Electronic Supplementary Information

New Metal Organic Frameworks Derived from pyridine-3,5-dicarboxylic acid: Structural Diversity Rising from the Addition of Templates in the Reaction Systems

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1. Experimental

Materials. Reagent grade chemicals were obtained from Aldrich and used without further purification. Water was distilled in-house.

Physical Measurements. Elemental analysis (C, H, N) was performed by the in-house facilities of the University of Cyprus, Chemistry Department on a Eurovector EA3000 Elemental Analyzer. IR spectra were recorded on KBr pellets in the 4000–400 cm^{-1} range using a Shimadzu Prestige –21 spectrometer. PXRD diffraction pattern was recorded on a Shimazdu 6000 Series X-ray diffractometer (Cu Kα radiation, λ = 1.5418 Å). Thermal stability studies were performed with a Shimadzu TGA 50 thermogravimetric analyzer.

Single Crystal X-ray Crystallography. Single crystal X-ray diffraction data were collected on an Oxford-Diffraction Supernova diffractometer, equipped with an Atlas CCD area detector utilizing Cu Kα (λ = (1.54184 Å) radiation. Suitable crystal was attached to Hampton cryoloops using paratone-N oil and transferred to the goniostat where they were cooled for data collection. Empirical absorption corrections (multiscan based on symmetry-related measurements) were applied using CrysAlis RED software.[1] The same software package was used for data collection, cell refinement and data reduction. The structures were solved by direct methods using either SIR2014[2] or SHELXS,[3] via the WinGX[4] interface. They are refined on F^2 using full-matrix least-squares with SHELXL-2016/6[5] via the ShelXle[6] interface. The non-H atoms were treated anisotropically, whereas the aromatic H atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms. Some of the O–H hydrogen atoms were located from difference Fourier maps and refined isotropically using SHELX restraints; others could not be located and they were placed in calculated positions using CALC-OH.[7] Electron density contributions from disordered guest molecules (and dimethylammonium cations in case of **[1]**) were handled using the SQUEEZE procedure from the PLATON software suit.[8] PLATON and DIAMOND[9] were used for geometric calculations, and X-Seed[10] for molecular graphics. The topological evaluation of the networks was performed with ToposPro.[11] Solvent accessible volumes were calculated with Mercury.[12] Selected crystal data for **[1]** – **[9]** are summarized in Table S1. Selected bond distances (Å) and angles (°) are presented in Tables S2 – S10, respectively. CCDC 1958501-1958509 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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Synthesis of $[[(CH_3)_2NH_2]_2[Cd_2(PDC)_3]]_n \cdot 4nDMF \cdot 6nH_2O$, [1]. *Method A:* $PDCH_2$ (0.050 g, 0.299 mmol) was dissolved (after sonication for 3 minutes) in DMF (8 mL) in a 20 mL glass vial and to this solution was added $deaH_2$ (2.00 mL, 20.734 mmol). The mixture was sonicated for 3 minutes and to

the resulting solution was added solid $CdCl_2$ (0.100 g, 0.545 mmol). The mixture was sonicated for 3 min, sealed and then, heated without stirring at 100 °C for 48 h. During this period, white polyhedral-like crystals of **[1]** were formed. They were isolated by filtration, washed several times with DMF and diethylether, and dried under vacuum. Yield: 75 mg (62 % based on $PDCH_2$). Elemental analysis: Anal. Calc. for $C_{37}H_{65}N_9O_{22}Cd_2$ ([**1**]) C 36.64, H 5.40, N 10.39, Found: C 36.78, H 5.51, N 10.61 %. IR data (cm^{-1}): 3300mbr ν(OH), 3080w $\nu(CH)_{ar}$, 2958w $\nu(CH)_{al}$, 2812w ν(NH), 1667m $\nu(CO)_{DMF}$, 1603s ν(CC), 1560s, 1387ms $\nu(CO_2)$, 1429m $\nu(CN)_{ar}$.

Method B: The same procedure was repeated replacing $deaH_2$ with $teoaH_3$ (2.00 mL, 15.068 mmol). Yield: ~ 61 %.

Synthesis of $[Mn(PDC)(DMF)]_n$, [2]. *Method A:* $PDCH_2$ (0.050 g, 0.299 mmol) was dissolved (after sonication for 3 minutes) in DMF (8 mL) in a 20 mL glass vial and to this solution was added $phdeaH_2$ (0.200 g, 1.104 mmol). The mixture was sonicated for 3 minutes and to the resulting solution was added solid $Mn(NO_3)_2{\cdot}4H_2O$ (0.100 g, 0.398 mmol). The mixture was sonicated for 3 min, sealed and then, heated without stirring at 100 °C for 48 h. During this period, pinkish polyhedral-like crystals of **[2]** were formed. They were isolated by filtration, washed several times with DMF and diethylether, and dried under vacuum. Yield: 52 mg (59 % based on $PDCH_2$). Elemental analysis: Anal. Calc. for $C_{10}H_{10}N_2O_5Mn$ ([**2**]) C 40.97, H 3.44, N 9.56, Found: C 40.80, H 3.51, N 9.30 %. IR data (cm^{-1}): 3072w $\nu(CH)_{ar}$, 1670s $\nu(CO)_{DMF}$, 1605m ν(CC), 1560s, 1391ms $\nu(CO_2)$, 1431m $\nu(CN)_{ar}$

Methods B, C, D: Method A was repeated, using 2hmpH (200 µL, 2.073 mmol)(B) or 3hmpH (200 µL, 2.073 mmol)(C) or 3hppH (200 µL, 1.545 mmol)(D) instead of $phdeaH_2$. The yields span the range 58 – 59 %.

Method E: **[2]** can be synthesized successfully in the absence of any template molecule with similar yield.

Synthesis of $[Mn_3(PDC)_2(INA)_2(DMF)_{1.5}(H_2O)_{0.5}]_n{\cdot}nDMF{\cdot}2nH_2O$, [3]. $PDCH_2$ (0.050 g, 0.299 mmol) was dissolved (after sonication for 3 minutes) in DMF (8 mL) in a 20 mL glass vial and to this solution was added 4hmpH (0.200 g, 1.833 mmol). The mixture was sonicated for 3 minutes and to the resulting solution was added solid $Mn(NO_3)_2{\cdot}4H_2O$ (0.100 g, 0.398 mmol). The mixture was sonicated for 3 min, sealed and then, heated without stirring at 100 °C for 48 h. During this period, very pale pink polyhedral-like crystals of **[3]** were formed. They were isolated by filtration, washed several times with DMF and diethylether, and dried under vacuum. Yield: 105 mg (72 % based on $PDCH_2$). Elemental analysis: Anal. Calc. for $C_{33.5}H_{36.5}N_{6.5}O_{17}Mn_3$ ([**3**]) C 41.61, H 3.80, N 9.42, Found: C 41.83, H 3.65, N 9.59 %. IR data (cm^{-1}): 3317mbr ν(OH), 3072w $\nu(CH)_{ar}$, 2927w $\nu(CH)_{al}$, 1667s $\nu(CO)_{DMF}$, 1600m ν(CC), 1552s, 1384ms $\nu(CO_2)$.

Synthesis of $[Zn(PDC)(NMP)]_n{\cdot}nH_2O$, [4]. $PDCH_2$ (0.050 g, 0.299 mmol) was dissolved (after sonication for 3 minutes) in NMP (8 mL) and to this solution was added pdH_2 (200 µL, 2.786 mmol). The mixture was sonicated for 3 minutes and to the resulting solution was added solid $Zn(O_2CMe)_2{\cdot}2H_2O$ (0.100 g, 0.455 mmol). The mixture was sonicated for 3 min, and sealed in a 23 mL Teflon-lined autoclave and then, heated at 150 °C for 48 h. The autoclave left to cool slowly at room temperature. Colourless polyhedral-like crystals of **[4]** were formed. They were isolated by filtration, washed several times successively with NMP, DMF and diethylether, and dried under vacuum. Yield: 84 mg (81 % based on $PDCH_2$). Elemental analysis: Anal. Calc. for $C_{12}H_{14}N_2O_6Zn$ (**[4]**) C 41.46, H 4.06, N 8.06, Found: C 41.44, H 4.23, N 8.10 %. IR data (cm^{-1}): 3279mbr, 2889wbr ν(OH), 3100w $\nu(CH)_{ar}$, 2969w $\nu(CH)_{al}$, 1667m $\nu(CO)_{NMP}$, 1609s ν(CC), 1567s, 1407ms $\nu(CO_2)$, 1430m $\nu(CN)_{ar}$.

Synthesis of $[Zn(PDC)(H_2O)(DMF)]_n$, [5]. *Method A*: $PDCH_2$ (0.050 g, 0.299 mmol) was dissolved (after sonication for 3 minutes) in DMF (8 mL) in a 20 mL glass vial and to this solution was added $phdeaH_2$ (0.200 g, 1.104 mmol). The mixture was sonicated for 3 minutes and to the resulting solution was added solid $Zn(NO_3)_2{\cdot}6H_2O$ (0.100 g, 0.336 mmol). The mixture was sonicated for 3 min, sealed and then, heated without stirring at 100 °C for 48 h. During this period, colourless

polyhedral-like crystals of **[5]** were formed. They were isolated by filtration, washed several times with DMF and diethylether, and dried under vacuum. Yield: 64 mg (67 % based on $PDCH_2$). Elemental analysis: Anal. Calc. for $C_{10}H_{12}N_2O_6Zn$ ([**5**]) C 37.35, H 3.76, N 8.71, Found: C 37.51, H 3.99, N 8.52 %. IR data (cm^{-1}): 3278mbr, ν(OH), 3103w $\nu(CH)_{ar}$, 1694m $\nu(CO)_{DMF}$, 1605s ν(CC), 1551s, 1399ms $\nu(CO_2)$, 1436m $\nu(CN)_{ar}$.

Methods B, C, D: Method A was repeated, using $deaH_3$ (200 µL, 2.087 mmol)(B) or $teoaH_3$ (200 µL, 1.507 mmol)(C) or pdH_2 (200 µL, 2.768 mmol)(D) instead of $phdeaH_2$. The yields span the range 65 – 68 %.

Synthesis of $[Zn(PDC)(3hmpH)]_n \cdot nDMF \cdot 0.5nH_2O$, [6]. $PDCH_2$ (0.050 g, 0.299 mmol) was dissolved (after sonication for 3 minutes) in DMF (8 mL) in a 20 mL glass vial and to this solution was added 3hmpH (900 µL, 9.327 mmol). The mixture was sonicated for 3 minutes and to the resulting solution was added solid $Zn(O_2CMe)_2 \cdot 2H_2O$ (0.300 g, 1.367 mmol). The mixture was sonicated for 3 min, sealed and then, heated without stirring at 100 °C for 48 h. During this period, white polyhedral-like crystals of **[6]** were formed. They were isolated by filtration, washed several times with DMF and diethylether, and dried under vacuum. Yield: 96 mg (76 % based on $PDCH_2$). Elemental analysis: Anal. Calc. for $C_{16}H_{18}N_3O_{6.5}Zn$ (**[6]**) C 45.57, H 4.30, N 9.96, Found: C 48.43, H 4.11, N 9.69 %. IR data (cm^{-1}): 3340mbr, ν(OH), 3085w $\nu(CH)_{ar}$, 2942w $\nu(CH_3)_{DMF}$, 2874w $\nu(CH_2)$, 1626s $\nu(CO)_{DMF}$, 1590s $\nu(CC)_{ring}$, 1568s, 1376s $\nu(CO_2)$, 1436m $\nu(CN)_{ar}$, 1026m ν(C-OH).

Synthesis of $[Zn(PDC)(2hmpH)_2]_2 \cdot 2DMF$, [7]. $PDCH_2$ (0.050 g, 0.299 mmol) was dissolved (after sonication for 3 minutes) in DMF (8 mL) in a 20 mL glass vial and to this solution was added 2hmpH (500 µL, 5.182 mmol). The mixture was sonicated for 3 minutes and to the resulting solution was added solid $Zn(O_2CMe)_2 \cdot 2H_2O$ (0.100 g, 0.455 mmol). The mixture was sonicated for 3 min, sealed and then, heated without stirring at 100 °C for 48 h. During this period, colourless polyhedral-like crystals of **[7]** were formed. They were isolated by filtration, washed several times with DMF and diethylether, and dried under vacuum. Yield: 80 mg (51 % based on $PDCH_2$). Elemental analysis: Anal. Calc. for $C_{22}H_{24}N_4O_7Zn$ (**[7]**) C 50.64, H 4.64, N 10.74, Found: C 50.93, H 4.70, N 10.41 %. IR data (cm^{-1}): 3355mbr, ν(OH), 3083w $\nu(CH)_{ar}$, 2940w $\nu(CH_3)_{DMF}$, 2873w $\nu(CH_2)$, 1665s $\nu(CO)_{DMF}$, 1589s $\nu(CC)_{ring}$, 1588s, 1372s $\nu(CO_2)$, 1438m $\nu(CN)_{ar}$, 1029m ν(C-OH).

Synthesis of $[Co(PDC)(3hmpH)_2]_n \cdot 0.25nDMF$, [8]. $PDCH_2$ (0.050 g, 0.299 mmol) was dissolved (after sonication for 3 minutes) in DMF (8 mL) in a 20 mL glass vial and to this solution was added 3hmpH (1.50 mL, 15.467 mmol). The mixture was sonicated for 3 minutes and to the resulting solution was added solid $Co(NO_3)_2 \cdot 6H_2O$ (0.100 g, 0.343 mmol). The mixture was sonicated for 3 min, sealed and then, heated without stirring at 100 °C for 48 h. During this period, pink polyhedral-like crystals of **[8]** were formed. They were isolated by filtration, washed several times with DMF and diethylether, and dried under vacuum. Yield: 95 mg (69 % based on $PDCH_2$). Elemental analysis: Anal. Calc. for $C_{19.75}H_{18.75}N_{3.25}O_{6.25}Co$ (**[8]**) C 51.50, H 4.10, N 9.88, Found: C 51.81, H 4.38, N 10.07 %. IR data (cm^{-1}): 3326mbr, ν(OH), 3077w $\nu(CH)_{ar}$, 2891w $\nu(CH_2)$, 1587s $\nu(CC)_{ring}$, 1569s, 1377s $\nu(CO_2)$, 1446m $\nu(CN)_{ar}$, 1023m ν(C-OH).

Synthesis of $[Cu(PDC)(3hmpH)_2]_n \cdot 0.5nDMF$, [9]. $PDCH_2$ (0.050 g, 0.299 mmol) was dissolved (after sonication for 3 minutes) in DMF (8 mL) in a 20 mL glass vial and to this solution was added 3hmpH (1.50 mL, 15.467 mmol). The mixture was sonicated for 3 minutes and to the resulting solution was added solid $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.100 g, 0.429 mmol). The mixture was sonicated for 3 min, sealed and then, heated without stirring at 100 °C for 48 h. During this period, blue polyhedral-like crystals of **[9]** were formed. They were isolated by filtration, washed several times with DMF and diethylether, and dried under vacuum. Yield: 87 mg (57 % based on $PDCH_2$). Elemental analysis: Anal. Calc. for $C_{20.5}H_{20.5}N_{3.5}O_{6.5}Cu$ (**[9]**) C 50.93, H 4.27, N 10.14, Found: C 50.48, H 4.55, N 9.79 %. IR data (cm^{-1}): 3295mbr, ν(OH), 3078w $\nu(CH)_{ar}$, 2882w $\nu(CH_2)$, 1591s $\nu(CC)_{ring}$, 1557s, 1356s $\nu(CO_2)$, 1435m $\nu(CN)_{ar}$, 1031m ν(C-OH).

Table S1 Selected crystal data and refinement details for the prepared compounds.

Compound	**[1]**	**[2]**	**[3]**	**[4]**	**[5]**	**[6]**	**[7]**	**[8]**	**[9]**
Empirical formula	$C_{21}H_9N_3O_{12}Cd_2$	$C_{30}H_{30}N_6O_{15}Mn_3$	$C_{30.97}H_{24.94}Mn_3N_{5.66}O_{14}$	$C_{12}H_{12}N_2O_5Zn$	$C_{10}H_{11}N_2O_6Zn$	$C_{13}H_9N_2O_5Zn$	$C_{44}H_{48}N_8O_{14}Zn_2$	$C_{19}H_{17}CoN_3O_6$	$C_{57}H_{51}Cu_3N_9O_{18}$
Formula weight	720.13	879.42	864.87	329.63	320.60	338.61	1043.68	442.29	1340.72
Temperature (K)	100	113	101	100	100	100	100	100	100
Crystal System	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
Space group	$Cmc2_1$	$P2_1/n$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_12_12_1$	P-1	$P2_1$	$C2/c$
a (Å)	10.1522(3)	12.3457(2)	11.5931(6)	11.203(5)	11.0431(6)	7.878(5)	9.0778(8)	7.7534(3)	11.1680(8)
b (Å)	33.2337(12)	11.3248(2)	13.5663(5)	11.394(5)	9.7384(5)	12.877(5)	9.6883(8)	15.3166(4)	25.2917(18)
c (Å)	12.3547(4)	29.2277(4)	27.2835(13)	14.313(5)	12.1390(5)	17.325(5)	13.9491(13)	8.7169(4)	21.2081(19)
α (°)	90	90	90	90	90	90	76.153(8)	90	90
β (°)	90	98.689(1)	89.922(5)	90	90.252(4)	90	73.459(8)	112.728(5)	96.363(7)
γ (°)	90	90	90	90	90	90	84.233(7)	90	90
V (Å^3)	4168.4(2)	4039.50(11)	4291.0(3)	1827.0(13)	1305.44(11)	1757.5(14)	1141.17(18)	954.80(7)	5953.5(8)
Z	4	4	4	4	4	4	1	2	4
D_c (g cm^{-3})	1.148	1.446	1.339	1.198	1.631	1.280	1.519	1.538	1.496
μ (mm^{-1})	8.546	8.131	7.628	1.359	1.905	2.124	1.946	7.428	1.921
F(000)	1392	1788	1750	672	652	684	540	454	2748
Refls collected	11467	15902	28319	7256	7436	3968	7215	5627	11010
Unique refls	3050	7822	8198	3211	2304	2623	4055	2197	5731
R_{int}	0.034	0.036	0.085	0.034	0.036	0.029	0.027	0.040	0.023
R_1	0.0198	0.0393	0.0897	0.0315	0.0439	0.0485	0.0305	0.0374	0.0350
wR_2	0.0512	0.1073	0.3064	0.0756	0.1232	0.1394	0.0840	0.0916	0.0971
GOF	1.015	1.028	1.122	1.052	1.078	1.083	0.898	1.034	1.038
$\Delta\rho_{min/max}$ (e Å^{-3})	-0.33, 0.35	-0.52, 0.89	-1.61, 0.91	-0.27, 0.62	-1.25, 0.91	-0.63, 1.12	-0.44, 0.34	-0.48, 0.55	-0.46, 1.02

Table S2 Selected bond distances (Å) and angles (°) for $[[(CH_3)_2NH_2]_2[Cd_2(PDC)_3]]_n \cdot 4nDMF \cdot 6nH_2O$, **[1]**.

Bond distances			
Cd(1) – O(3)	2.224(6)	Cd(1) – O(7)	2.538(3)
Cd(1) – O(8)	2.341(3)	Cd(1) – N(1)	2.362(5)
Cd(1) – O(3)_d	2.224(6)	Cd(1) – O(7)_d	2.538(3)
Cd(1) – O(8)_d	2.341(3)	Cd(1) – N(3)_h	2.359(5)
Cd(2) – N(2)	2.302(8)	Cd(2) – O(5)_a	2.371(5)
Cd(2) – O(6)_a	2.331(7)	Cd(2) – N(2)_d	2.302(8)
Cd(2) – O(5)_e	2.371(5)	Cd(2) – O(6)_e	2.331(6)
Cd(2) – O(1)_h	2.261(3)	Cd(2) – O(2)_h	2.532(3)
Cd(2) – O(1)_l	2.261(3)	Cd(2) – O(2)_l	2.532(3)
Bond angles			
O(3) – Cd(1) – O(7)	85.9(5)	O(3)_d – Cd(1) – N(3)_h	81.4(2)
O(3) – Cd(1) – O(8)	97.8(4)	O(7)_d – Cd(1) – O(8)_d	53.35(14)
O(3) – Cd(1) – N(1)	165.5(3)	O(7)_d – Cd(1) – N(3)_h	86.27(11)
O(3) – Cd(1) – O(3)_d	10.2(7)	O(8)_d – Cd(1) – N(3)_h	139.39(8)
O(3) – Cd(1) – O(7)_d	96.1(5)	O(5)_a – Cd(2) – N(2)	89.3(2)
O(3) – Cd(1) – O(8)_d	104.5(3)	O(6)_a – Cd(2) – N(2)	143.8(2)
O(3) – Cd(1) – N(3)_h	81.4(2)	N(2) – Cd(2) – N(2)_d	8.1(11)
O(7) – Cd(1) – O(8)	53.35(14)	O(5)_e – Cd(2) – N(2)	88.6(2)
O(7) – Cd(1) – N(1)	88.14(7)	O(6)_e – Cd(2) – N(2)	142.9(3)
O(3)_d – Cd(1) – O(7)	96.1(5)	O(1)_h – Cd(2) – N(2)	96.4(5)
O(7) – Cd(1) – O(7)_d	171.92(14)	O(2)_h – Cd(2) – N(2)	84.6(8)
O(7) – Cd(1) – O(8)_d	133.75(14)	O(1)_l – Cd(2) – N(2)	101.9(5)
O(7) – Cd(1) – N(3)_h	86.27(11)	O(2)_l – Cd(2) – N(2)	92.6(8)
O(8) – Cd(1) – N(1)	89.16(12)	O(5)_a – Cd(2) – O(6)_a	54.6(2)
O(3)_d – Cd(1) – O(8)	104.5(3)	O(5)_a – Cd(2) – N(2)_d	88.6(2)
O(7)_d – Cd(1) – O(8)	133.75(14)	O(5)_a – Cd(2) – O(5)_e	9.3(7)
O(8) – Cd(1) – O(8)_d	80.46(12)	O(5)_a – Cd(2) – O(6)_e	55.3(3)
O(8) – Cd(1) – N(3)_h	139.39(8)	O(1)_h – Cd(2) – O(5)_a	140.8(5)
O(3)_d – Cd(1) – N(1)	165.5(3)	O(2)_h – Cd(2) – O(5)_a	88.8(5)
O(7)_d – Cd(1) – N(1)	88.14(7)	O(1)_l – Cd(2) – O(5)_a	131.7(5)
O(8)_d – Cd(1) – N(1)	89.16(12)	O(2)_l – Cd(2) – O(5)_a	79.5(5)
N(1) – Cd(1) – N(3)_h	84.98(17)	O(6)_a – Cd(2) – N(2)_d	142.9(4)
O(3)_d – Cd(1) – O(7)_d	85.9(5)	O(5)_e – Cd(2) – O(6)_a	55.3(3)
O(3)_d – Cd(1) – O(8)_d	97.8(4)	O(1)_l – Cd(2) – O(2)_l	53.52(11)
O(6)_a – Cd(2) – O(6)_e	7.5(18)	O(2)_h – Cd(2) – O(5)_e	79.5(5)
O(1)_h – Cd(2) – O(6)_a	110.0(9)	O(1)_l – Cd(2) – O(5)_e	105.9(5)
O(2)_h – Cd(2) – O(6)_a	91.4(12)	O(2)_l – Cd(2) – O(5)_e	88.8(5)
O(1)_l – Cd(2) – O(6)_a	104.7(9)	O(1)_h – Cd(2) – O(6)_e	104.7(9)
O(2)_l – Cd(2) – O(6)_a	84.0(12)	O(2)_h – Cd(2) – O(6)_e	84.0(12)
O(5)_e – Cd(2) – N(2)_d	89.3(2)	O(1)_l – Cd(2) – O(6)_e	110.0(9)
O(6)_e – Cd(2) – N(2)_d	143.8(2)	O(2)_l – Cd(2) – O(6)_e	91.4(12)
O(1)_h – Cd(2) – N(2)_d	101.9(5)	O(1)_h – Cd(2) – O(2)_h	53.52(11)
O(2)_h – Cd(2) – N(2)_d	92.6(8)	O(1)_h – Cd(2) – O(1)_l	84.97(11)
O(1)_l – Cd(2) – N(2)_d	96.4(5)	O(1)_h – Cd(2) – O(2)_l	138.49(11)
O(2)_l – Cd(2) – N(2)_d	84.6(8)	O(1)_l – Cd(2) – O(2)_h	138.49(11)
O(5)_e – Cd(2) – O(6)_e	54.6(2)	O(2)_h – Cd(2) – O(2)_l	167.99(12)
O(1)_h – Cd(2) – O(5)_e	131.7(5)		

Translation of Symmetry Code to Equivalent Positions: a = -x,1-y,-1/2+z, b = -x,1-y,1/2+z, c = -1-x,y,z, d = -x,y,z, e = x,1-y,-1/2+z, f = x,1-y,1/2+z, g = 1/2+x,-1/2+y,z, h = -1/2-x,1/2-y,-1/2+z, i = -1/2-x,1/2-y,1/2+z, j = 1/2-x,-1/2+y,z, k = -1/2+x,1/2-y,1/2+z, l = 1/2+x,1/2-y,-1/2+z.

Table S3 Selected bond distances (Å) and angles (°) for $[Mn(PDC)(DMF)]_n$ **[2]**

Bond distances			
Mn(1) – O(3S)	2.154(14)	Mn(2) – O(10)_a	2.1247(18)
Mn(1) – O(7)	2.2670(18)	Mn(2) – O(3)_d	2.1806(19)
Mn(1) – O(8)	2.2922(18)	Mn(2) – O(6)_e	2.1412(19)
Mn(1) – O(12)	2.0933(18)	Mn(3) – O(1)	2.1193(19)
Mn(1) – O(3S)	2.164(17)	Mn(3) – O(1S)	2.1891(19)
Mn(1) – N(3)_b	2.264(2)	Mn(3) – O(2S)	2.223(2)
Mn(1) – O(4)_d	2.1585(19)	Mn(3) – O(9)_a	2.1904(18)
Mn(2) – O(2)	2.1388(19)	Mn(3) – N(1)_c	2.305(2)
Mn(2) – O(8)	2.2836(19)	Mn(3) – O(5)_e	2.1491(19)
Mn(2) – O(11)	2.1581(19)		
Bond angles			
O(3S)_1 – Mn(1) – O(7)	88.8(3)	O(8) – Mn(2) – O(11)	83.68(7)
O(3S)_1 – Mn(1) – O(8)	103.8(4)	O(8) – Mn(2) – O(10)_a	87.53(7)
O(3S)_1 – Mn(1) – O(12)	88.6(3)	O(3)_d – Mn(2) – O(8)	97.48(7)
O(3S)_1 – Mn(1) – N(3)_b	87.4(4)	O(6)_e – Mn(2) – O(8)	87.76(7)
O(3S)_1 – Mn(1) – O(4)_d	163.2(4)	O(10)_a – Mn(2) – O(11)	90.43(7)
O(7) – Mn(1) – O(8)	57.89(6)	O(3)_d – Mn(2) – O(11)	90.88(7)
O(7) – Mn(1) – O(12)	156.30(7)	O(6)_e – Mn(2) – O(11)	168.31(7)
O(3S)_2 – Mn(1) – O(7)	84.5(5)	O(3)_d – Mn(2) – O(10)_a	174.93(7)
O(7) – Mn(1) – N(3)_b	113.04(7)	O(6)_e – Mn(2) – O(10)_a	97.16(7)
O(4)_d – Mn(1) – O(7)	84.49(7)	O(3)_d – Mn(2) – O(6)_e	82.34(7)
O(8) – Mn(1) – O(12)	100.04(7)	O(1) – Mn(3) – O(1S)	170.21(8)
O(3S)_2 – Mn(1) – O(8)	96.5(5)	O(1) – Mn(3) – O(2S)	87.13(8)
O(8) – Mn(1) – N(3)_b	164.76(7)	O(1) – Mn(3) – O(9)_a	90.22(7)
O(4)_d – Mn(1) – O(8)	85.64(7)	O(1) – Mn(3) – N(1)_c	86.39(8)
O(3S)_2 – Mn(1) – O(12)	90.2(5)	O(1) – Mn(3) – O(5)_e	105.68(7)
O(12) – Mn(1) – N(3)_b	90.37(7)	O(1S) – Mn(3) – O(2S)	97.08(8)
O(4)_d – Mn(1) – O(12)	103.65(7)	O(1S) – Mn(3) – O(9)_a	85.88(7)
O(3S)_2 – Mn(1) – N(3)_b	94.6(5)	O(1S) – Mn(3) – N(1)_c	84.80(7)
O(3S)_2 – Mn(1) – O(4)_d	165.5(5)	O(1S) – Mn(3) – O(5)_e	83.57(7)
O(4)_d – Mn(1) – N(3)_b	81.06(8)	O(2S) – Mn(3) – O(9)_a	176.58(8)
O(2) – Mn(2) – O(8)	168.89(7)	O(2S) – Mn(3) – N(1)_c	89.71(8)
O(2) – Mn(2) – O(11)	85.26(7)	O(2S) – Mn(3) – O(5)_e	84.91(8)
O(2) – Mn(2) – O(10)_a	93.63(7)	O(9)_a – Mn(3) – N(1)_c	92.26(7)
O(2) – Mn(2) – O(3)_d	81.61(7)	O(5)_e – Mn(3) – O(9)_a	93.76(7)
O(2) – Mn(2) – O(6)_e	103.04(7)	O(5)_e – Mn(3) – N(1)_c	166.47(8)

Translation of Symmetry Code to Equivalent Positions: a = 1/2-x,-1/2+y,3/2-z, b = 1/2-x,1/2+y,3/2-z, c = 3/2-x,-1/2+y,3/2-z, d = 3/2-x,1/2+y,3/2-z, e = 1-x,1-y,1-z.

Table S4 Selected bond distances (Å) and angles (°) for $[Mn_3(PDC)_2(INA)_2(DMF)_{1.5}(H_2O)_{0.5}]_n \cdot nDMF \cdot 2nH_2O$, **[3].**

Bond distances			
Mn(1) – O(1)	2.133(9)	Mn(2) – O(3)_e	2.115(11)
Mn(1) – O(2S)	2.211(8)	Mn(2) – O(5)_g	2.181(8)
Mn(1) – N(4)	2.363(9)	Mn(2) – O(12)_h	2.137(9)
Mn(1) – N(3)_b	2.325(12)	Mn(3) – O(1S)	2.196(8)
Mn(1) – O(4)_e	2.161(8)	Mn(3) – O(10)	2.170(7)
Mn(1) – O(6)_g	2.137(10)	Mn(3) – N(2)	2.275(9)
Mn(2) – O(2)	2.146(8)	Mn(3) – O(7)_c	2.137(9)
Mn(2) – O(9)	2.117(10)	Mn(3) – N(1)_c	2.320(12)
Mn(2) – O(8)_c	2.184(8)	Mn(3) – O(11)_h	2.133(10)
Bond angles			
O(1) – Mn(1) – O(2S)	90.7(4)	O(9) – Mn(2) – O(12)_h	108.4(4)
O(1) – Mn(1) – N(4)	178.1(4)	O(3)_e – Mn(2) – O(8)_c	80.2(4)
O(1) – Mn(1) – N(3)_b	91.3(4)	O(5)_g – Mn(2) – O(8)_c	165.9(4)
O(1) – Mn(1) – O(4)_e	100.8(3)	O(8)_c – Mn(2) – O(12)_h	94.7(3)
O(1) – Mn(1) – O(6)_g	100.4(4)	O(3)_e – Mn(2) – O(5)_g	112.9(4)
O(2S) – Mn(1) – N(4)	88.2(4)	O(3)_e – Mn(2) – O(12)_h	87.7(5)
O(2S) – Mn(1) – N(3)_b	84.9(4)	O(5)_g – Mn(2) – O(12)_h	81.2(3)
O(2S) – Mn(1) – O(4)_e	164.1(4)	O(1S) – Mn(3) – O(10)	167.0(4)
O(2S) – Mn(1) – O(6)_g	88.0(4)	O(1S) – Mn(3) – N(2)	84.9(3)
N(3)_b – Mn(1) – N(4)	87.1(4)	O(1S) – Mn(3) – O(7)_c	85.8(3)
O(4)_e – Mn(1) – N(4)	80.1(3)	O(1S) – Mn(3) – N(1)_c	84.0(4)
O(6)_g – Mn(1) – N(4)	81.1(4)	O(1S) – Mn(3) – O(11)_h	85.1(4)
O(4)_e – Mn(1) – N(3)_b	83.9(3)	O(10) – Mn(3) – N(2)	85.6(3)
O(6)_g – Mn(1) – N(3)_b	166.4(4)	O(7)_c – Mn(3) – O(10)	103.1(3)
O(4)_e – Mn(1) – O(6)_g	100.5(3)	O(10) – Mn(3) – N(1)_c	86.9(3)
O(2) – Mn(2) – O(9)	83.9(3)	O(10) – Mn(3) – O(11)_h	103.0(4)
O(2) – Mn(2) – O(8)_c	101.4(3)	O(7)_c – Mn(3) – N(2)	170.2(3)
O(2) – Mn(2) – O(3)_e	84.3(4)	N(1)_c – Mn(3) – N(2)	88.5(4)
O(2) – Mn(2) – O(5)_g	85.7(3)	O(11)_h – Mn(3) – N(2)	85.8(4)
O(2) – Mn(2) – O(12)_h	160.5(4)	O(7)_c – Mn(3) – N(1)_c	87.5(4)
O(8)_c – Mn(2) – O(9)	86.2(3)	O(7)_c – Mn(3) – O(11)_h	96.5(4)
O(3)_e – Mn(2) – O(9)	159.8(4)	O(11)_h – Mn(3) – N(1)_c	168.1(4)
O(5)_g – Mn(2) – O(9)	82.4(4)		

Translation of Symmetry Code to Equivalent Positions: a = -1+x,y,z, b = 1+x,y,z, c = -x,-1/2+y,3/2-z, d = -x,1/2+y,3/2-z, e = 1-x,-1/2+y,3/2-z, f = 1-x,1/2+y,3/2-z, g = -x,-y,1-z, h = 1-x,-y,1-z

Table S5 Selected bond distances (Å) and angles (°) for $[Zn(PDC)(NMP)]_n \cdot nH_2O$, **[4]**.

Bond distances			
Zn(1) – O(1)	1.946(3)	Zn(1) – O(4)_a	1.954(3)
Zn(1) – O(5)	1.975(3)	Zn(1) – N(1)_c	2.049(3)
Bond angles			
O(1) – Zn(1) – O(5)	105.71(13)	O(4)_a – Zn(1) – O(5)	119.60(13)
O(1) – Zn(1) – O(4)_a	116.44(12)	O(5) – Zn(1) – N(1)_c	94.70(14)
O(1) – Zn(1) – N(1)_c	121.22(12)	O(4)_a – Zn(1) – N(1)_c	97.98(14)

Translation of Symmetry Code to Equivalent Positions: a = 1/2-x,1-y,-1/2+z, c = -1/2+x,3/2-y,1-z

Table S6 Selected bond distances (Å) and angles (°) for $[Zn(PDC)(H_2O)(DMF)]_n$, **[5]**.

Bond distances			
Zn(1) – O(1)	1.993(3)	Zn(1) – O(3)_b	2.035(3)
Zn(1) – O(5)	2.154(3)	Zn(1) – N(1)_c	2.098(4)
Zn(1) – O(6)	2.075(3)		
Bond angles			
O(1) – Zn(1) – O(5)	90.82(13)	O(3)_b – Zn(1) – O(5)	92.58(12)
O(1) – Zn(1) – O(6)	89.92(13)	O(5) – Zn(1) – N(1)_c	87.04(13)
O(1) – Zn(1) – O(3)_b	125.76(11)	O(3)_b – Zn(1) – O(6)	91.42(13)
O(1) – Zn(1) – N(1)_c	137.78(11)	O(6) – Zn(1) – N(1)_c	88.74(14)
O(5) – Zn(1) – O(6)	174.49(13)	O(3)_b – Zn(1) – N(1)_c	96.46(11)

Translation of Symmetry Code to Equivalent Positions: b = x,1+y,z, c = x,5/2-y,-1/2+z.

Table S7 Selected bond distances (Å) and angles (°) for $[Zn(PDC)(3hmpH)]_n \cdot nDMF \cdot 0.5nH_2O$, **[6]**.

Bond distances			
Zn(1) – N(1)	2.009(5)	Zn(1) – O(3)_a	2.612(6)
Zn(1) – N(2)	2.040(5)	Zn(1) – O(4)_d	1.958(5)
Zn(1) – O(2)_a	1.981(4)		
Bond angles			
N(1) – Zn(1) – N(2)	106.4(2)	O(3)_a – Zn(1) – N(2)	155.46(18)
O(2)_a – Zn(1) – N(1)	120.2(2)	O(4)_d – Zn(1) – N(2)	111.09(19)
O(3)_a – Zn(1) – N(1)	81.3(2)	O(2)_a – Zn(1) – O(3)_a	55.52(17)
O(4)_d – Zn(1) – N(1)	114.5(2)	O(2)_a – Zn(1) – O(4)_d	102.07(18)
O(2)_a – Zn(1) – N(2)	101.90(19)	O(3)_a – Zn(1) – O(4)_d	85.34(17)

Translation of Symmetry Code to Equivalent Positions: a = -1+x,y,z, d = 2-x,1/2+y,3/2-z.

Table S8 Selected bond distances (Å) and angles (°) for $[Zn(PDC)(2hmpH)_2]_2 \cdot 2DMF$, **[7]**.

Bond distances			
Zn(1) – O(1)	2.1986(16)	Zn(1) – N(1)	2.0972(18)
Zn(1) – O(2)	2.2697(16)	Zn(1) – N(2)	2.0888(17)
Zn(1) – O(3)	2.0711(14)	Zn(1) – O(5)_a	2.0406(15)
Bond angles			
O(1) – Zn(1) – O(2)	91.54(6)	O(2) – Zn(1) – O(5)_a	92.58(6)
O(1) – Zn(1) – O(3)	88.40(6)	O(3) – Zn(1) – N(1)	102.78(6)
O(1) – Zn(1) – N(1)	77.67(6)	O(3) – Zn(1) – N(2)	95.01(6)
O(1) – Zn(1) – N(2)	92.35(6)	O(3) – Zn(1) – O(5)_a	88.98(6)
O(1) – Zn(1) – O(5)_a	169.90(6)	N(1) – Zn(1) – N(2)	159.22(6)
O(2) – Zn(1) – O(3)	170.96(6)	O(5)_a – Zn(1) – N(1)	93.42(7)
O(2) – Zn(1) – N(1)	86.02(6)	O(5)_a – Zn(1) – N(2)	97.60(6)
O(2) – Zn(1) – N(2)	75.96(6)		

Translation of Symmetry Code to Equivalent Positions: a = -x,1-y,2-z

Table S9 Selected bond distances (Å) and angles (°) for $[Co(PDC)(3hmpH)_2]_n \cdot 0.25nDMF$, **[8]**.

Bond distances			
Co(1) – N(1)	2.121(3)	Co(1) – O(3)_a	2.163(3)
Co(1) – N(2)	2.158(3)	Co(1) – O(4)_a	2.214(3)
Co(1) – N(3)	2.149(3)	Co(1) – O(2)_d	2.037(3)
Bond angles			
N(1) – Co(1) – N(2)	94.33(14)	O(2)_d – Co(1) – N(2)	86.16(15)
N(1) – Co(1) – N(3)	94.23(14)	O(3)_a – Co(1) – N(3)	92.16(13)
O(3)_a – Co(1) – N(1)	90.46(13)	O(4)_a – Co(1) – N(3)	89.36(14)
O(4)_a – Co(1) – N(1)	150.76(12)	O(2)_d – Co(1) – N(3)	87.75(13)
O(2)_d – Co(1) – N(1)	109.66(13)	O(3)_a – Co(1) – O(4)_a	60.38(11)
N(2) – Co(1) – N(3)	170.79(15)	O(2)_d – Co(1) – O(3)_a	159.83(13)
O(3)_a – Co(1) – N(2)	91.19(14)	O(2)_d – Co(1) – O(4)_a	99.46(12)
O(4)_a – Co(1) – N(2)	84.84(12)		

Translation of Symmetry Code to Equivalent Positions: a = -1+x,y,z, d = 1-x,1/2+y,1-z

Table S10 Selected bond distances (Å) and angles (°) for $[Cu(PDC)(3hmpH)_2]_n \cdot 0.5nDMF \cdot 1.5nH_2O$, **[9]**.

Bond distances			
Cu(1) – O(1)	1.9781(14)	Cu(2) – O(5)	1.9656(14)
Cu(1) – O(3)	2.2153(16)	Cu(2) – N(1)	2.269(2)
Cu(1) – N(3)	2.0112(17)	Cu(2) – N(5)	2.0385(17)
Cu(1) – N(4)	2.0130(18)	Cu(2) – O(5)_a	1.9656(14)
Cu(1) – O(4)_b	1.9551(16)	Cu(2) – N(5)_a	2.0385(17)
Bond angles			
O(1) – Cu(1) – O(3)	87.39(6)	O(5) – Cu(2) – N(1)	86.03(4)
O(1) – Cu(1) – N(3)	88.55(6)	O(5) – Cu(2) – N(5)	89.61(6)
O(1) – Cu(1) – N(4)	88.44(6)	O(5) – Cu(2) – O(5)_a	172.06(6)
O(1) – Cu(1) – O(4)_b	156.19(7)	O(5) – Cu(2) – N(5)_a	91.82(6)
O(3) – Cu(1) – N(3)	94.90(7)	N(1) – Cu(2) – N(5)	100.36(5)
O(3) – Cu(1) – N(4)	90.05(7)	O(5)_a – Cu(2) – N(1)	86.03(4)
O(3) – Cu(1) – O(4)_b	116.15(6)	N(1) – Cu(2) – N(5)_a	100.36(5)
N(3) – Cu(1) – N(4)	174.09(8)	O(5)_a – Cu(2) – N(5)	91.82(6)
O(4)_b – Cu(1) – N(3)	92.71(7)	N(5) – Cu(2) – N(5)_a	159.29(8)
O(4)_b – Cu(1) – N(4)	88.01(7)	O(5)_a – Cu(2) – N(5)_a	89.61(6)

Translation of Symmetry Code to Equivalent Positions: a = 1-x,y,1/2-z, b = -x,-y,-z

Table S11 Geometrical characteristics (distances in Å and angles in °) of the conventional H-bonds found in $[Zn(PDC)(H_2O)(DMF)]_n$, **[5]**

D – H ··· A	D – H	H ··· A	D ··· A	∠ D – H ··· A	Symmetry
O(6) – H(6A) ··· O(4)	0.82(4)	1.88(4)	2.690(4)	169(4)	1-x,2-y,1-z
O(6) – H(6B) ··· O(2)	0.81(4)	1.90(4)	2.703(4)	169(5)	1-x,1/2+y,1/2-z

Table S12 Geometrical characteristics (distances in Å and angles in °) of the conventional H-bonds found in $[Zn(PDC)(2hmpH)_2]_2$·2DMF, **[7]**.

D – H ··· A	D – H	H ··· A	D ··· A	∠ D – H ··· A	Symmetry
O(1) – H(1A) ··· O(4)	0.82(3)	1.78(3)	2.586(2)	170(2)	
O(2) – H(2A) ··· O(6)	0.82(3)	1.79(3)	2.609(2)	172(5)	-x,1-y,2-z

Table S13 Geometrical characteristics (distances in Å and angles in °) of the conventional H-bonds found in $[Co(PDC)(3hmpH)_2]_n$·0.25nDMF, **[8]**.

D – H ··· A	D – H	H ··· A	D ··· A	∠ D – H ··· A	Symmetry
O(6) – H(6) ··· O(5)	0.82	2.05	2.801(6)	153	x,y,1+z
O(5) – H(7A) ··· O(1)	0.80(2)	2.38(3)	2.725(5)	107(3)	-x,1/2+y,-z

Table S14 Geometrical characteristics (distances in Å and angles in °) of the conventional H-bonds found in $[Cu(PDC)(3hmpH)_2]_n$·0.5nDMF·1.5nH_2O, **[9]**.

D – H ··· A	D – H	H ··· A	D ··· A	∠ D – H ··· A	Symmetry
O(7) – H(7A) ··· O(6)	0.98(3)	1.68(2)	2.651(2)	172(3)	-1/2+x,1/2+y,z
O(8A) – H(8A) ··· O(7)	0.92	1.81	2.722(4)	168	1+x,y,z
O(9) – H(9A) ··· O(2)	0.94(4)	1.76(4)	2.691(2)	174(3)	1/2+x,-1/2+y,z

Table S15 Thermogravimetric analysis (TG) data for the prepared compounds.

Compound	Lattice solvent loss (°C)		Coordinated solvent or pyridinealcohol loss (°C)		PDC^{2-} decomposition (°C)		Final residue reached (°C) (MO)	
	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)
$[[(CH_3)_2NH_2]_2[Cd_2(PDC)_3]]_n$· 4nDMF·6n$H_2O$, **[1]**	8.5 24.5 RT – 110, 130-220[a]	8.9(H_2O) 24.1(DMF)	9.5[b] 280 – 325	7.6	38.1 375 – 440	40.8	21.2 440	22.5
$[Mn(PDC)(DMF)]_n$, **[2]**			25.0 120 – 300	24.9	52.0 350 – 470	50.8	24.0 470	24.2
$[Mn_3(PDC)_2(INA)_2(DMF)_{1.5}(H_2O)_{0.5}]_n$· nDMF·2n$H_2O$, **[3]**	4.0 RT – 110	4.7	18.9 140 – 330[c]	19.0	55.0 335 – 445[d]	54.5	22.9 450	22.0
$[Zn(PDC)(NMP)]_n$·nH_2O, **[4]**			35.0 RT – 195[e]	33.7	43.0 390 – 480	42.9	22.5 480	23.4
$[Zn(PDC)(H_2O)(DMF)]_n$, **[5]**			28.0 90 – 240	28.3	46.5 400 – 510	46.4	25.5 510	25.3
$[Zn(PDC)(3hmpH)]_n$· nDMF·0.5nH_2O, **[6]**	19.0 30 – 250	19.5	25.0 280 – 370	25.9	36.9 380 – 480	35.5	18.1 480	19.4
$[Zn(PDC)(2hmpH)_2]_2$· 2DMF, **[7]**	12.9 70 – 150	14.0	40.1 180 – 290	41.8	28.6 355 – 390	30.5	15.5 420	15.6
$[Co(PDC)(3hmpH)_2]_n$· 0.25nDMF, **[8]**	3.8 RT – 120	4.0	46.1 235 – 310	47.4	31.0 315 – 430	32.4	18.0 430	16.3
$[Cu(PDC)(3hmpH)_2]_n$· 0.5nDMF, **[9]**	7.3 RT – 205	7.6			76.0 230 – 380	76.0[f]	17.0 380	16.5

[a] H_2O and DMF were lost in two distinguishable steps.

[b] In this case is the decomposition of the cation $(CH_3)_2NH_2$.

[c] The loss of lattice and coordinated DMF is not distinguishable.

[d] Both PDC^{2-} and INA^- are decomposed over this temperature range.

[e] H_2O and NMP loss is indistinguishable.

[f] This is assigned to the loss (and/or decomposition) of both 3hmph and pdc^{2-} ; it is a 4-step procedure but no assignments could be done for the individual steps.

Table S16. PDC^{2-} 2D coordination polymers with honeycomb topology.

		Lattice dimensions							
	Compound	*a*	*b*	*c*	*α*	*β*	*γ*	Space Group	Ref.
1	$[Cd(PDC)(H_2O)_2]_n$	10.21	12.32	7.53	90	106.3	90	*C*2/*c*	53
2	$[Cd(PDC)(DMA)_2]_n$	9.29	11.97	16.35	90	101.7	90	$P2_1$	54
3	$[Mn(PDC)(H_2O)_2]_n$	10.07	12.17	7.37	90	106.1	90	*C*2/*c*	55
4	$[Zn(PDC)(H_2O)_2]_n$	10.01	11.91	7.33	90	105.1	90	*C*2/*c*	56
5	$[Co(PDC)(H_2O)(py)]_n$	10.87	9.87	11.91	90	91.5	90	$P2_1/c$	57
6	$[Co(PDC)(H_2O)_2]_n$	9.89	11.96	7.39	90	105.1	90	*C*2/*c*	58
7	$[Cu(PDC)(im)_2]_n$	15.78	12.38	7.86	90	90	90	*Pnma*	59
8	$[Cu(PDC)(py)_2]_n$	10.09	11.60	14.68	90	93.7	90	$P2_1/n$	60
9	$[Cu(PDC)(H_2O)_2]_n$	10.11	11.86	7.06	90	105.4	90	*C*2/*c*	61
10	$[Fe(PDC)(H_2O)_2]_n$	9.95	12.07	7.41	90	105.9	90	*C*2/*c*	62
11	$[Mg(PDC)(H_2O)_2]_n$	9.24	12.07	7.28	90	106.5	90	*C*2/*c*	63
12	$[Ca(PDC)(H_2O)_2]_n$	10.25	12.68	7.53	90	106.3	90	*Cc*	64
13	$[Zn(PDC)(H_2O)(DMF)]_n$	11.04	9.74	12.14	90	90.3	90	$P2_1/c$	**[5]***
14	$[Co(PDC)(3hmpH)_2]_n$	7.75	15.32	8.72	90	112.7	90	$P2_1$	**[8]***

* This work

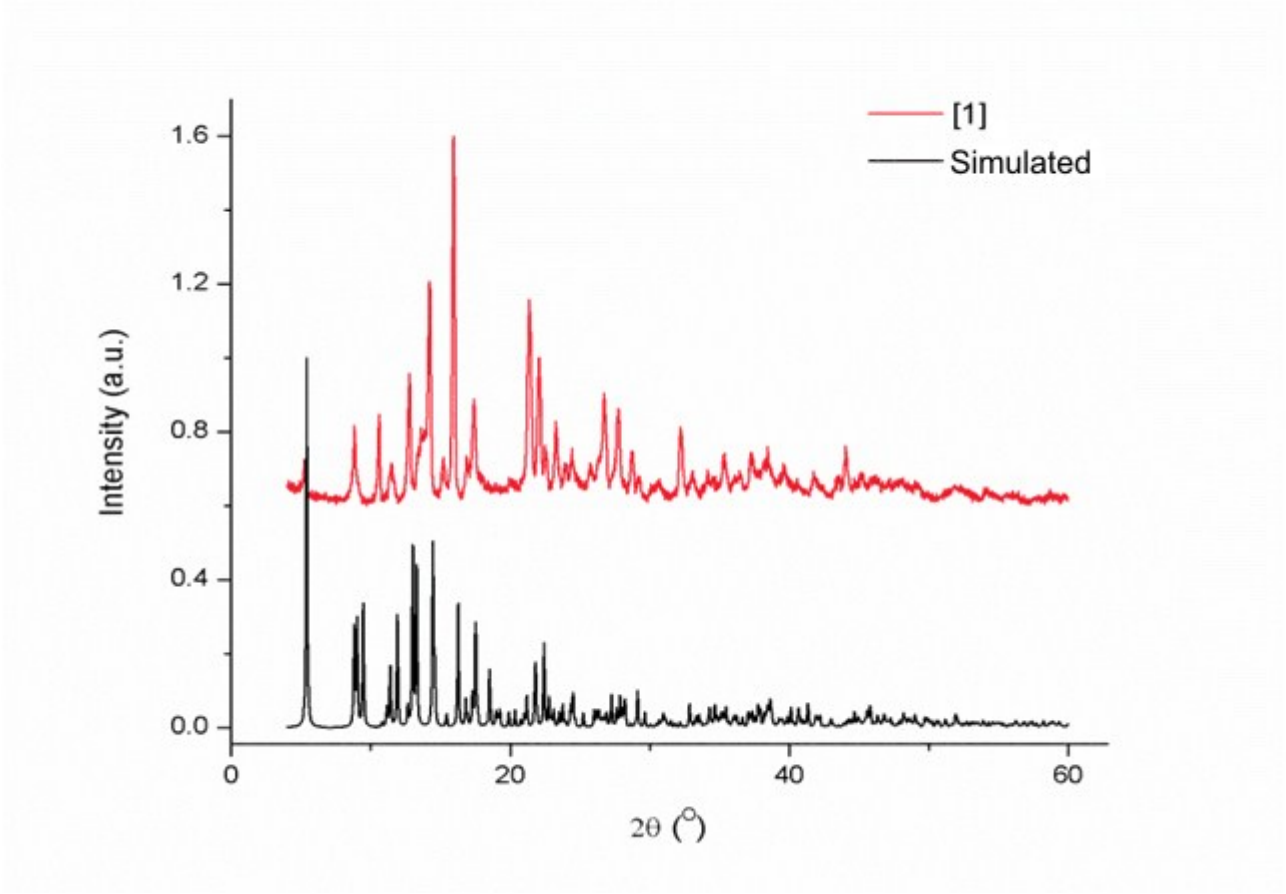


Fig. S1 The simulated and experimental XRD powder patterns for **[1]**.

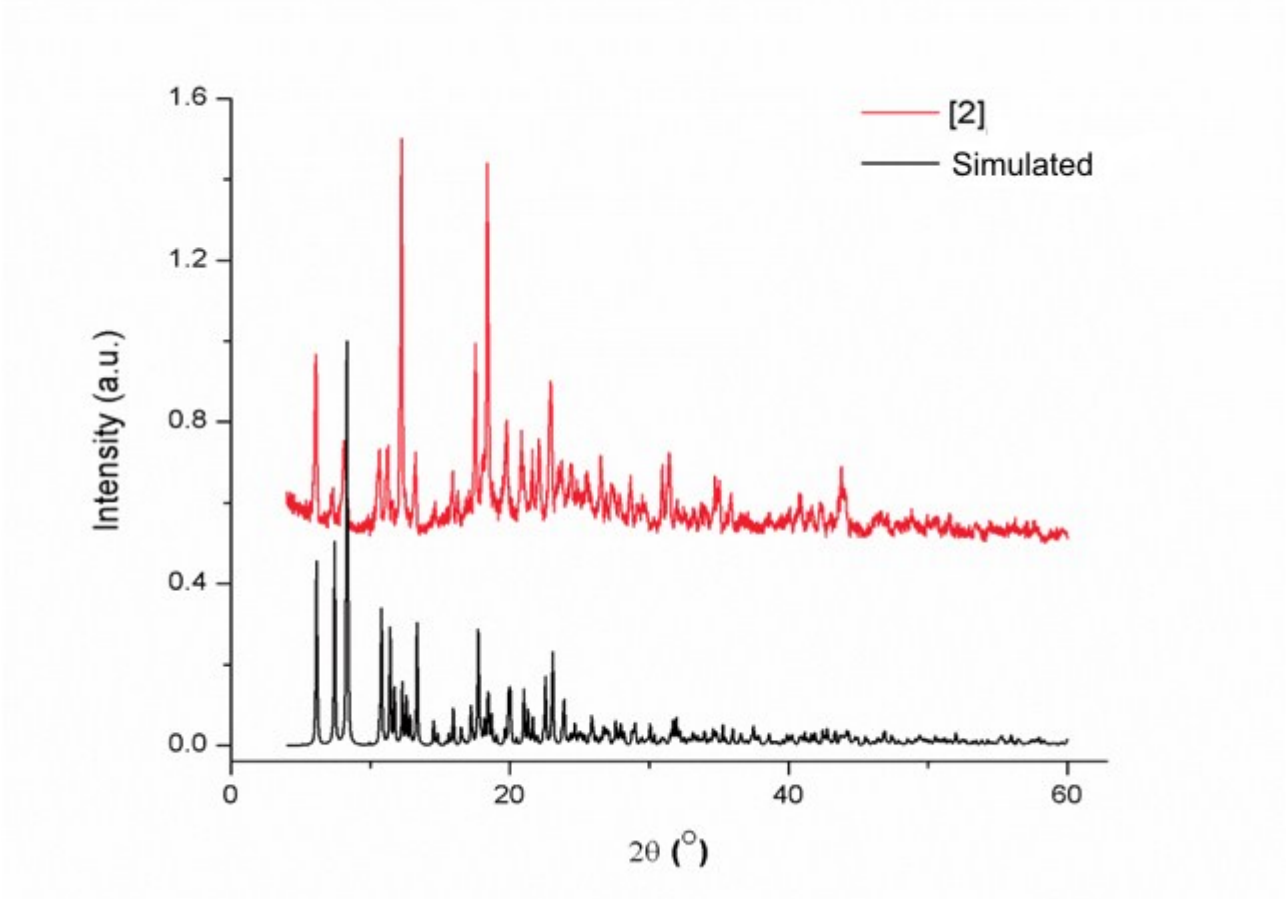


Fig. S2 The simulated and experimental XRD powder patterns for **[2]**.

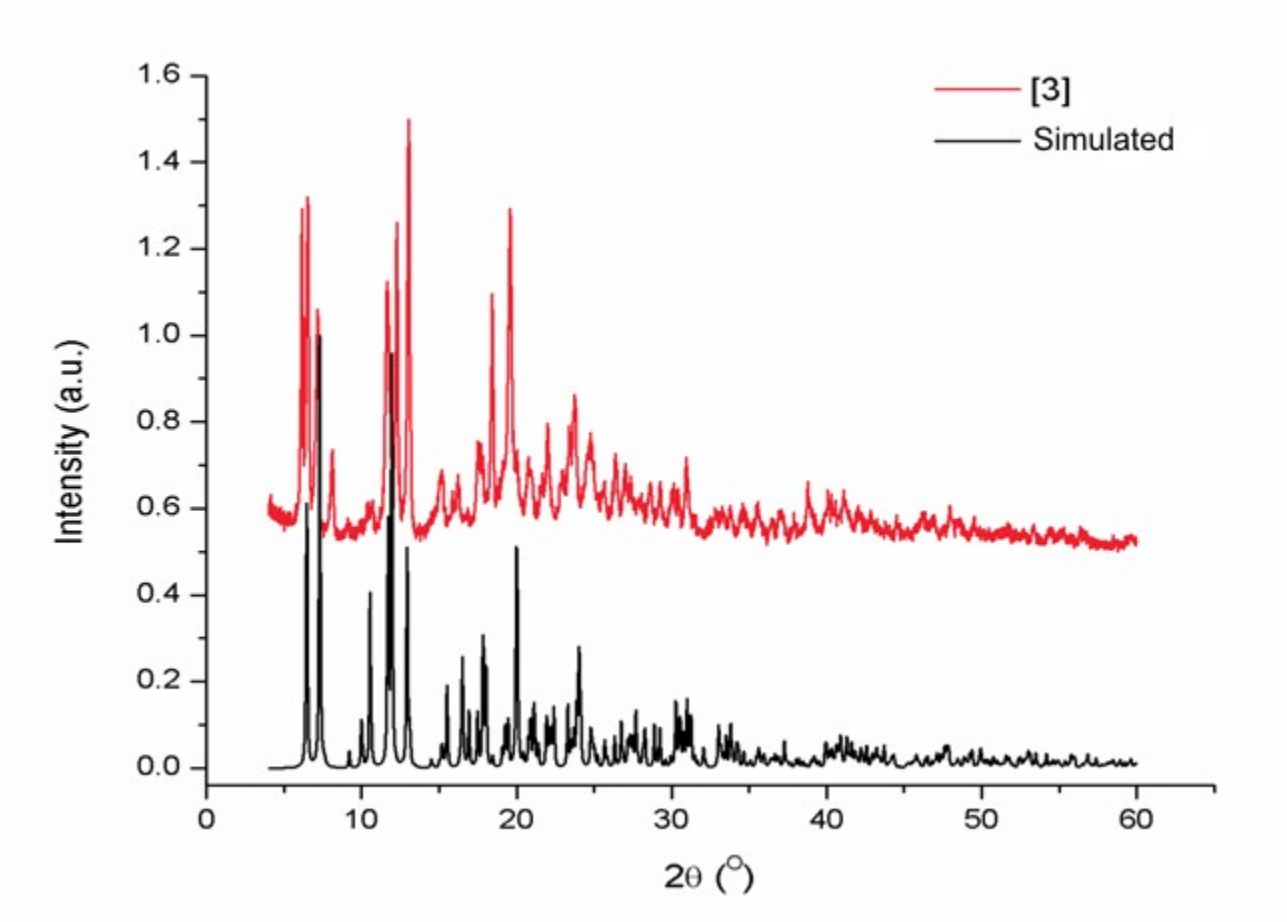


Fig. S3 The simulated and experimental XRD powder patterns for **[3]**.

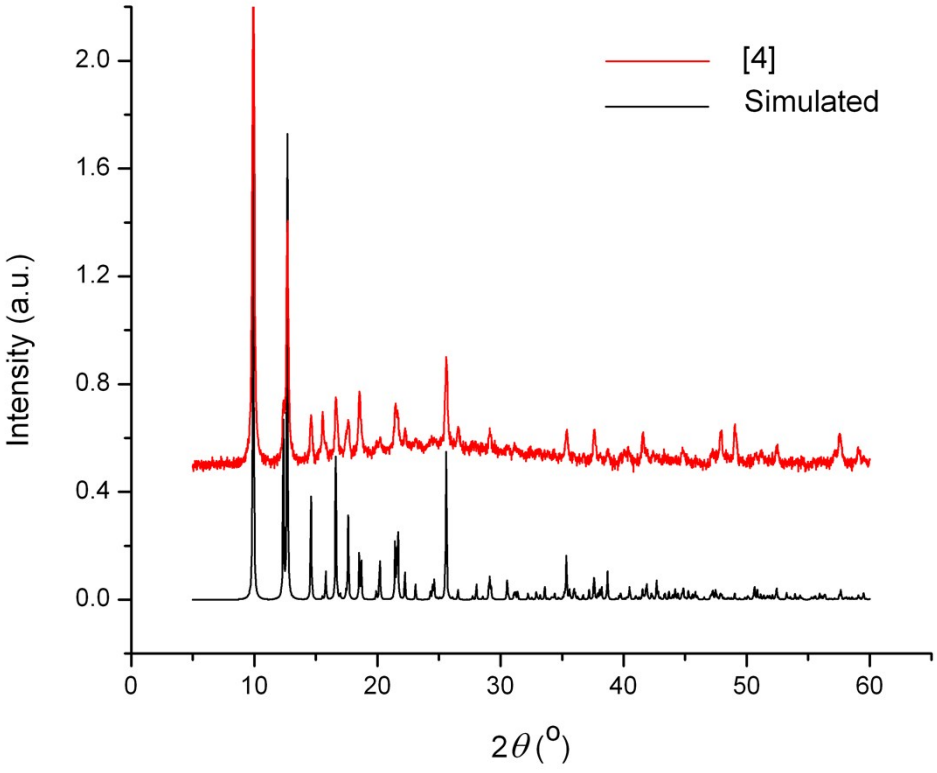


Fig. S4 The simulated and experimental XRD powder patterns for **[4]**.

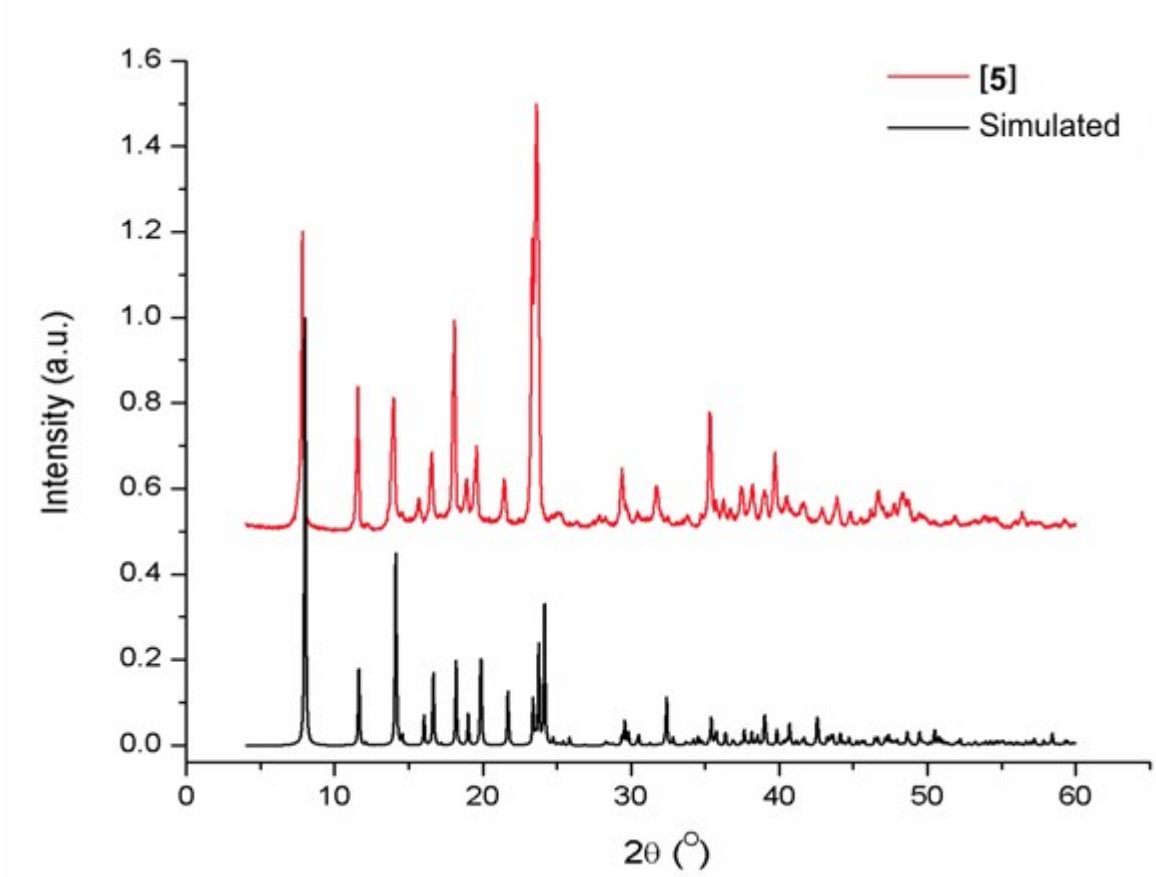


Fig. S5 The simulated and experimental XRD powder patterns for **[5]**.

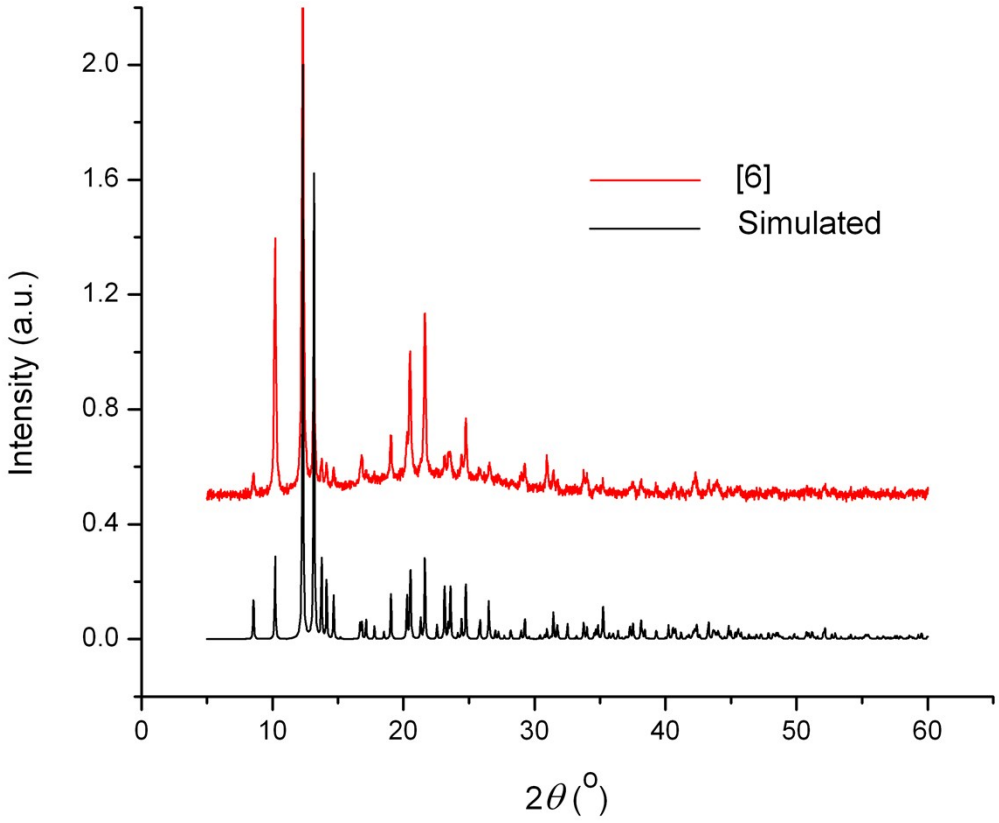


Fig. S6 The simulated and experimental XRD powder patterns for **[6]**.

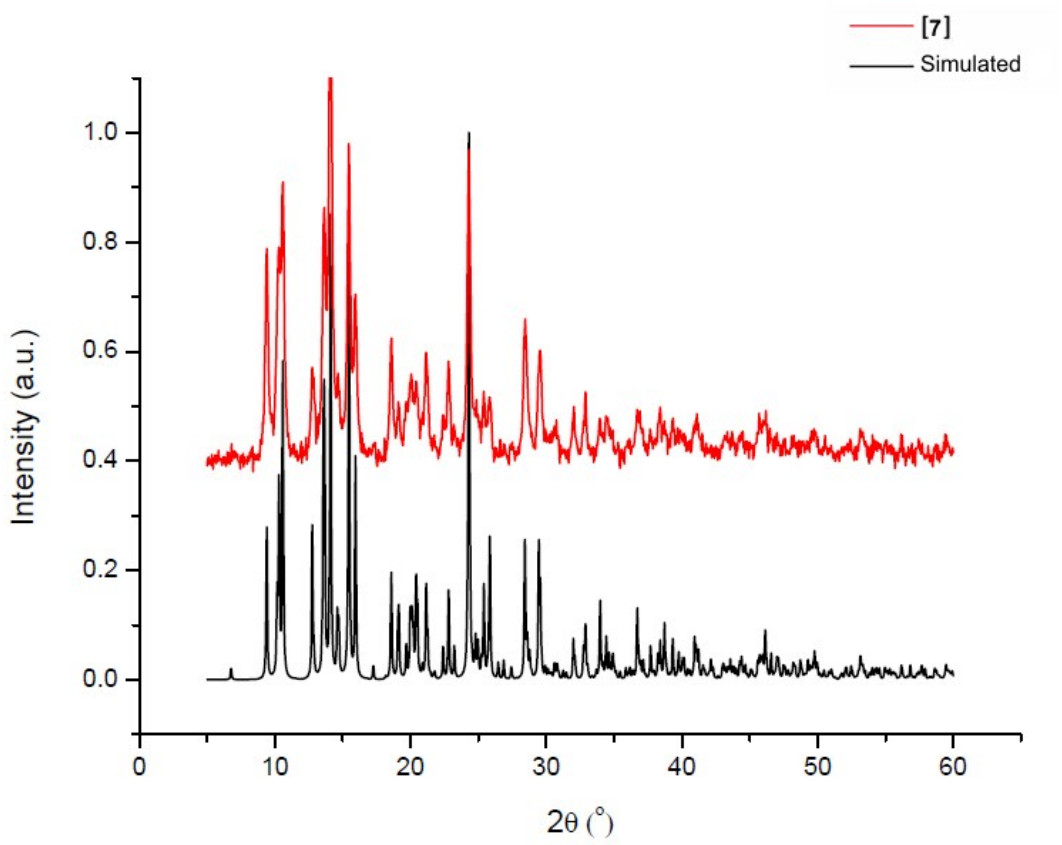


Fig. S7 The simulated and experimental XRD powder patterns for **[7]**.

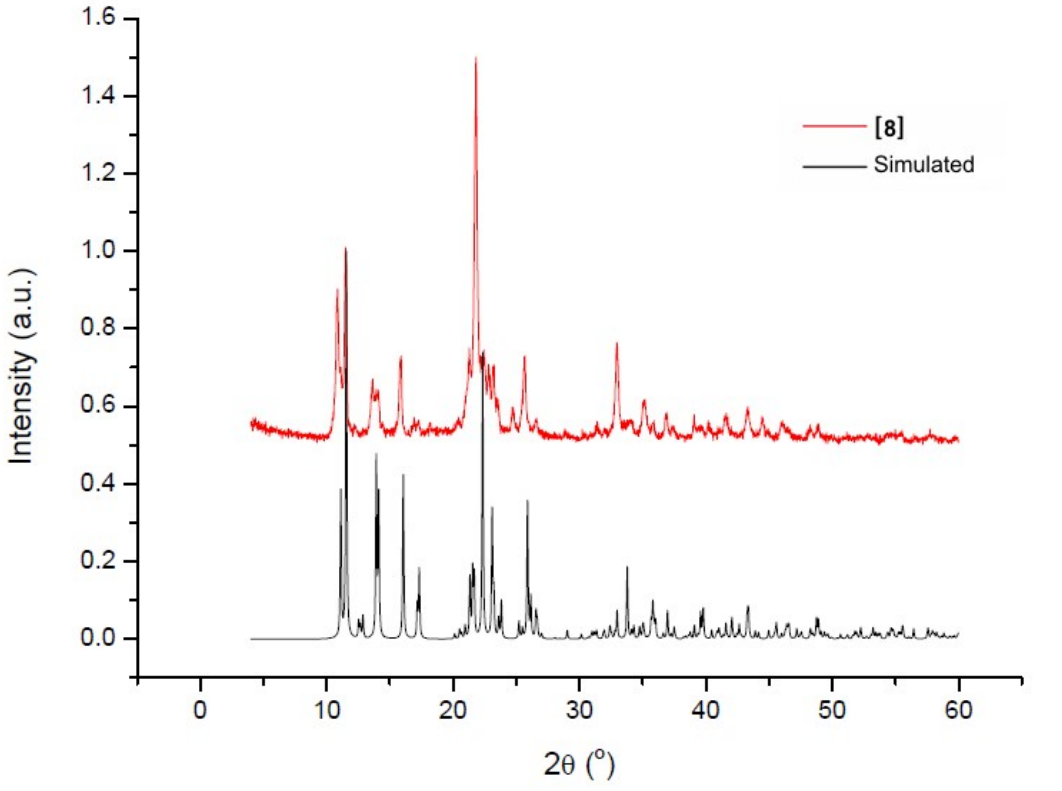


Fig. S8 The simulated and experimental XRD powder patterns for **[8]**.

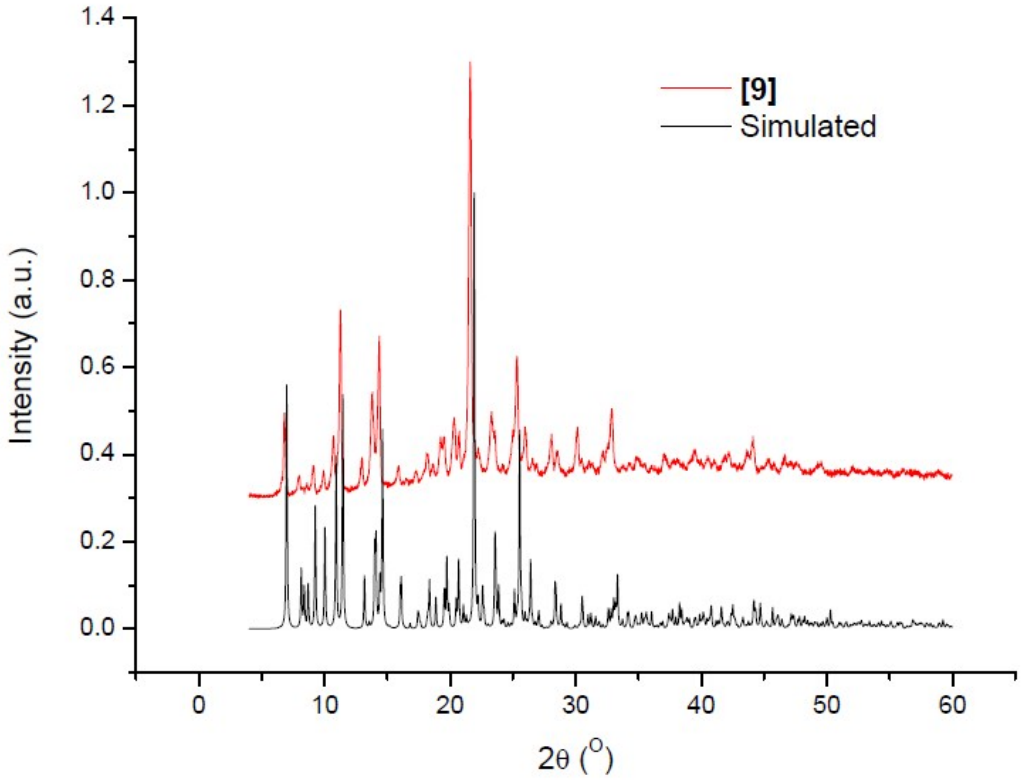
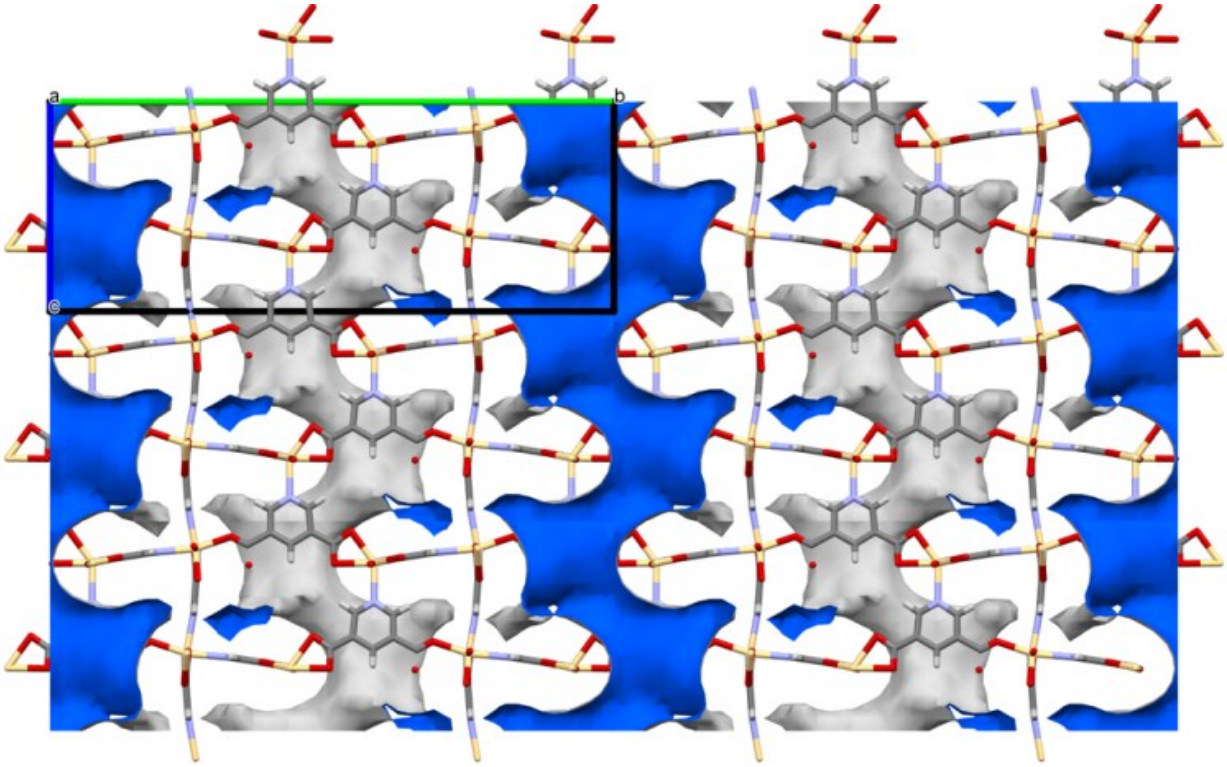
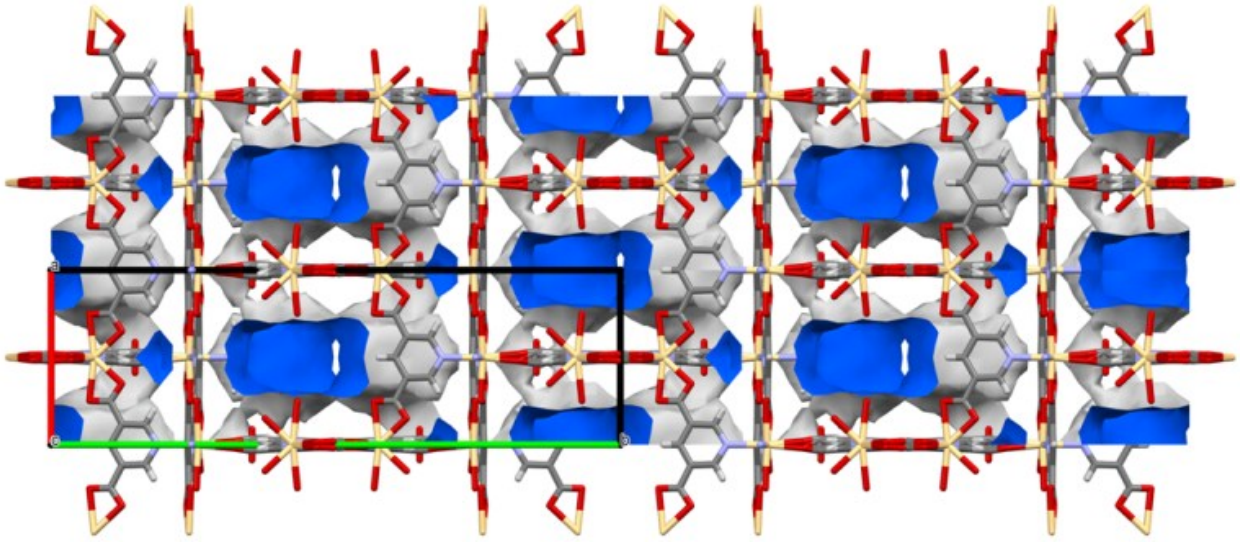


Fig. S9 The simulated and experimental XRD powder patterns for **[9]**.

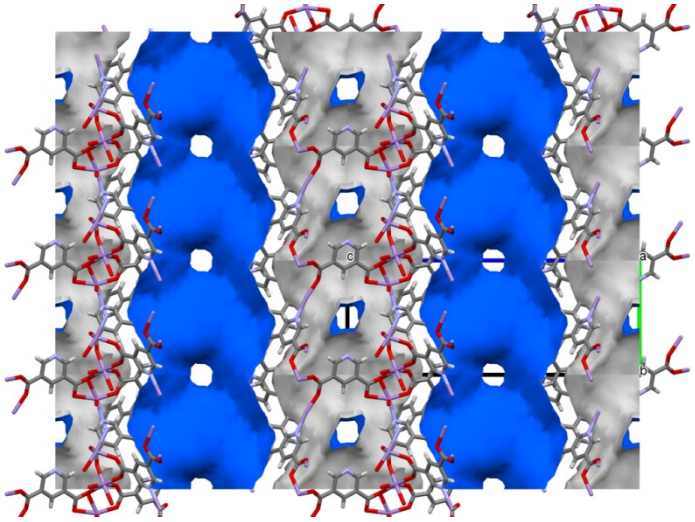


(a)

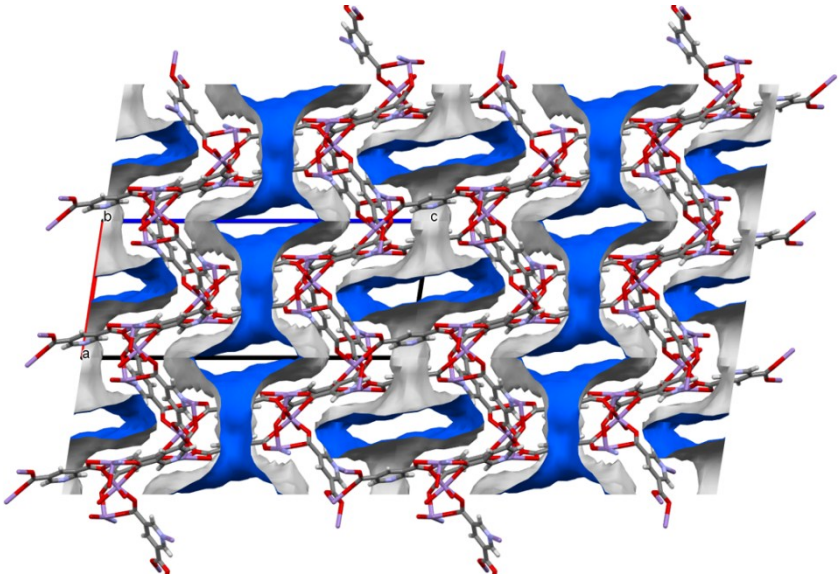


(b)

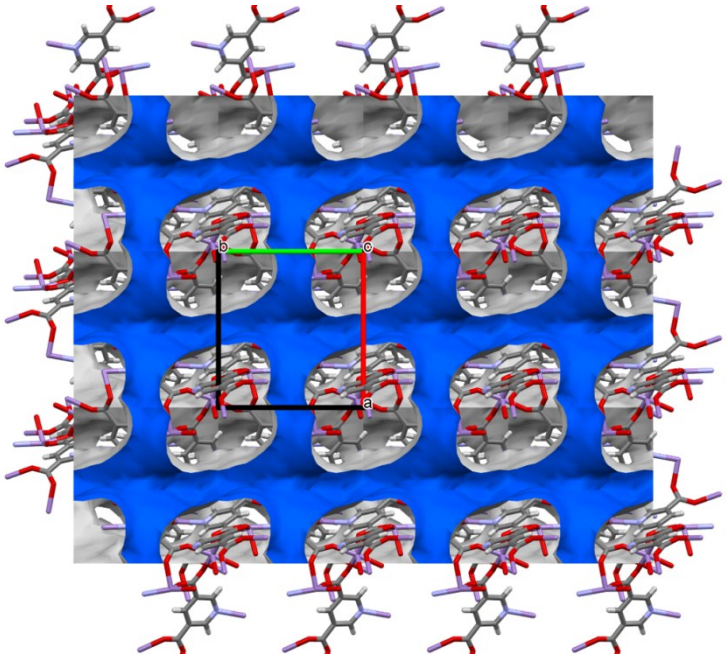
Fig. S10 Solvent accessible void space (internal wall is blue) in the anionic network in **[1]** down to *a* (a) and to *c* (b). The diameter of the channels is approximately7 – 8 Å. This is where the cations and the solvated molecules are accommodated.



(a)



(b)



(c)

Fig. S11 Solvent accessible void space in the network in **[2]** after the removal of the coordinated DMF molecules down to *a* (a), *b* (b), and *c* (c). (The internal wall is blue). The parallelogram channels formed have approximate dimensions 9 x 4 Å.

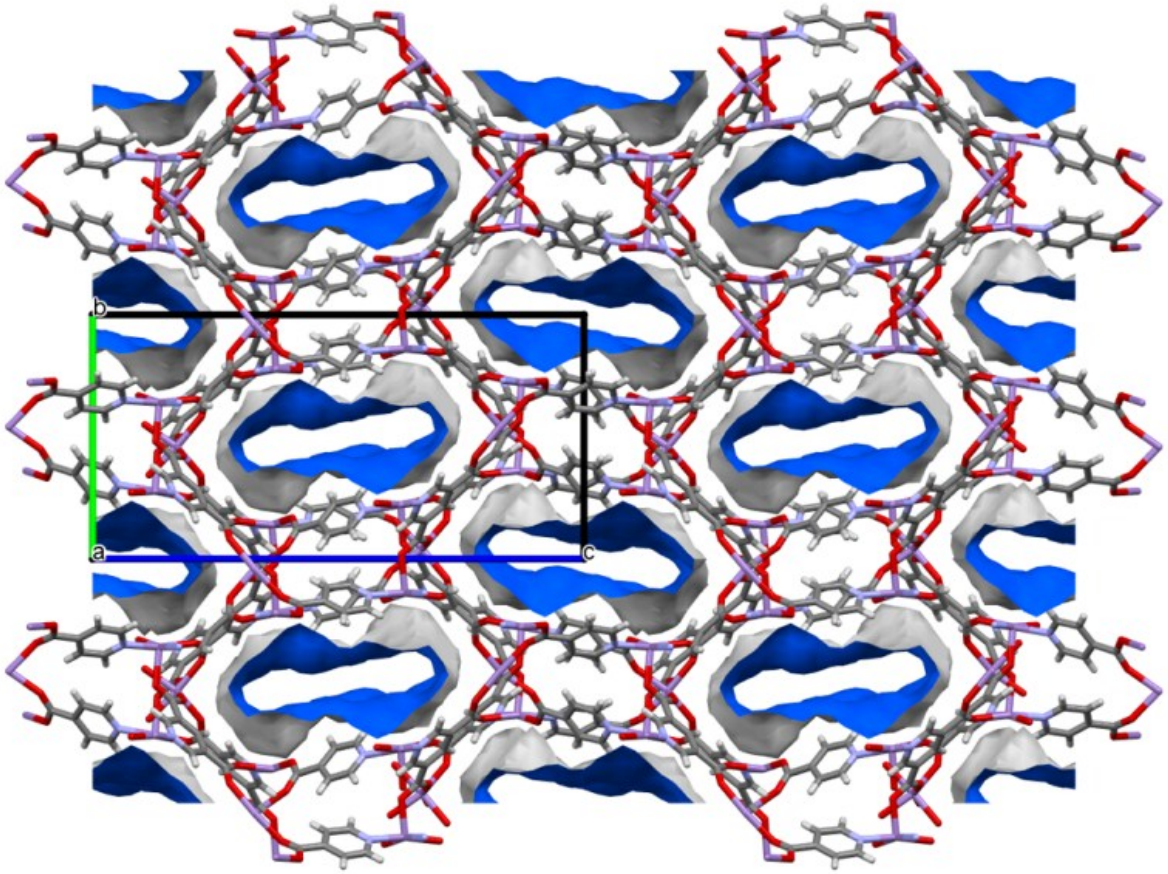


Fig. S12 Solvent accessible void space in the network in **[3]** after the removal of the coordinated DMF molecules down to *a* (a). (The internal wall is blue). The approximate dimensions of the channels are 17 x 9 Å.

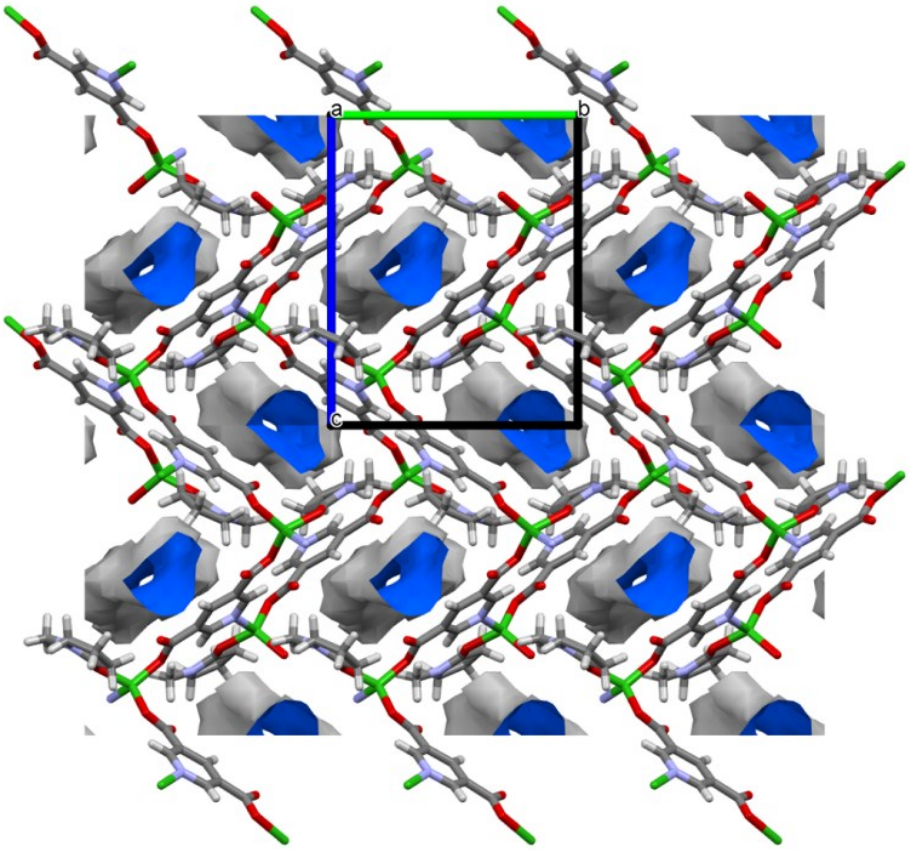


Fig. S13 Solvent accessible void space in the network in **[4]** down to *a* (a). (The internal wall is blue). The diameter of the channels is approximately 4 – 5 Å.

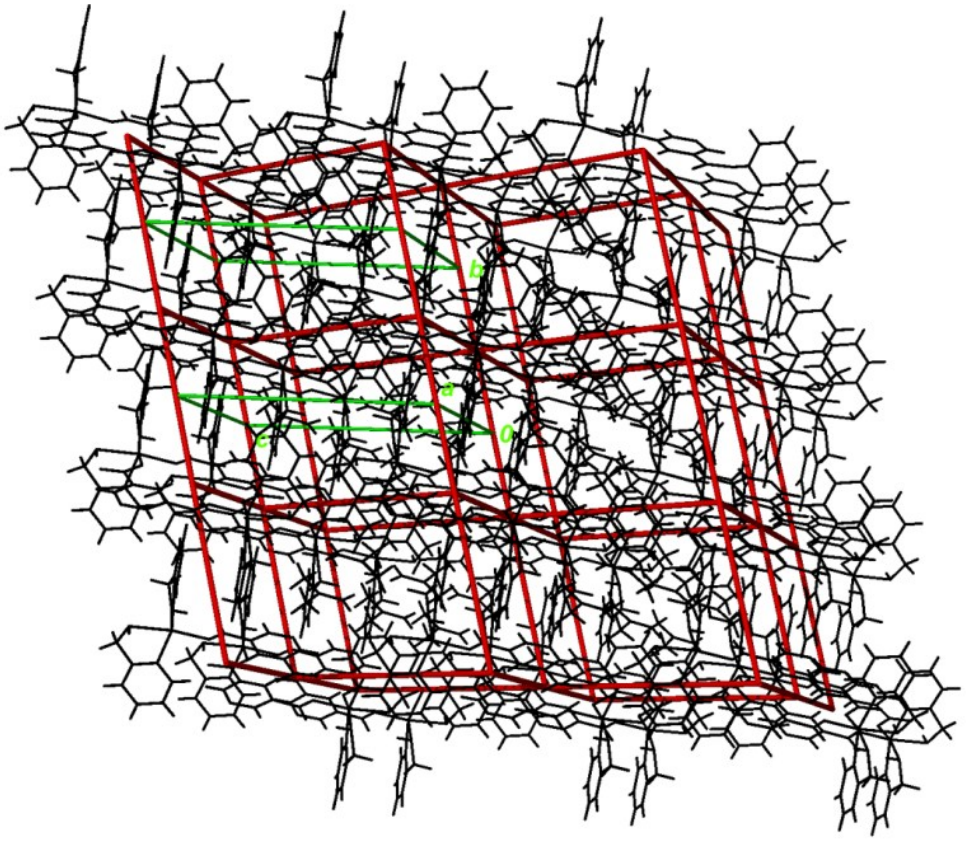


Fig. S14 A perspective view of the **pcu** framework formed in **[7]** via $\pi - \pi$ stacking interactions. The network nodes are located on the centroids of the binuclear complex.

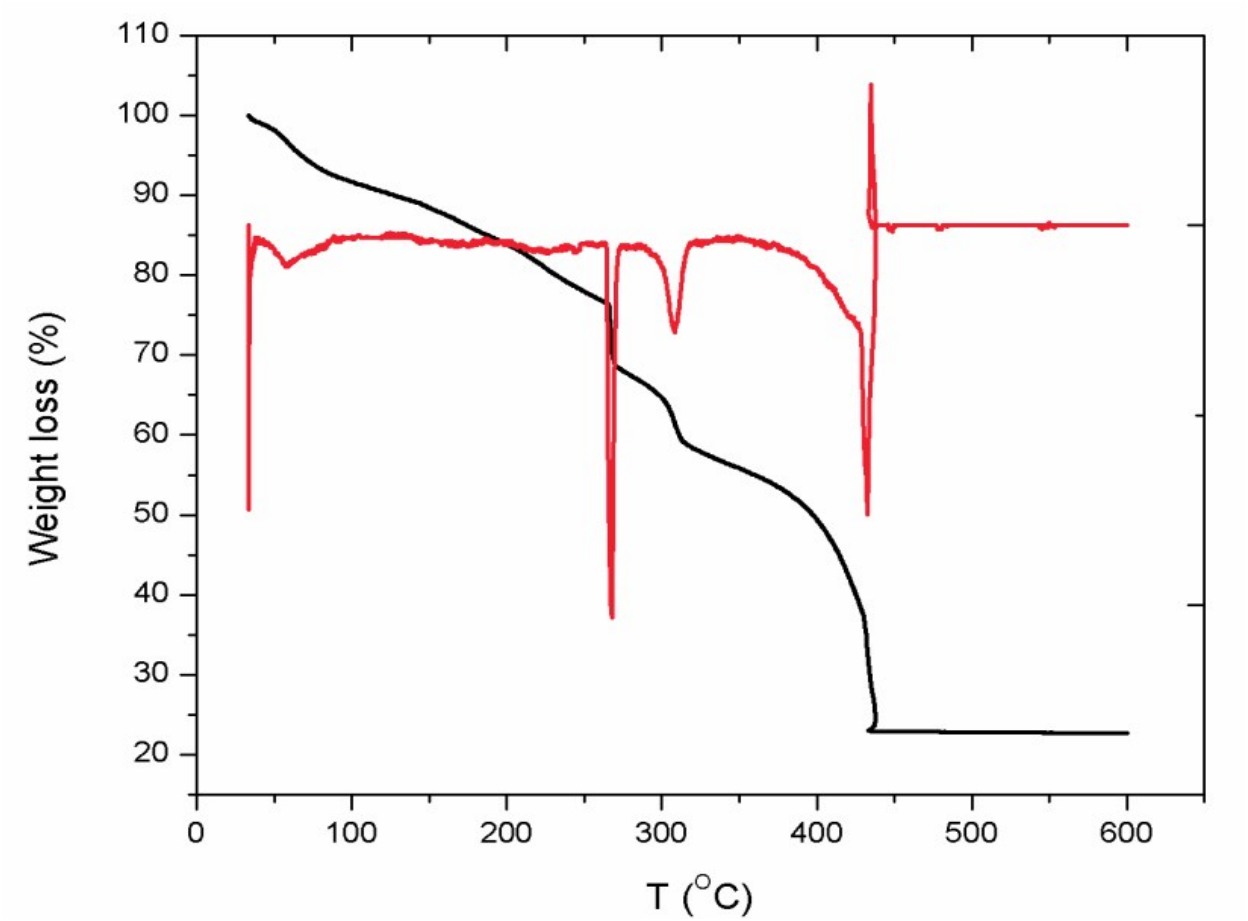


Fig. S15 The TG/DTG curves for $[[(CH_3)_2NH_2]_2[Cd_2(PDC)_3]]_n \cdot 4nDMF \cdot 6nH_2O$, **[1].**

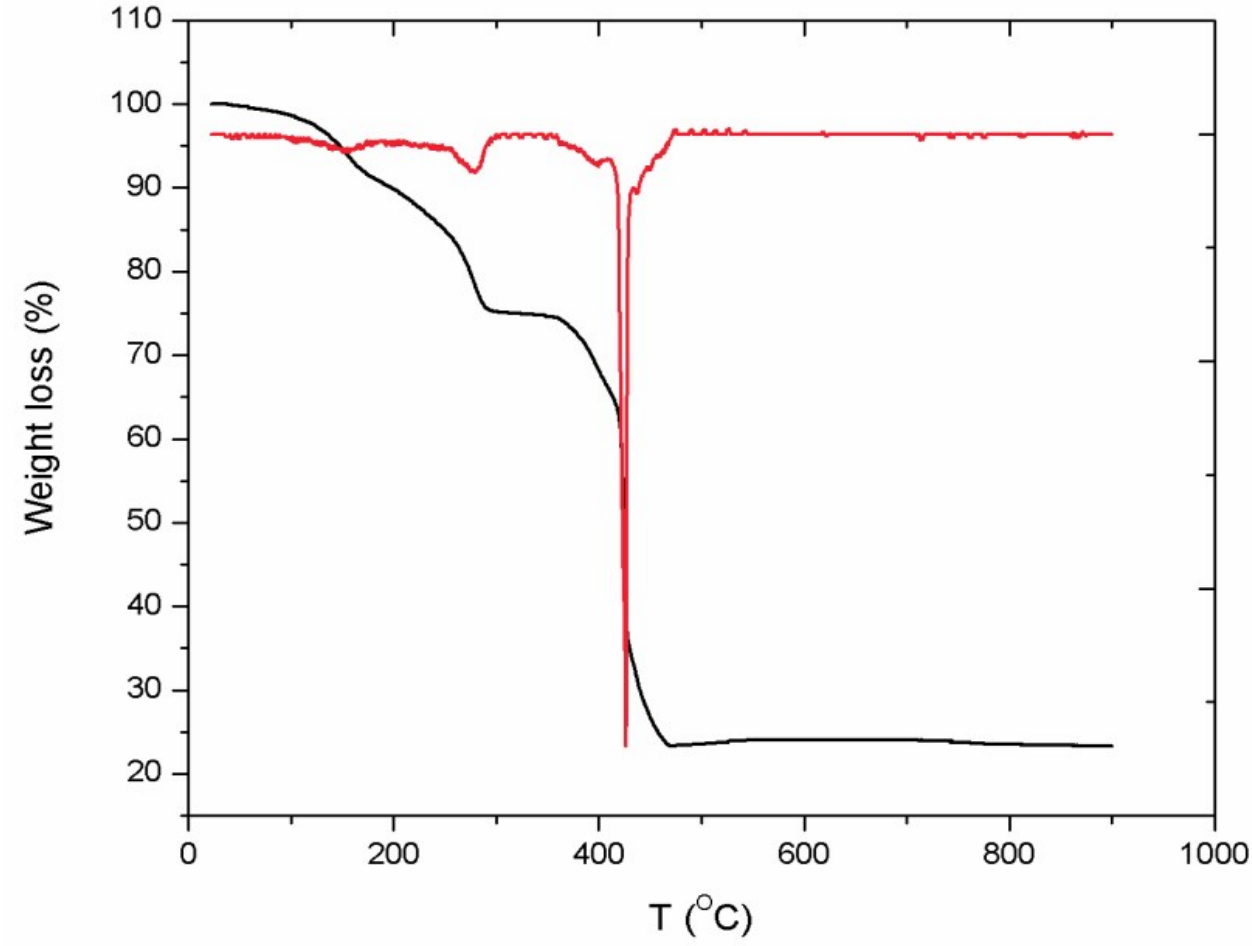


Fig. S16 The TG/DTG curves for $[Mn(PDC)(DMF)]_n$, **[2]**

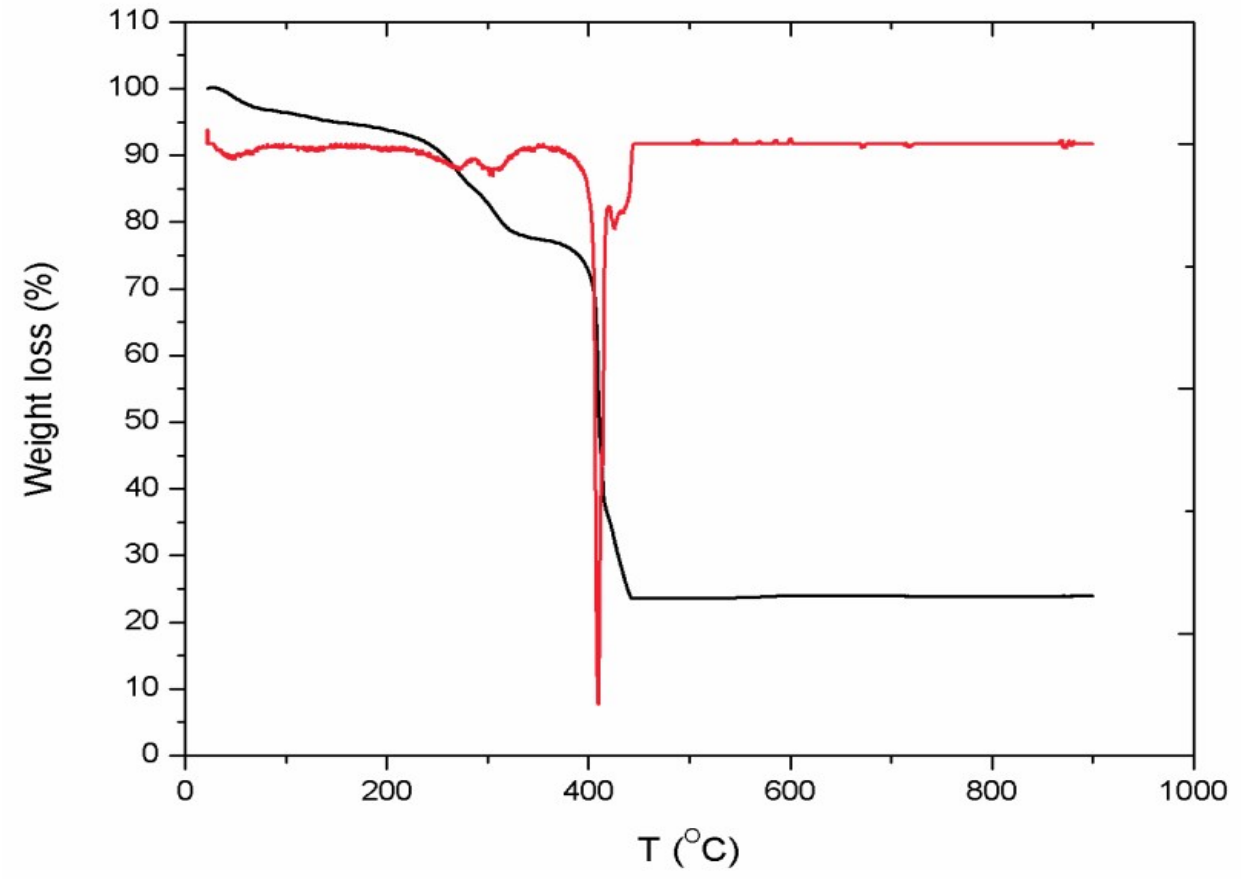


Fig. S17 The TG/DTG curves for $[Mn_3(PDC)_2(INA)_2(DMF)_{1.5}(H_2O)_{0.5}]_n \cdot nDMF \cdot 2nH_2O$, **[3].**

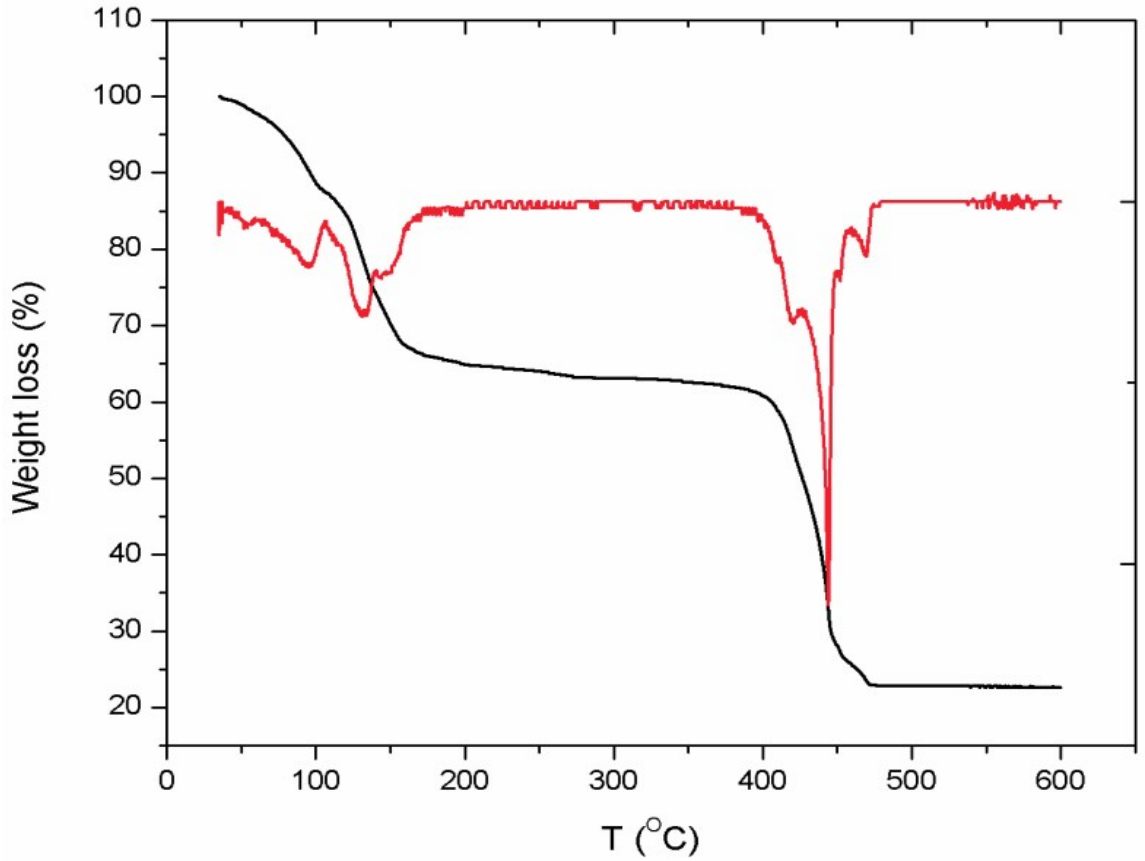


Fig. S18 The TG/DTG curves for $[Zn(PDC)(NMP)]_n \cdot nH_2O$, **[4]**.

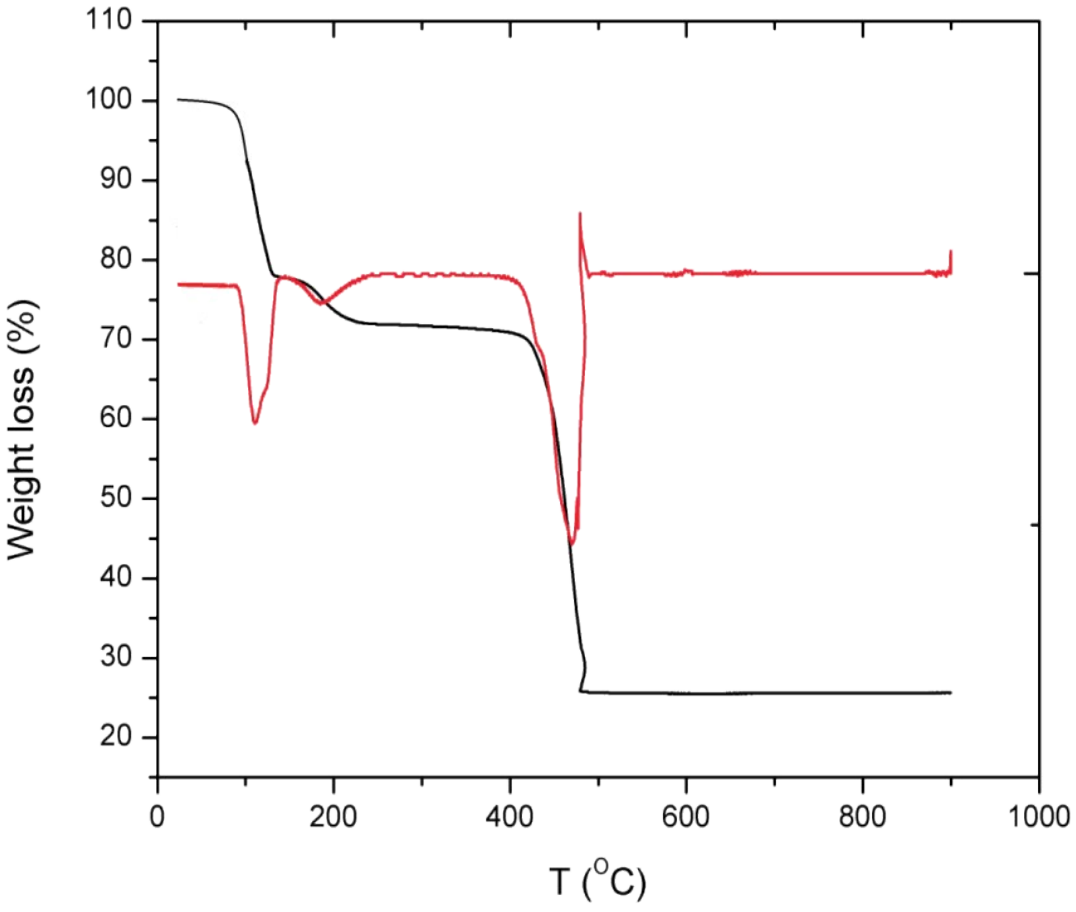


Fig. S19 The TG/DTG curves for $[Zn(PDC)(H_2O)(DMF)]_n$, **[5]**.

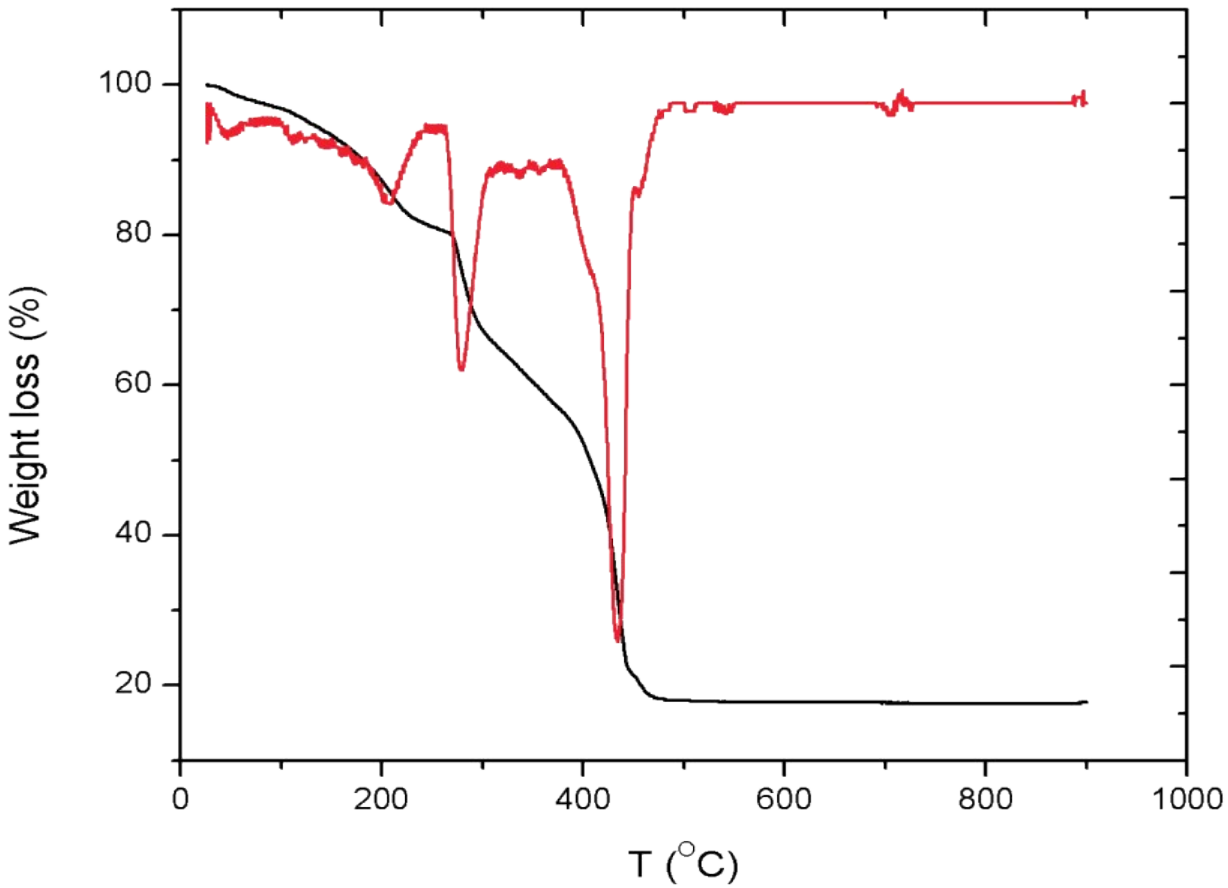


Fig. S20 The TG/DTG curves for $[Zn(PDC)(3hmpH)]_n \cdot nDMF \cdot 0.5nH_2O$, **[6]**.

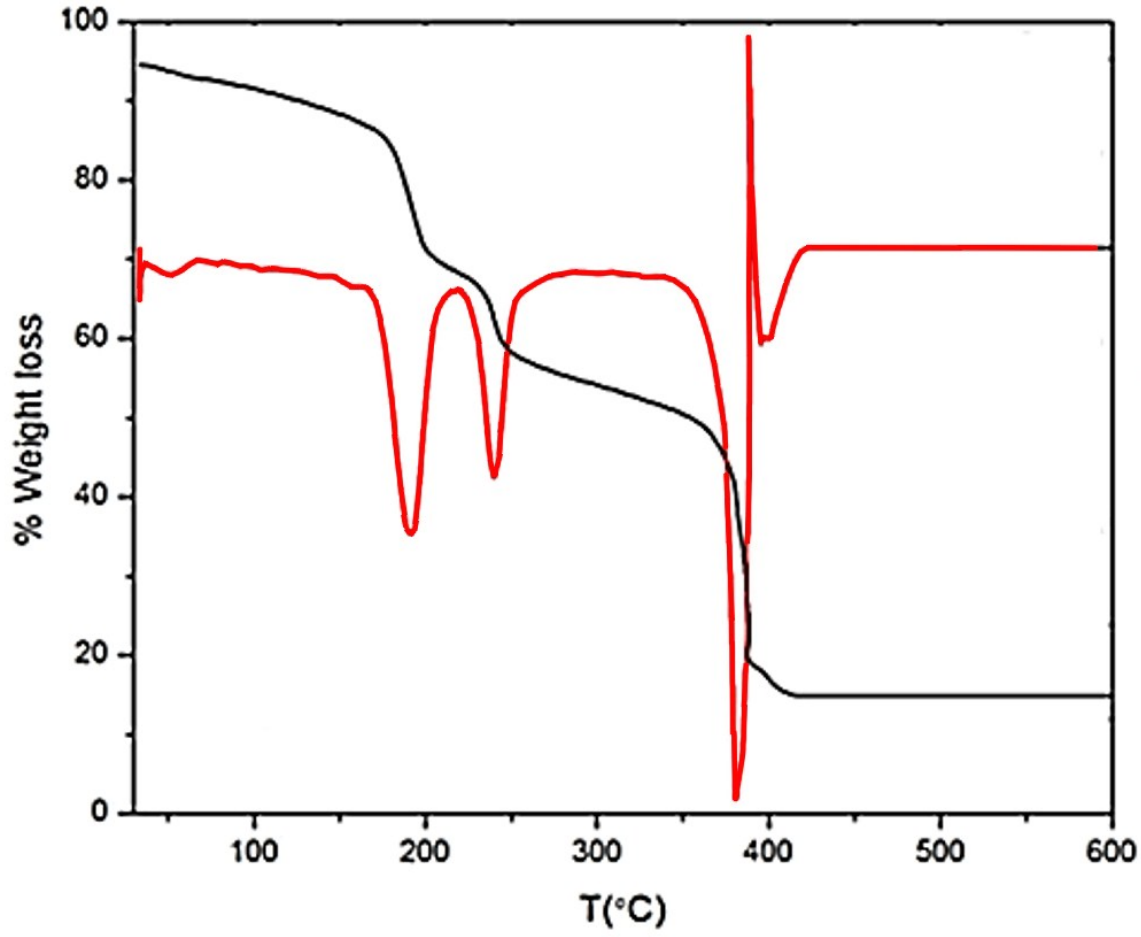


Fig. S21 The TG/DTG curves for $[Zn(PDC)(2hmpH)_2]_2 \cdot 2DMF$, **[7].**

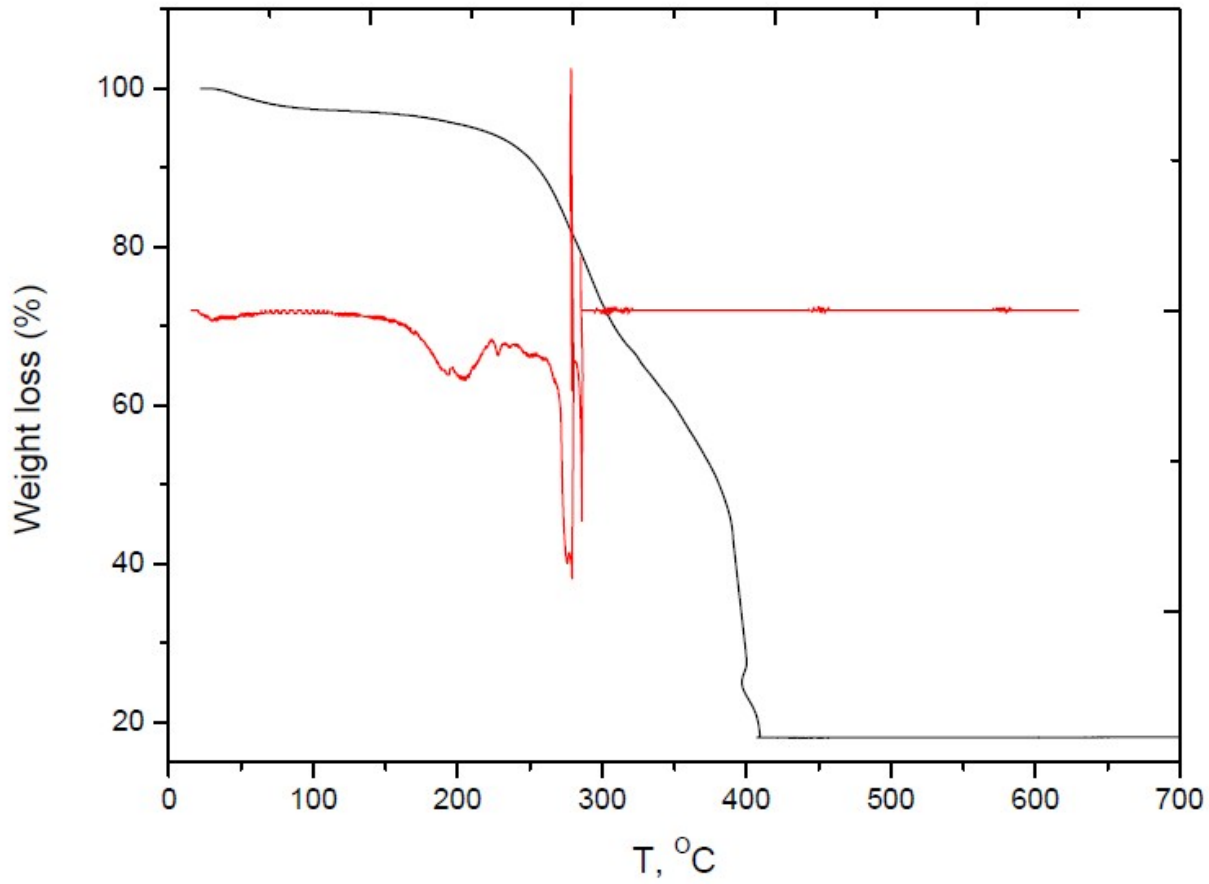


Fig. S22 The TG/DTG curves for $[Co(PDC)(3hmpH)_2]_n \cdot 0.25nDMF$, **[8].**

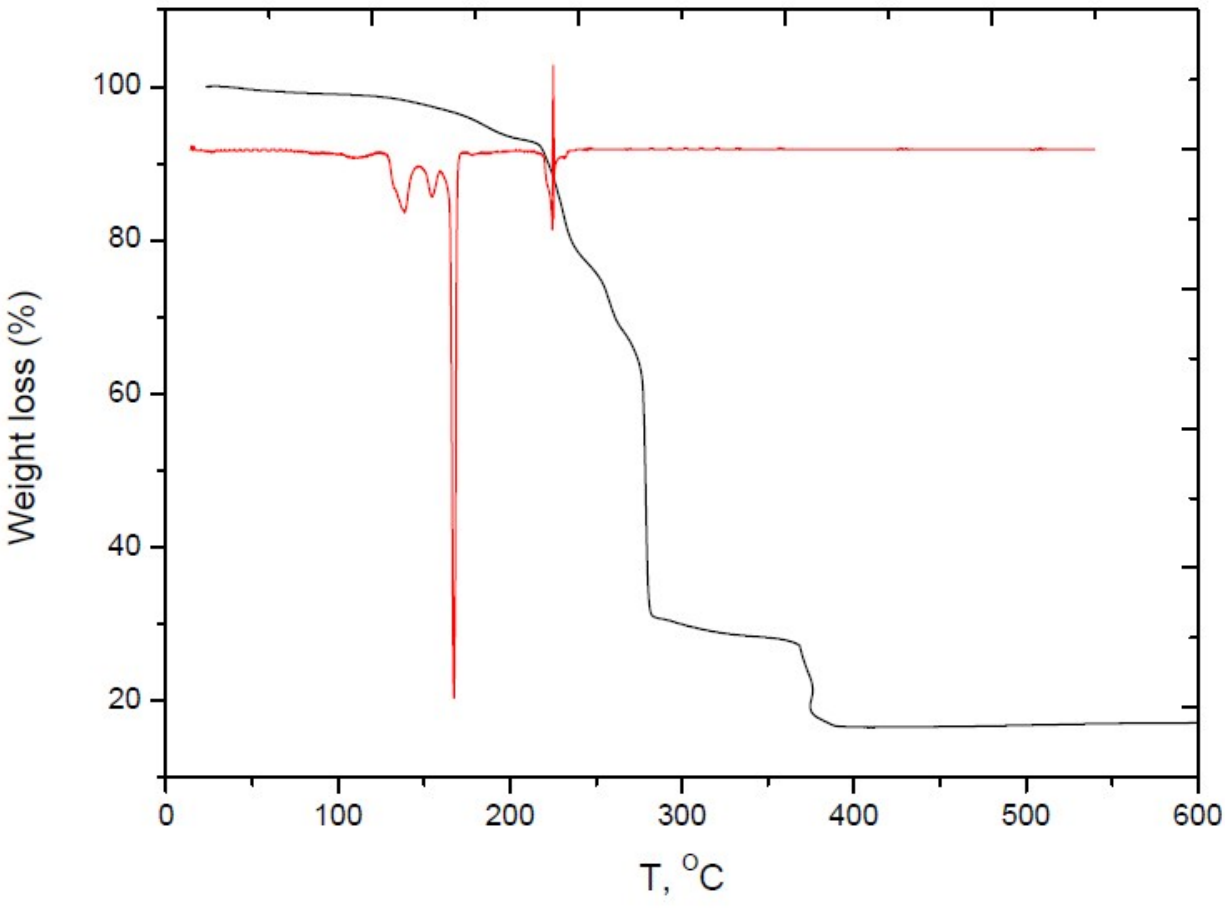


Fig. S23 The TG/DTG curves for $[Cu(PDC)(3hmpH)_2]_n \cdot 0.5nDMF$, **[9].**