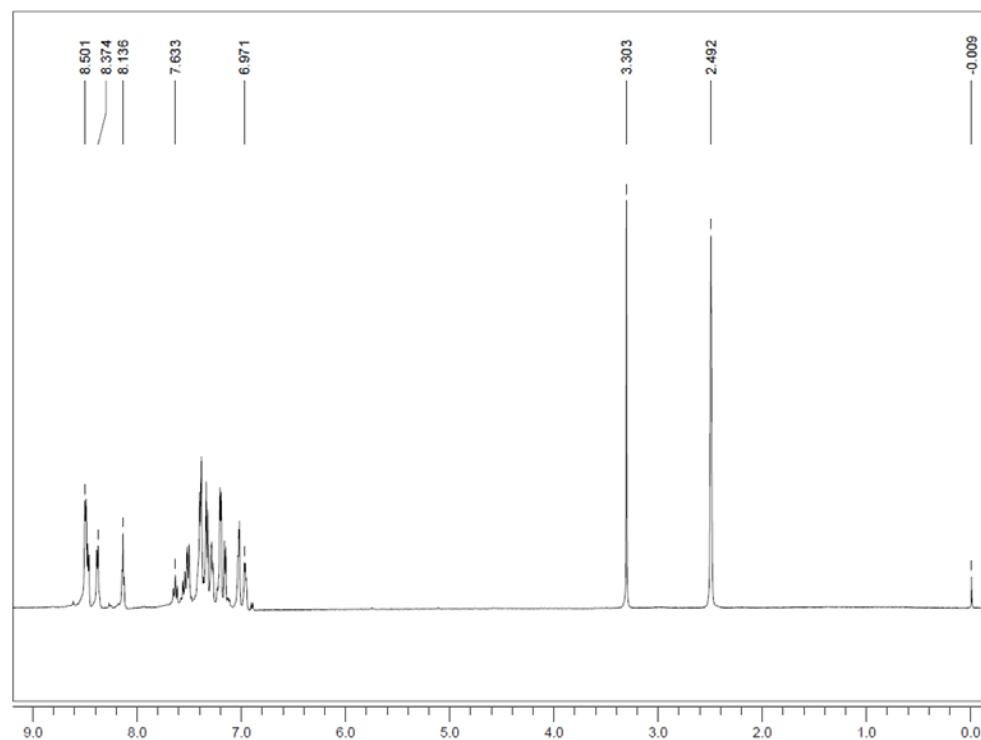
(c)



(d)



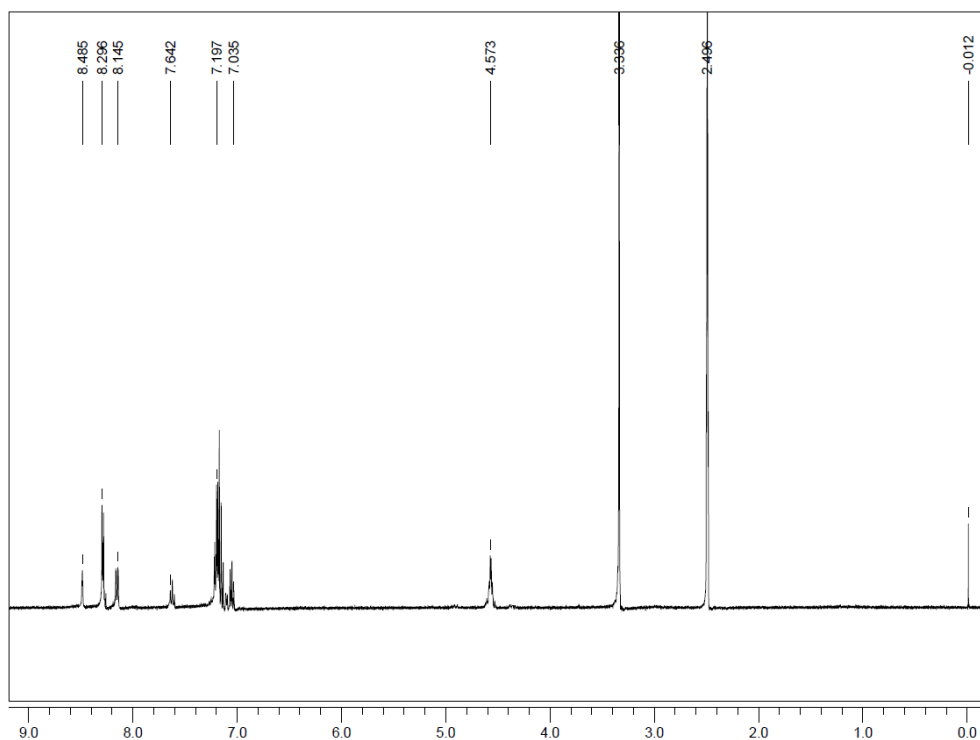
(e)



**Fig. S3.** The  $^1\text{H}$  NMR spectra of **1** (a), **2** (b), **HT-ppcb** (c), **3** (d) and **bpbf** (e) in  $\text{DMSO-}d_6$  at ambient temperature.

**NOTES:**

The  $^1\text{H}$  NMR spectrum of the irradiated product, **2**, dissolved in  $d_6$ -DMSO shows the presence of cyclobutane protons with a signal at 4.57 ppm. Shifts in the location of the signals for pyridyl protons from 8.55 and 7.56 ppm to 8.32 and 7.20 ppm respectively are noted upon dimer formation.

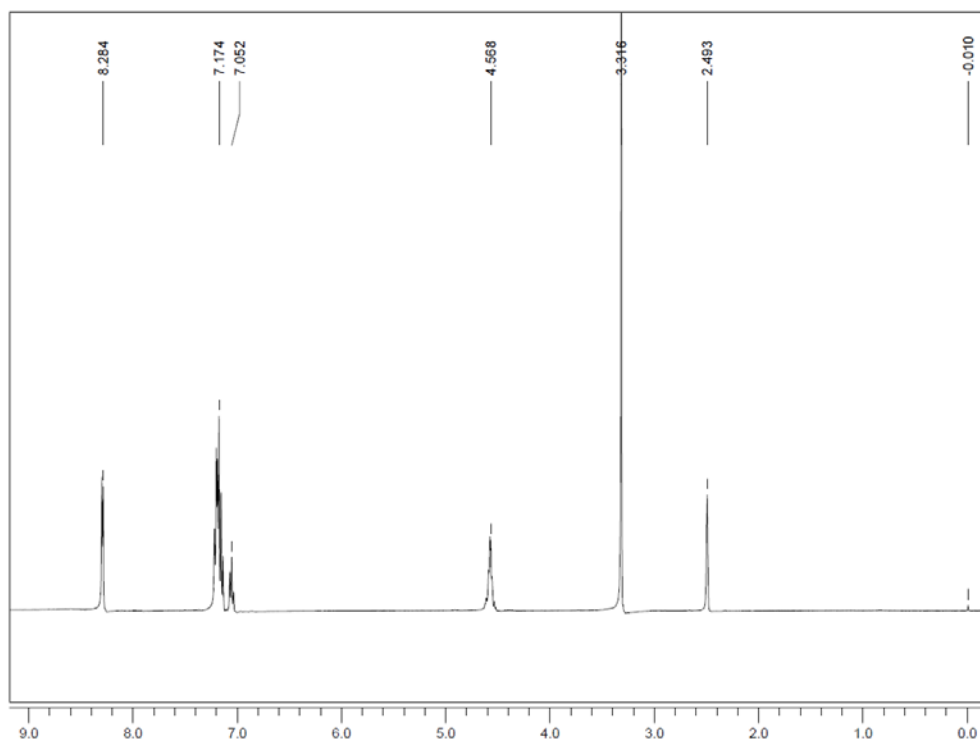


**Fig. S4.** The  $^1\text{H}$  NMR spectrum of the precipitation (after hydrothermal treatment of a mixture of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ , 1,3- $\text{H}_2\text{bdc}$  and HT-ppcb under nitrogen) in  $\text{DMSO-}d_6$  at ambient temperature.

$\delta = 8.49$  (s, 1H, Ph-H, 1,3-bdc), 8.30 (d, 4H, Py-H, 4-spy), 8.15 (d, 2H, Ph-H, 1,3-bdc), 7.64 (s, 1H, Ph-H, 1,3-bdc), 7.20–7.04 (m, 14H, Py-H and Ph-H of HT-ppcb), 4.57 (d, 4H, C-H, HT-ppcb).

**NOTES:**

The  $^1\text{H}$  NMR spectrum indicated that HT-ppcb ligand had not changed after hydrothermal treatment of a mixture of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ , 1,3- $\text{H}_2\text{bdc}$  and HT-ppcb under nitrogen.



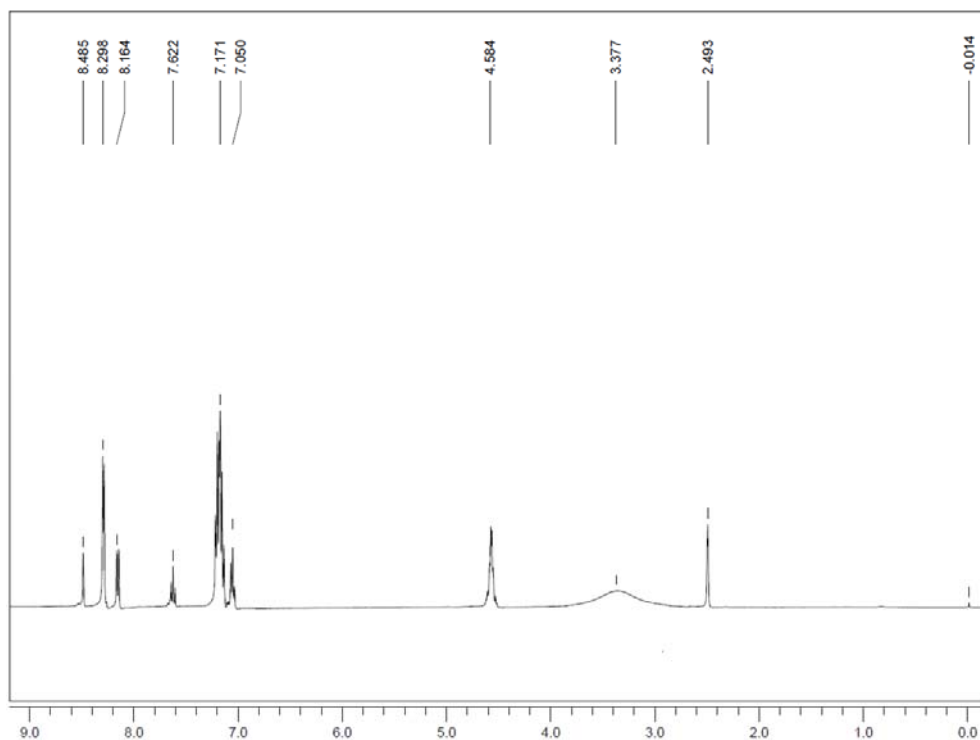
**Fig. S5.** The  $^1\text{H}$  NMR spectrum of the precipitation (after hydrothermal treatment of a mixture of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ , HT-ppcb and  $\text{H}_2\text{O}_2$ ) in  $\text{DMSO-}d_6$  at ambient temperature.

$\delta = 8.28$  (d, 4H, Py-H, HT-ppcb), 7.17–7.05 (m, 14H, Py-H and Ph-H of HT-ppcb), 4.57 (s, 4H, CH-CH, HT-ppcb).

**NOTES:**

The  $^1\text{H}$  NMR spectrum confirmed that the organic component of the precipitation is HT-ppcb.





**Fig. S6.** The  $^1\text{H}$  NMR spectrum of the precipitation (after hydrothermal treatment of a mixture of 1,3- $\text{H}_2\text{bdc}$ , HT-ppcb and  $\text{H}_2\text{O}_2$ ) in  $\text{DMSO-}d_6$  at ambient temperature.

$\delta = 8.49$  (s, 1H, Ph-H, 1,3-bdc), 8.30 (d, 4H, Py-H, 4-spy), 8.16 (d, 2H, Ph-H, 1,3-bdc), 7.62 (s, 1H, Ph-H, 1,3-bdc), 7.17–7.05 (m, 14H, Py-H and Ph-H of HT-ppcb), 4.58 (d, 4H, C-H, HT-ppcb).

**NOTES:**

The  $^1\text{H}$  NMR spectrum confirmed that the organic component of the precipitation is a mixture of 1,3- $\text{H}_2\text{bdc}$  and HT-ppcb.