

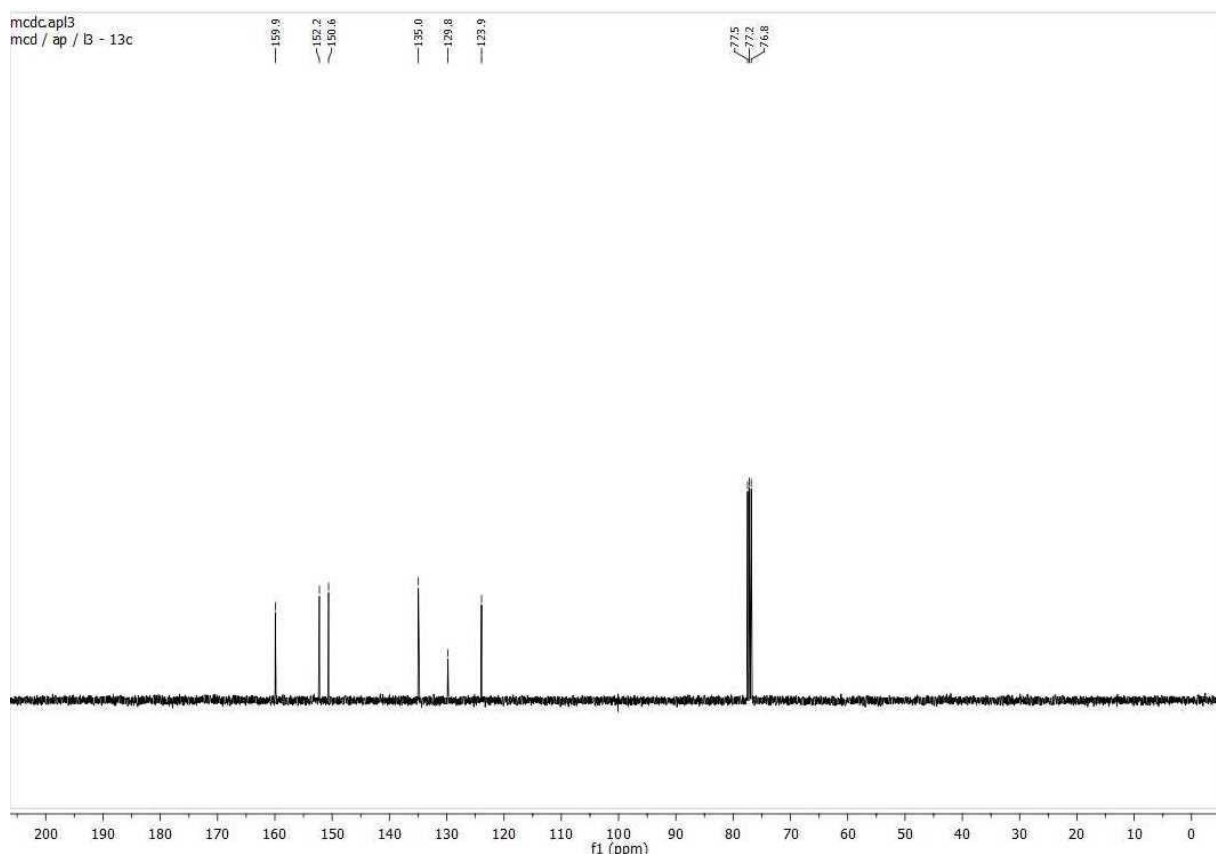
## Electronic Supplementary Information

### **Structural variation of transition metal coordination polymers based on bent carboxylate and flexible spacer ligand: polymorphism, gas adsorption and SC-SC transmetallation†‡**

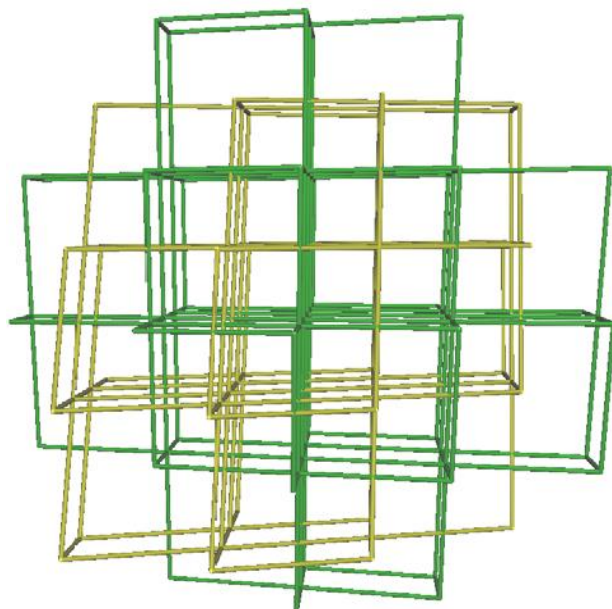
**Arun Pal,<sup>a</sup> Santanu Chand,<sup>a</sup> S. Senthilkumar,<sup>b</sup> Subhadip Neogi\*<sup>b</sup> and Madhab C. Das\*<sup>a</sup>**

<sup>a</sup>*Department of Chemistry, Indian Institute of Technology Kharagpur 721302, India, E-mail: [mcdas@chem.iitkgp.ernet.in](mailto:mcdas@chem.iitkgp.ernet.in)*

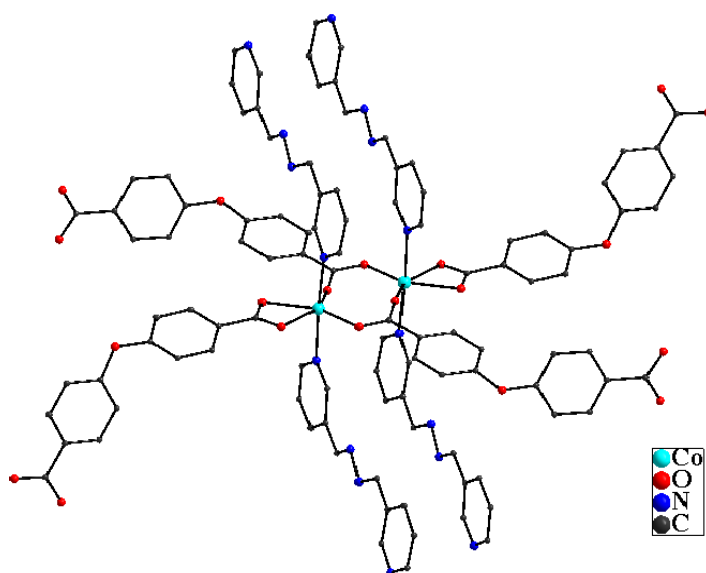
<sup>b</sup>*Inorganic Materials & Catalysis Division, Central Salt & Marine Chemicals Research Institute (CSIR), Bhavnagar-364002, Gujarat, India. E-mail: [sneogi@csmcri.org](mailto:sneogi@csmcri.org)*



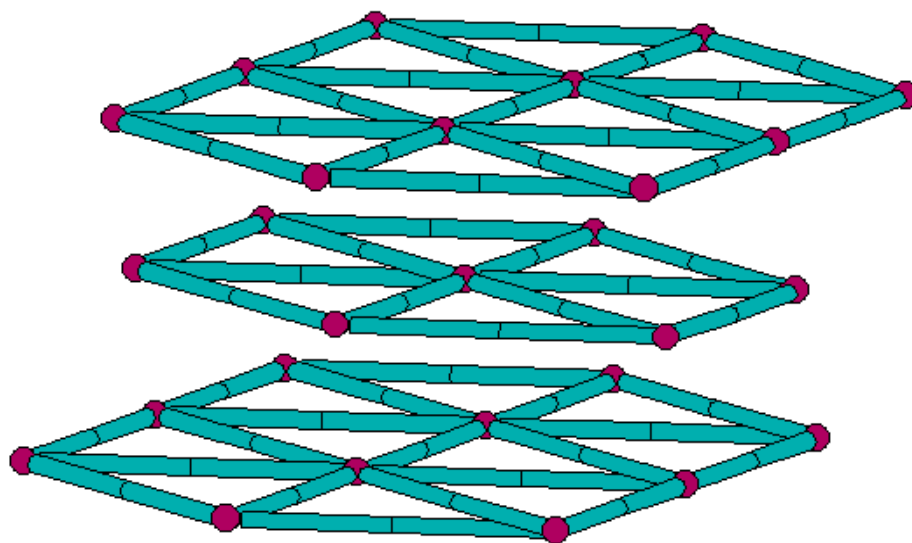
**Figure S1:** <sup>13</sup>C NMR spectra of ligand L<sub>1</sub>.



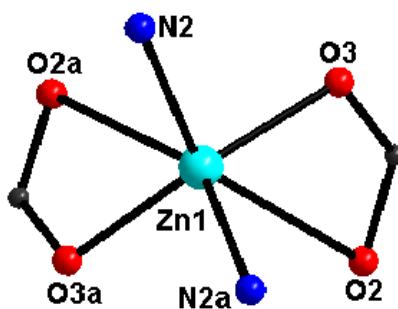
**Figure S2:** Representation of pcu alpha-Po primitive cubic topology of coordination polymer (CP) **1** {point symbol:  $4^{12}.6^3$ }.



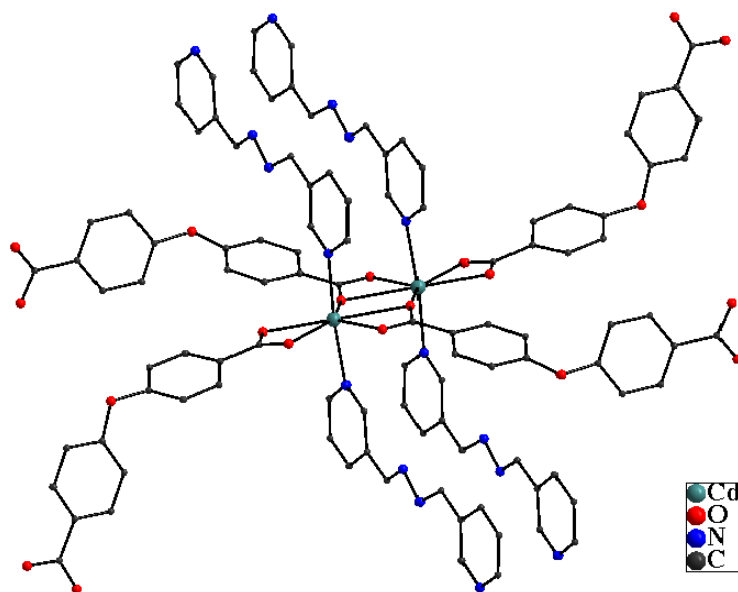
**Figure S3:** Coordination environment around Co metal of CP2. H atoms are omitted for clarity.



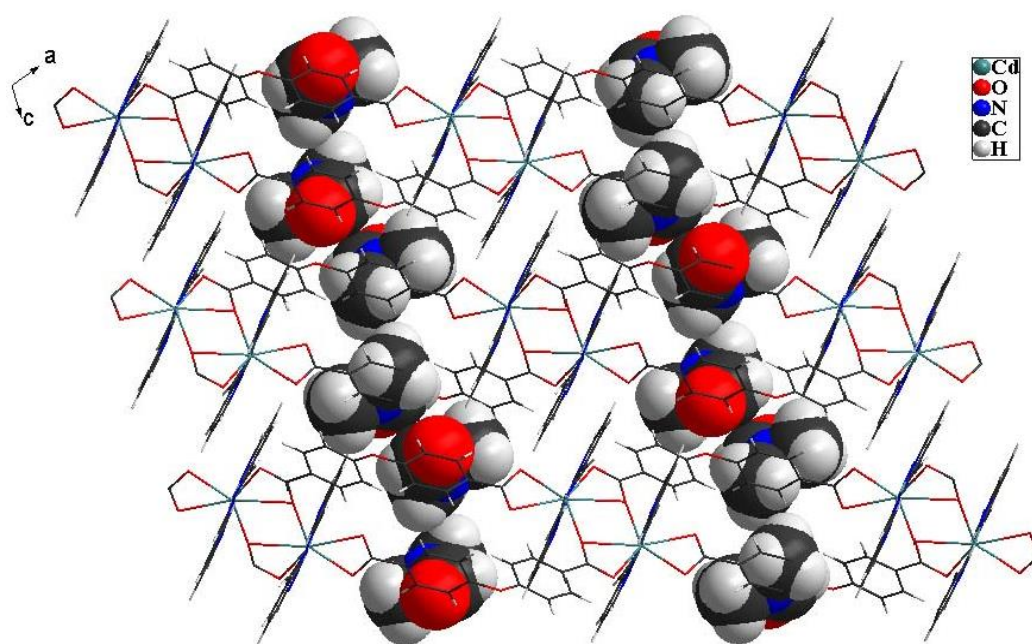
**Figure S4:** Representation of 6-c uninodal net topology having point symbol:  $\{3^6.4^6.5^3\}$  of CP2.



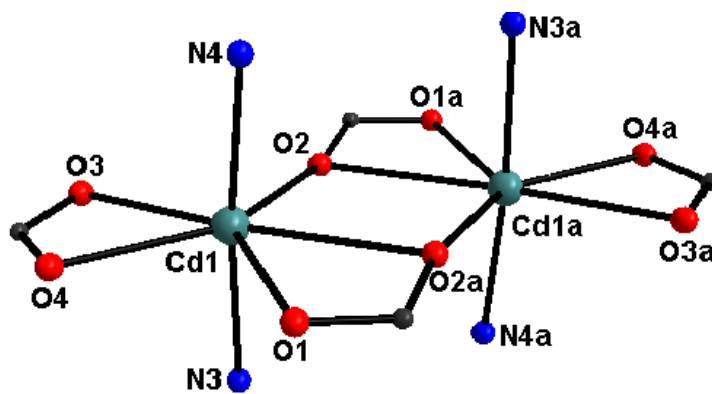
**Figure S5:** Core view of CP3 (symmetry operation (a):  $-x, y, 0.5-z$ ).



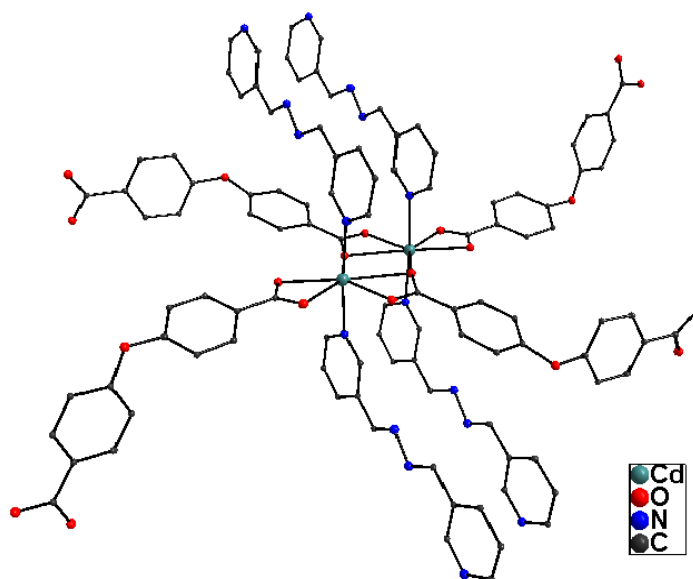
**Figure S6:** Coordination environment around Cd metal of CP4. H atoms are omitted for clarity.



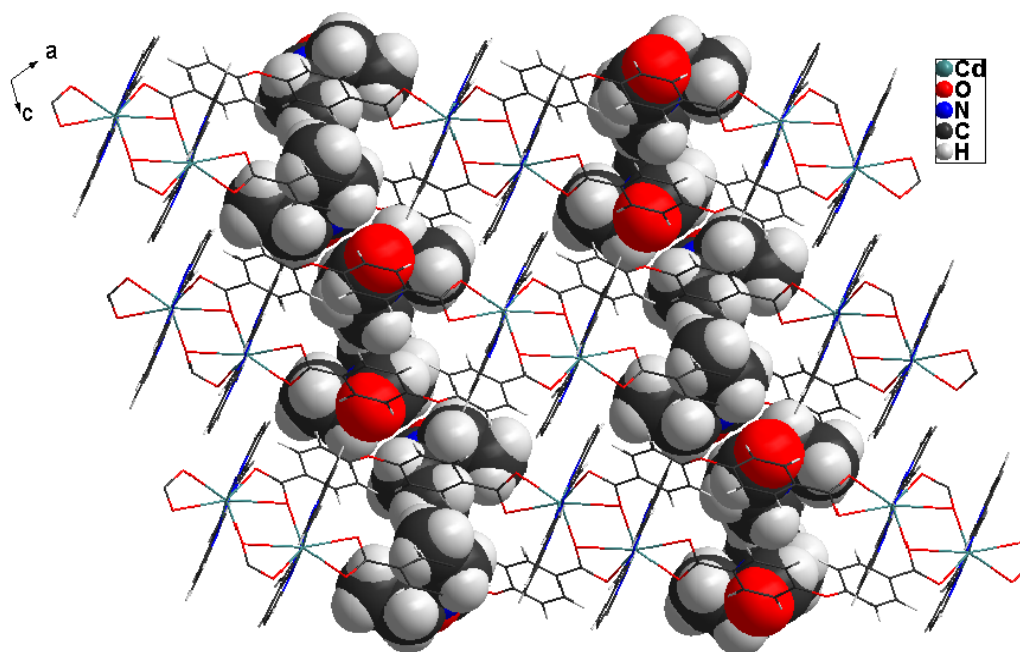
**Figure S7:** Representation of 2-D packing diagram of CP4 (lattice DMF molecules are shown in spacefilling model).



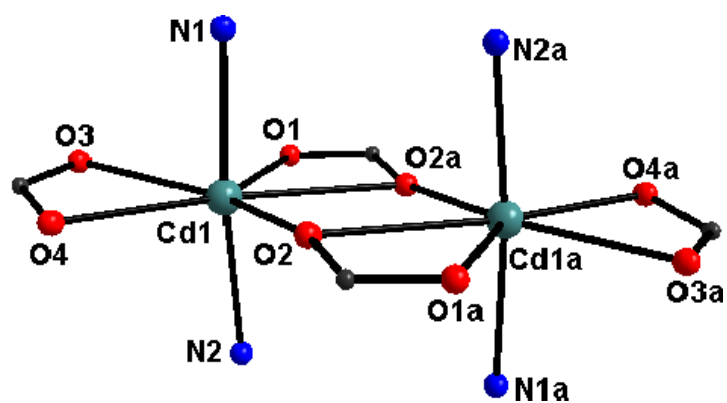
**Figure S8:** Core view of CP5 (symmetry operation (a):  $2-x, -y, 1-z$ ).



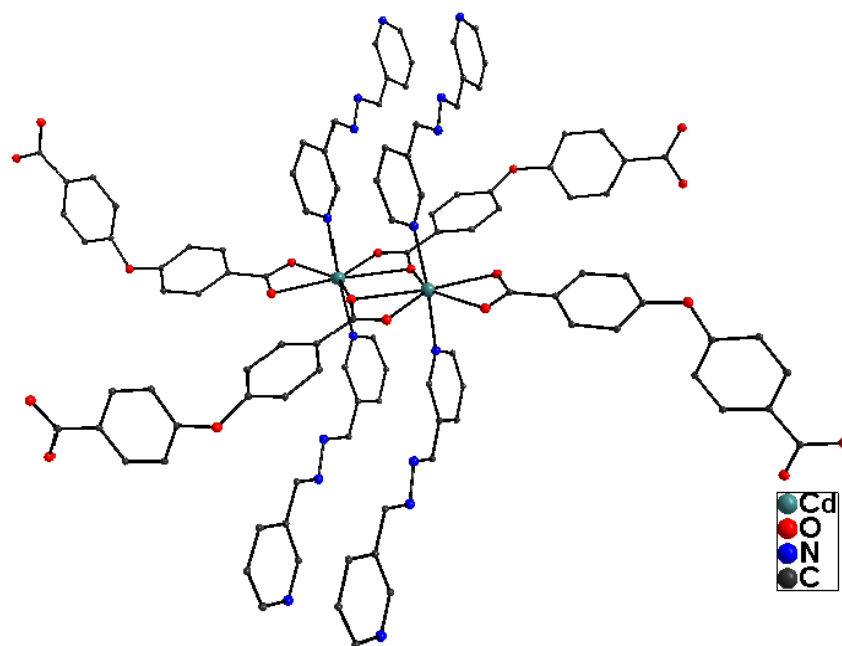
**Figure S9:** Coordination environment around Cd metal of CP5. H atoms are omitted for clarity.



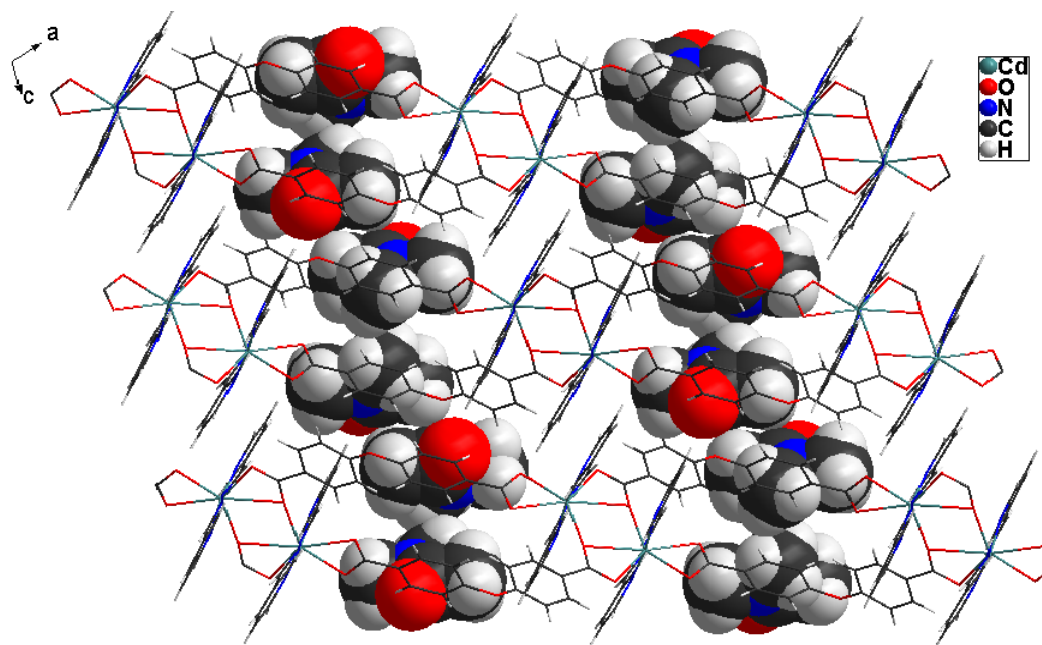
**Figure S10:** Representation of 2-D packing diagram of CP5 (lattice DEF molecules are shown in spacefilling model).



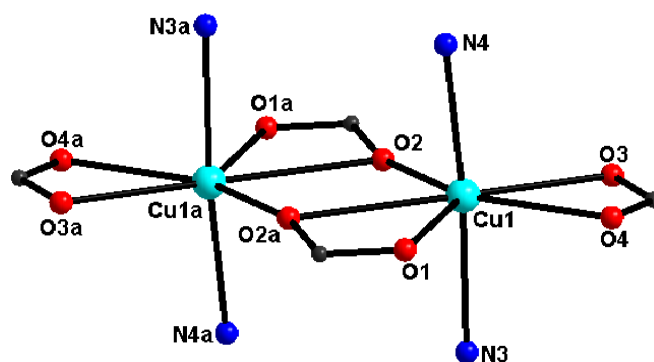
**Figure S11:** Core view of CP6 (symmetry operation (a):  $-x, -y, 1-z$ ).



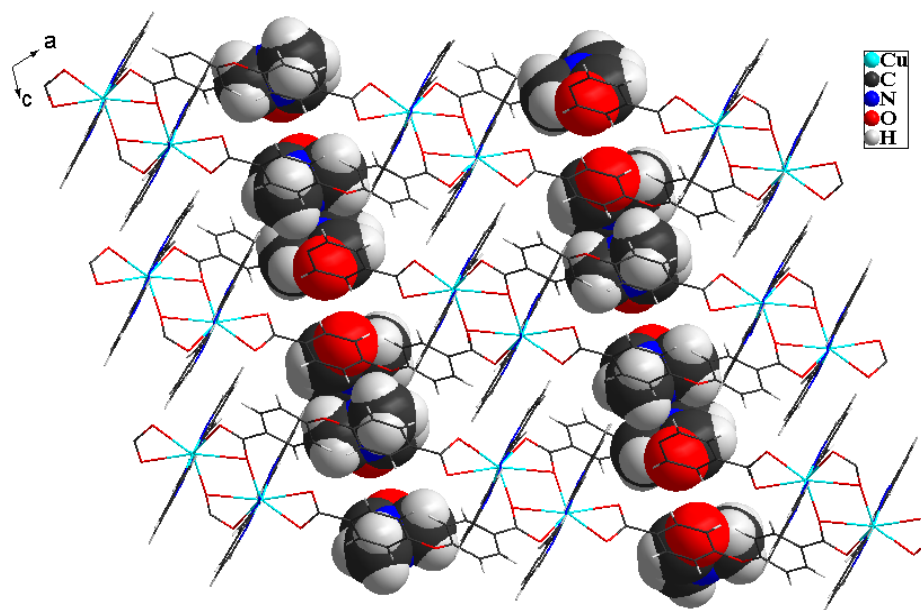
**Figure S12:** Coordination environment around Cd metal of CP6. H atoms are omitted for clarity.



**Figure S13:** Representation of 2-D packing diagram of CP6 (lattice DMA molecules are shown in spacefilling model).

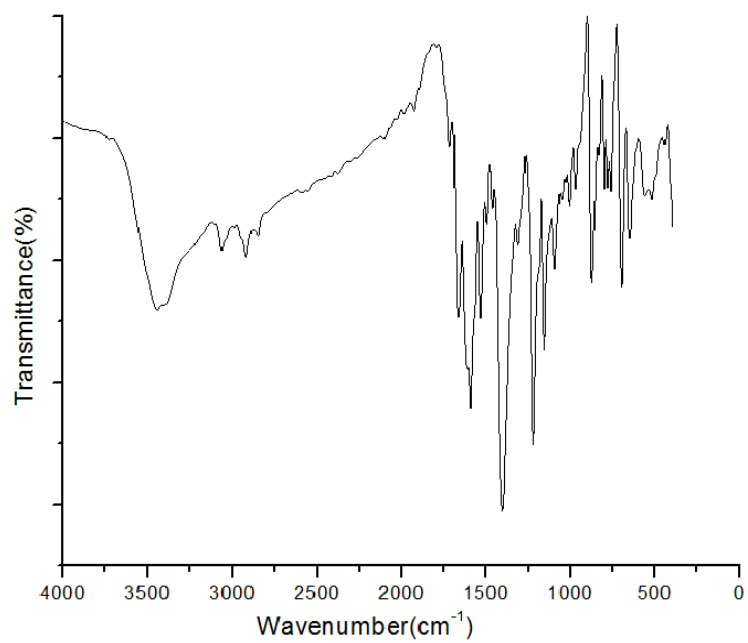


**Figure S14:** Core view of CP7 (symmetry operation (a):  $2-x, 2-y, 1-z$ ).

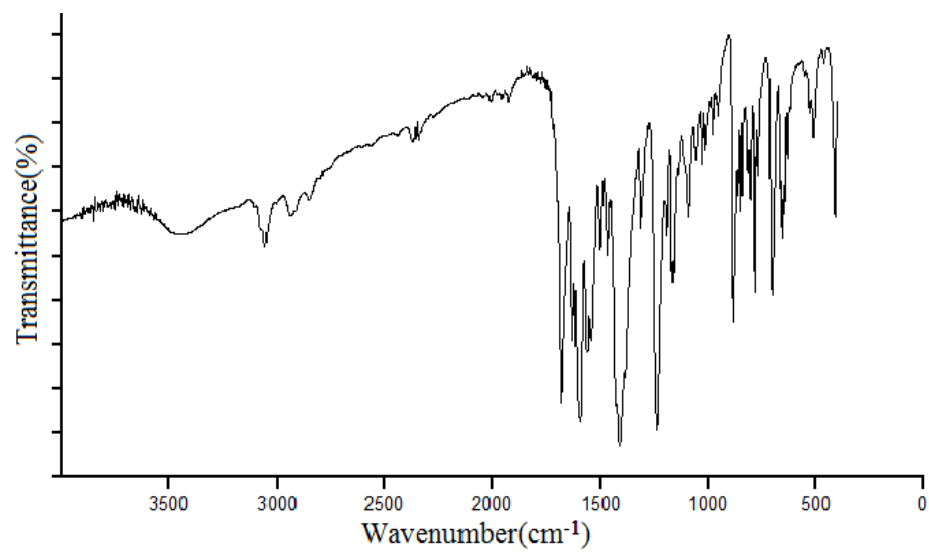


**Figure S15:** Representation of 2-D packing diagram of CP7 (lattice DMF molecules are shown in spacefilling model).

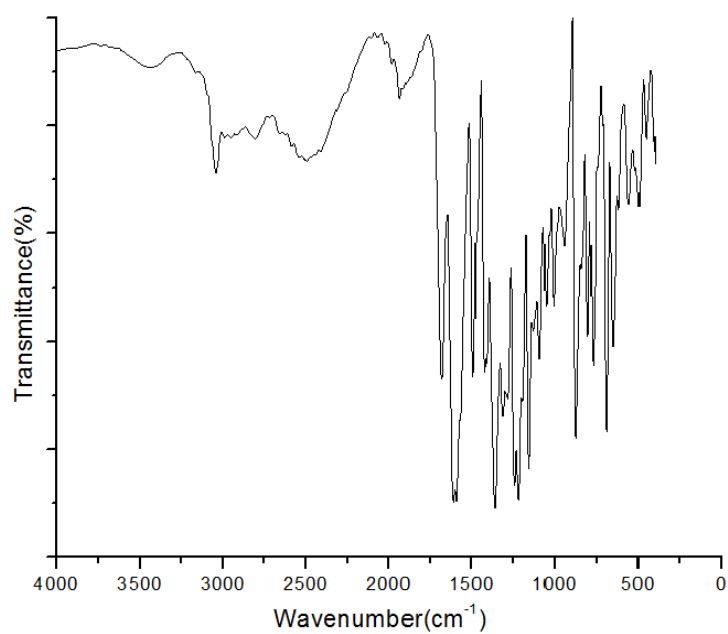




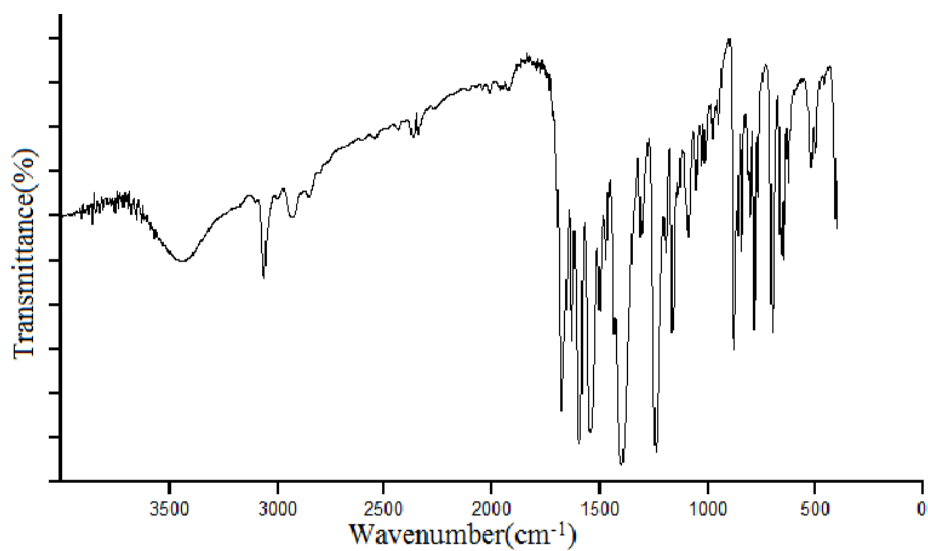
**Figure S16:** IR of CP1.



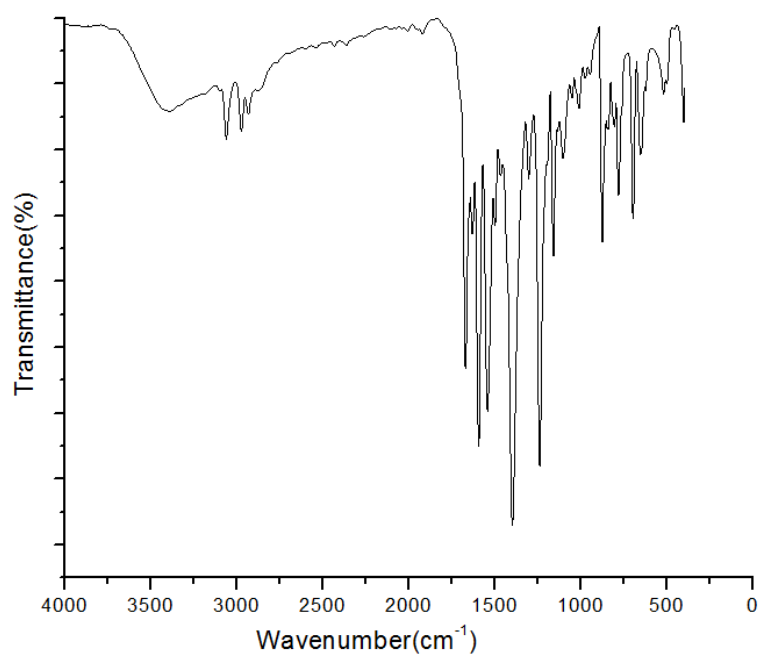
**Figure S17:** IR of CP2.



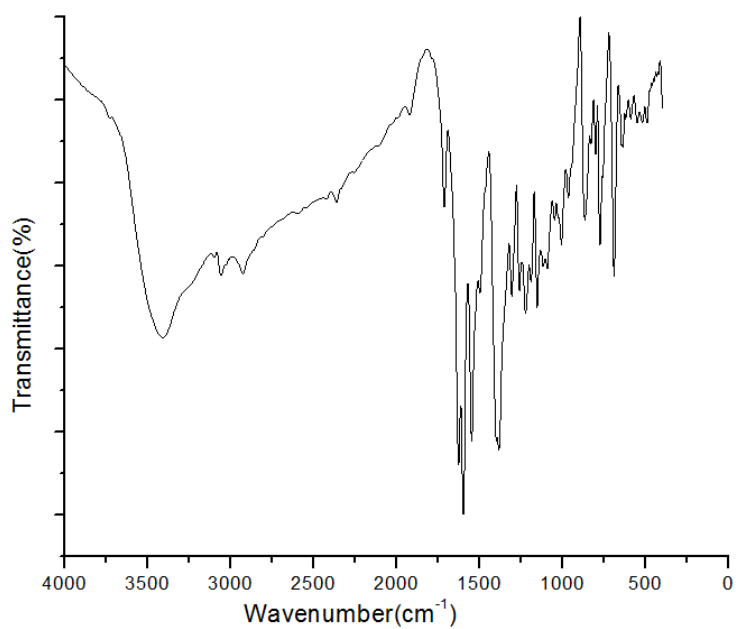
**Figure S18:** IR of CP3.



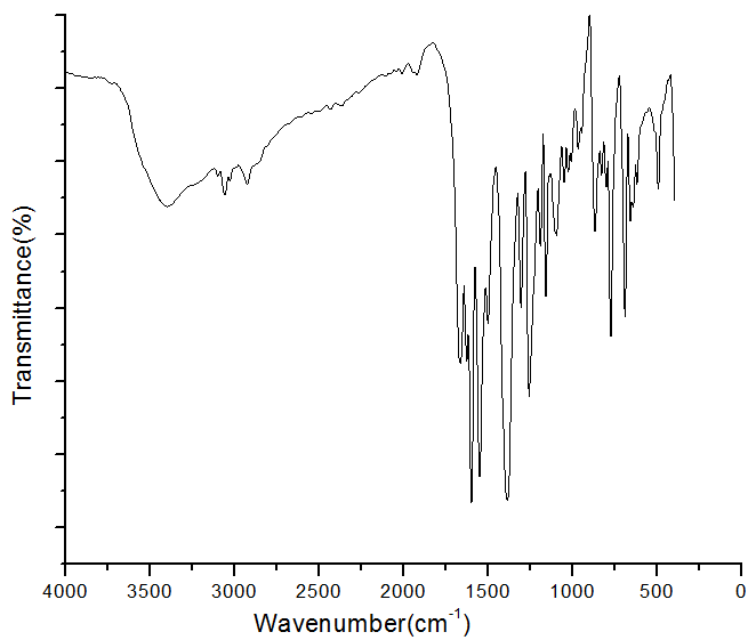
**Figure S19:** IR of CP4.



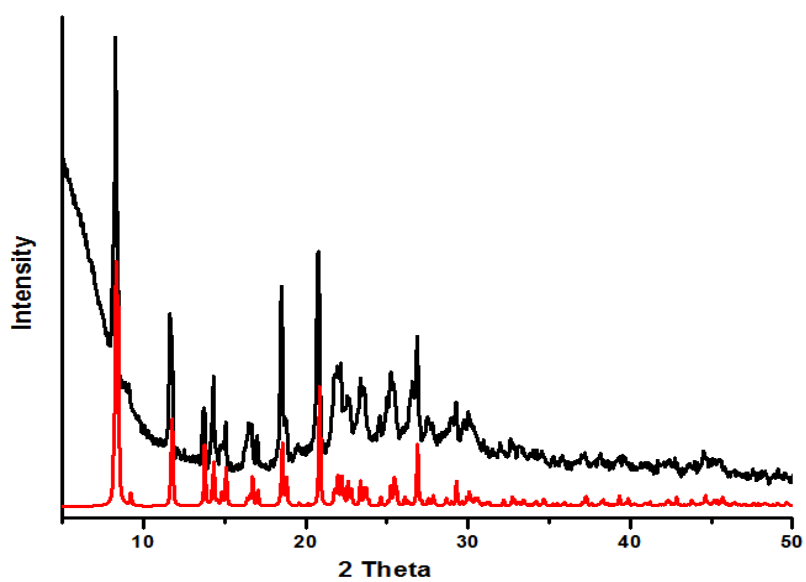
**Figure S20:** IR of CP5.



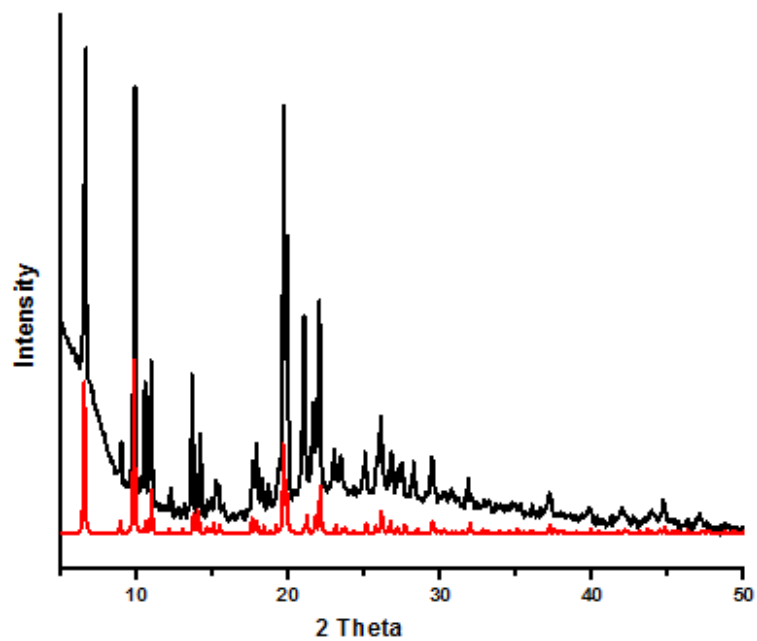
**Figure S21:** IR of CP6.



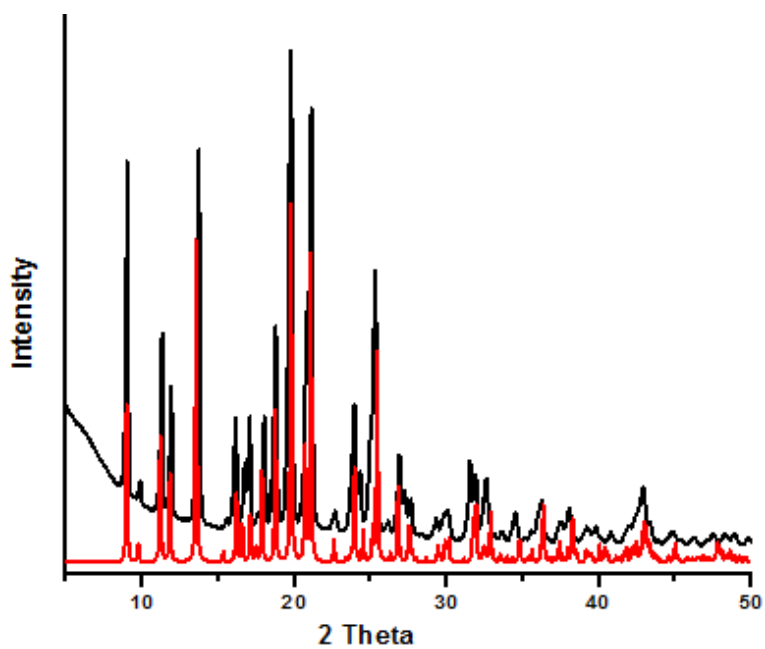
**Figure S22:** IR of CP7.



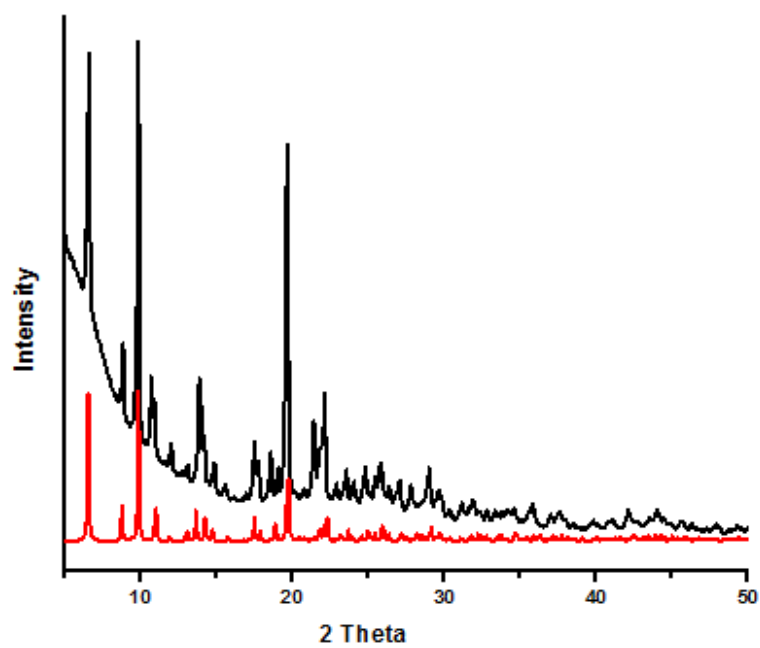
**Figure S23:** Simulated (red) and as synthesized (black) PXRD pattern of CP1.



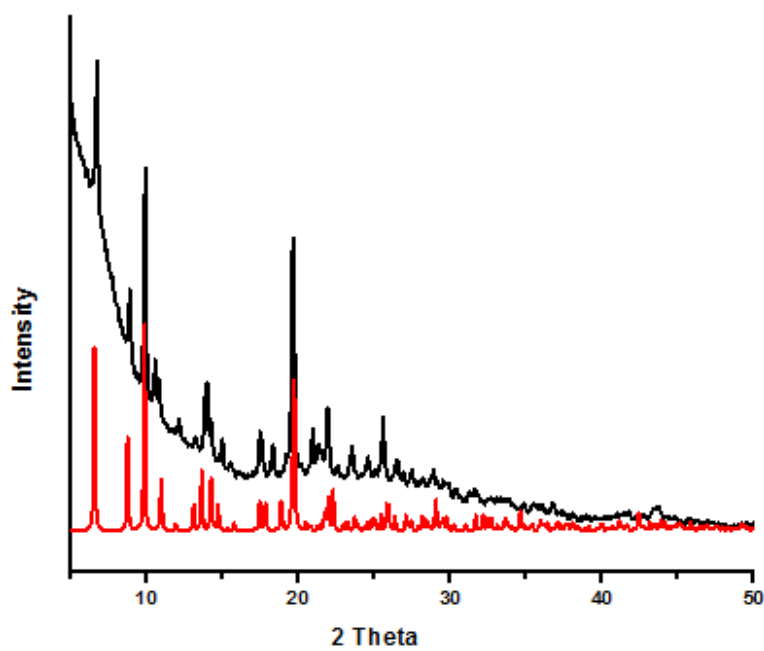
**Figure S24:** Simulated (red) and as synthesized (black) PXR D pattern of CP2.



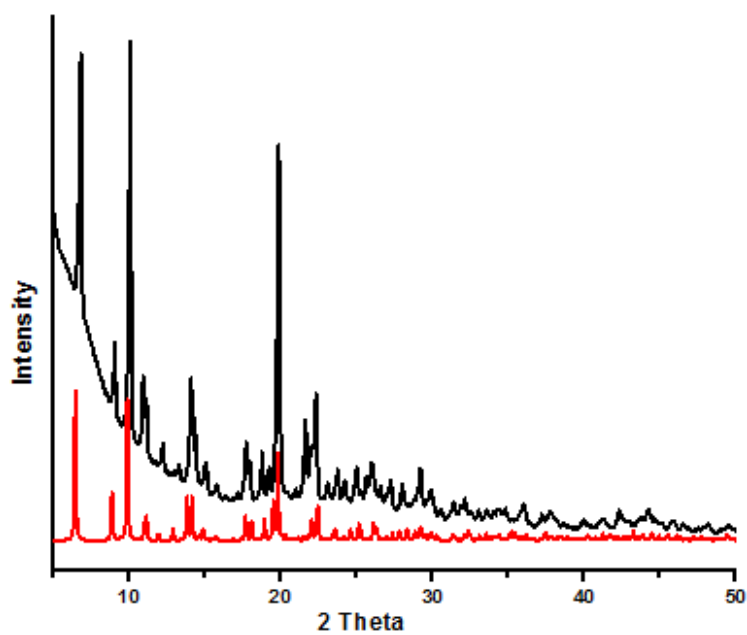
**Figure S25:** Simulated (red) and as synthesized (black) PXR D pattern of CP3.



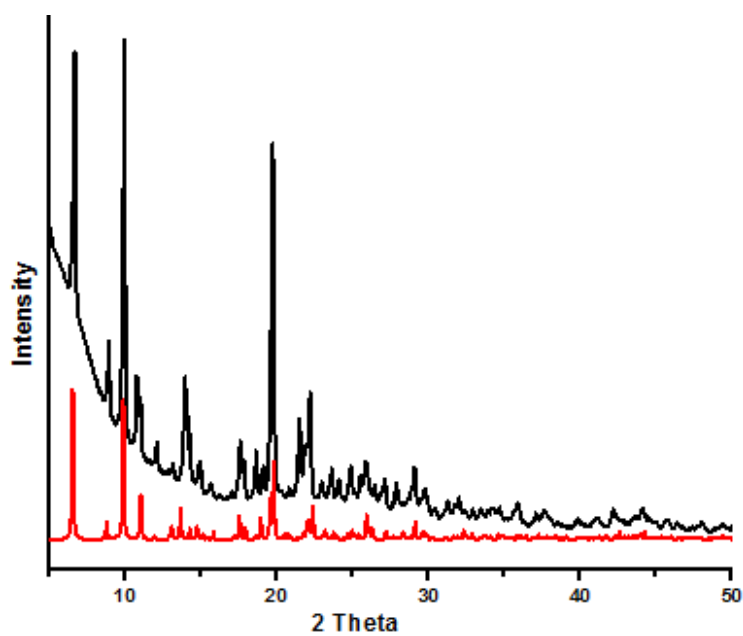
**Figure S26:** Simulated (red) and as synthesized (black) PXR D pattern of CP4.



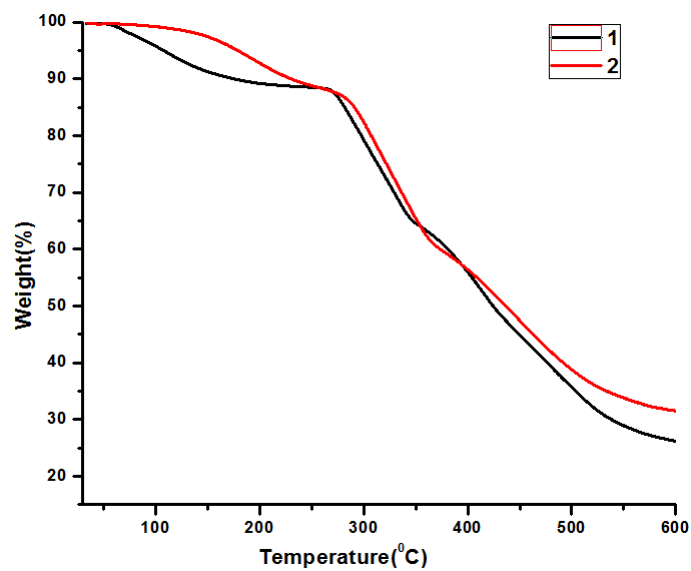
**Figure S27:** Simulated (red) and as synthesized (black) PXR D pattern of CP5.



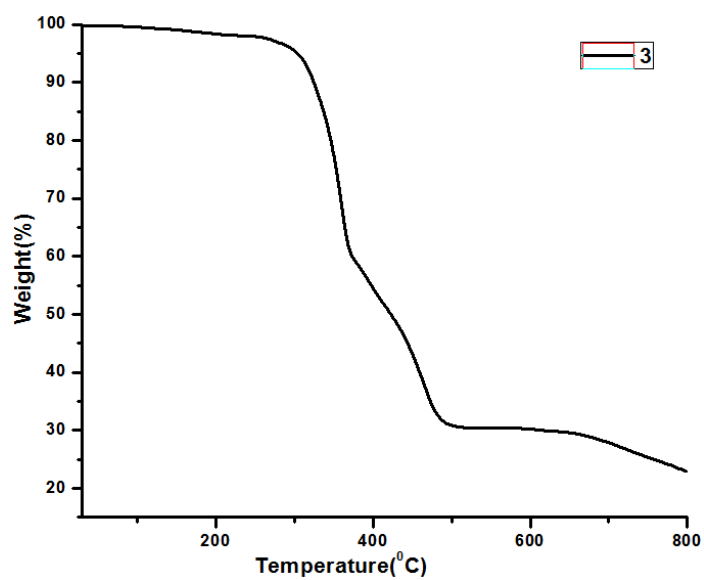
**Figure S28:** Simulated (red) and as synthesized (black) PXR D pattern of CP6.



**Figure S29:** Simulated (red) and as synthesized (black) PXR D pattern of CP7.

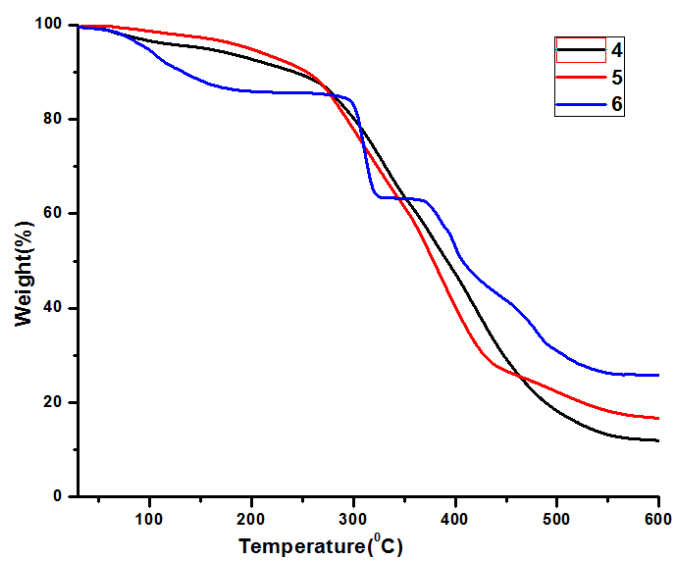


**Figure S30:** TGA of CP1 (black) and 2 (red).

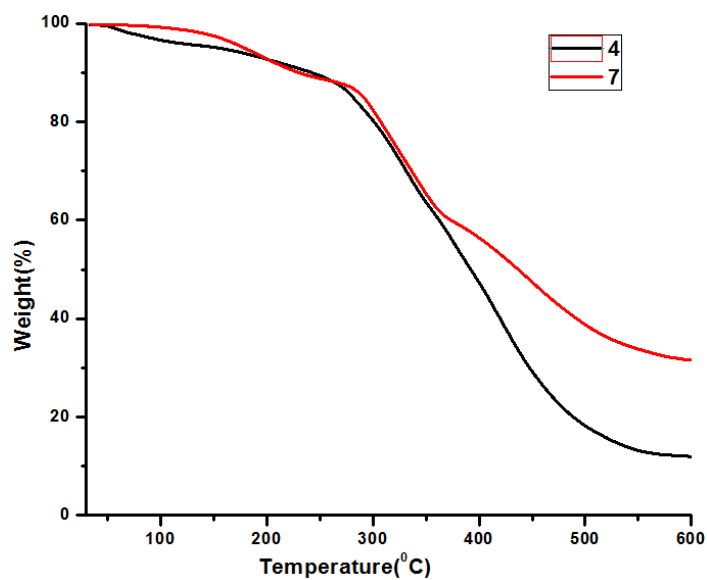


**Figure S31:** TGA of CP3.

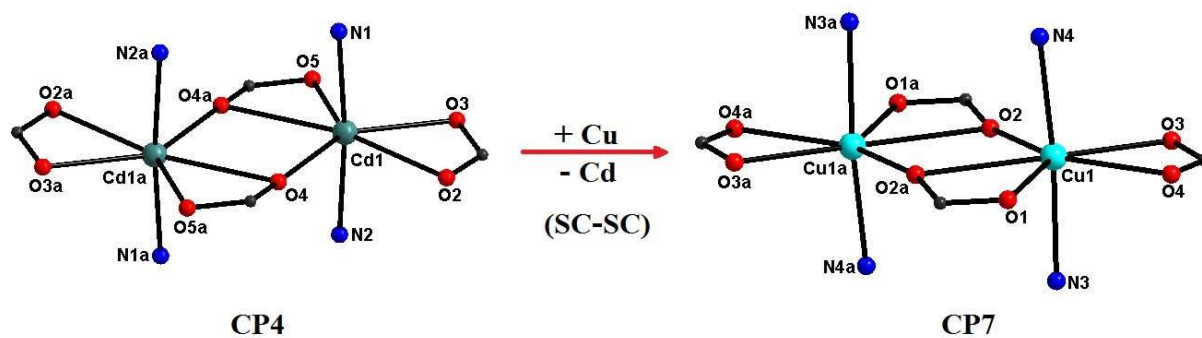




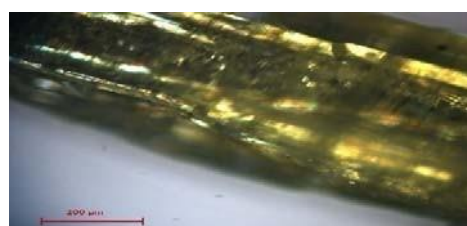
**Figure S32:** TGA of CP4 (black), 5 (red) and 6 (blue).



**Figure S33:** TGA of CP4 (black) and 7 (red).



**Figure S34:** Schematic illustration of the conversion of CP4 into CP7.



(a)



(b)

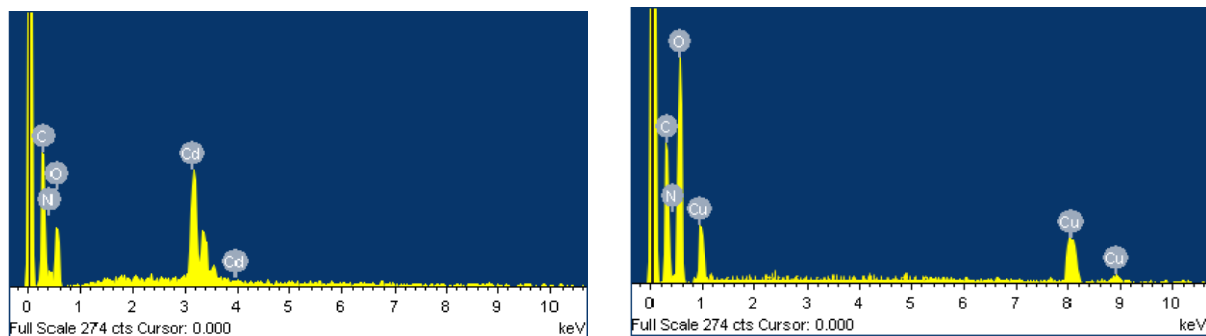


(c)

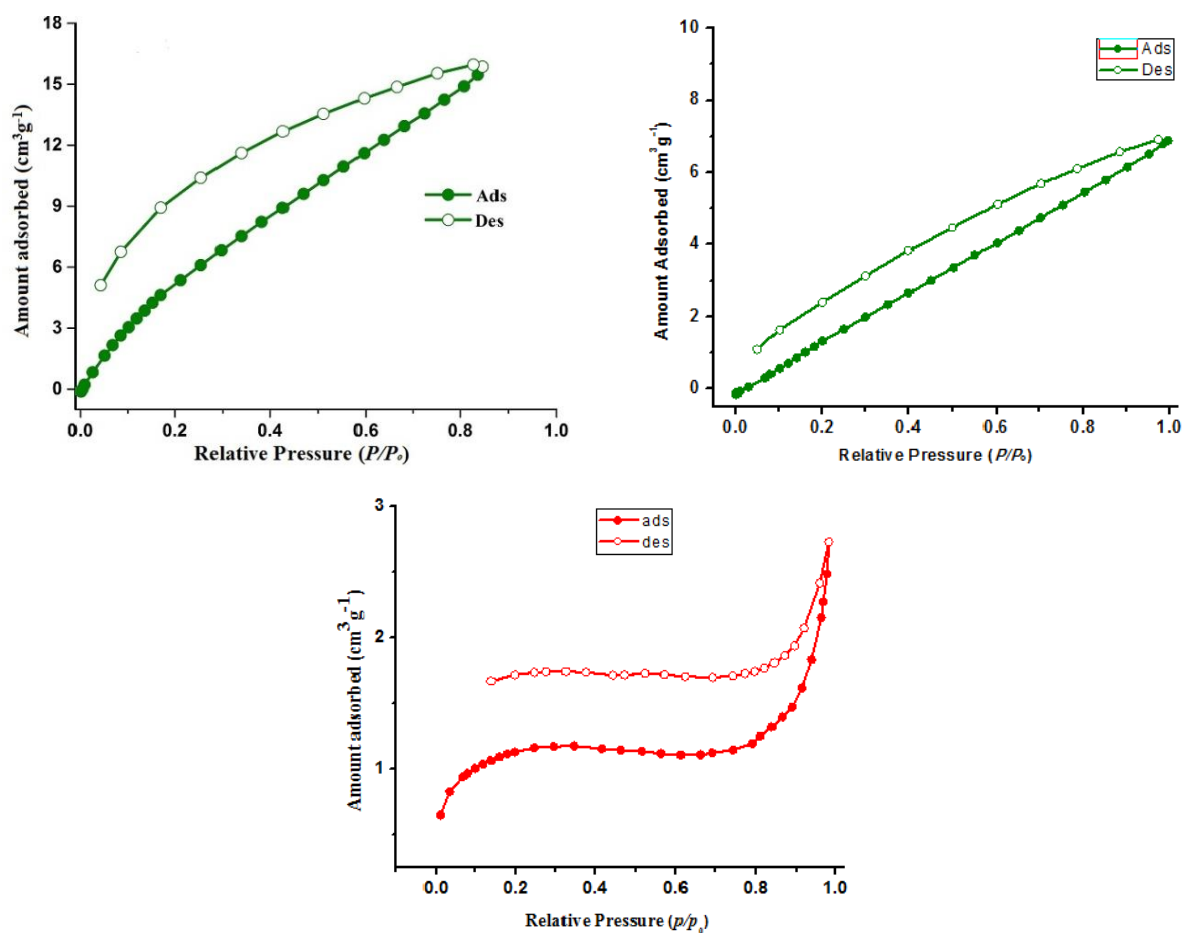


(d)

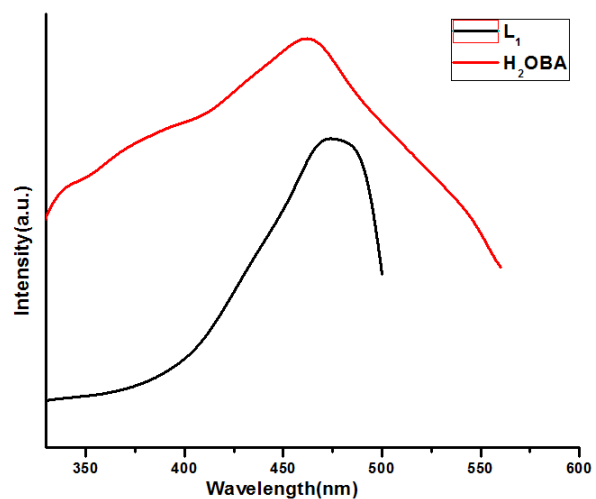
**Figure S35:** Optical microscopic images of a single crystal of CP4 (a) and Cu(II) trans-metallated crystal of 7 (b) after soaking of a crystal of 4 in 0.05 M  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  DMF solution for 5 days, confirming single crystal to single crystal transformation. Photographs of diffractometer-mounted single crystals of 4 (c) and 7 (d).



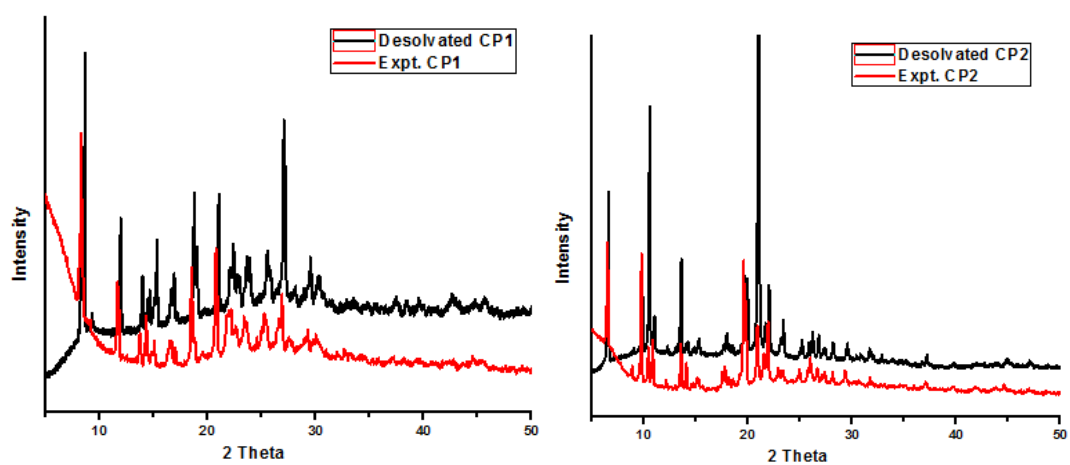
**Figure S36:** EDX spectra of **4** (left side) and trans-metallated Cu crystal of **7** (right side) after soaking of a crystal of **4** in 0.05 M  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  DMF solution for 5 days through single crystal to single crystal transformation process.



**Figure S37:** The  $\text{CO}_2$  (left),  $\text{CH}_4$  (right) and  $\text{N}_2$  (bottom) gas sorption isotherm of **1'** at 273 K, 273 K and 77 K respectively. Filled and open shapes indicate adsorption and desorption data points respectively.



**Figure S38:** Solid-state photoluminescent spectra of free ligands L<sub>1</sub> and H<sub>2</sub>OBA.



**Figure S39:** As-synthesized and desolvated PXRD patterns of CP 1 (left) and CP 2 (right).

**Table S1.** Selected Bond Distances (Å) and Bond Angles (°) in **1 – 7**.

<b>1</b>					
Co1–O4	2.0026(18)	Co1–O5	2.0240(18)	Co1–N3	2.156(2)
Co1–N4	2.157(2)	Co1–O3	2.1947(19)	Co1–O2	2.223(2)

O4–Co1–O5	120.02(8)	O4–Co1–N3	88.35(9)
O5–Co1–N3	89.25(8)	O4–Co1–N4	89.84(9)
O5–Co1–N4	90.21(8)	N3–Co1–N4	177.53(8)
O4–Co1–O3	150.17(8)	O5–Co1–O3	89.81(8)
N3–Co1–O3	92.50(9)	N4–Co1–O3	89.90(8)
O4–Co1–O2	91.31(8)	O5–Co1–O2	148.31(7)
N3–Co1–O2	86.84(9)	N4–Co1–O2	94.88(9)
O3–Co1–O2	59.01(7)		

<b>2</b>					
Co1–O5	2.030(3)	Co1–O4	2.061(3)	Co1–N4	2.135(4)
Co1–N1	2.155(4)	Co1–O3	2.179(3)	Co1–O2	2.191(3)

O5–Co1–O4	120.83(12)	O5–Co1–N4	91.59(14)
O4–Co1–N4	90.07(13)	O5–Co1–N1	87.57(14)
O4–Co1–N1	87.65(13)	N4–Co1–N1	176.72(13)
O5–Co1–O3	89.66(12)	O4–Co1–O3	149.27(12)
N4–Co1–O3	92.98(13)	N1–Co1–O3	90.19(14)
O5–Co1–O2	149.36(12)	O4–Co1–O2	89.26(12)
N4–Co1–O2	94.16(13)	N1–Co1–O2	88.16(13)
O3–Co1–O2	60.02(11)		

<b>3</b>					
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Zn1-O3	1.9505(15)	Zn1-O3a	1.9505(15)	Zn1-N2	2.0764(18)
Zn1-N2a	2.0764(18)	Zn1-O2	2.673(15)	Zn1-O2a	2.673(15)

O3-Zn1-O3a	135.53(9)	O3-Zn1-N2a	111.93(7)
O3-Zn1-N2	96.52(7)	O3a-Zn1-N2a	96.52(7)
O3a-Zn1-N2	111.93(7)	N2-Zn1-N2a	99.86(10)
O2-Zn1-O2a	95.10(5)	O2-Zn1-O3	54.65(6)
O2a-Zn1-O3a	54.65(6)	O3-Zn1-O2a	93.88(6)
N2-Zn1-O2	150.98(6)	N2a-Zn1-O2a	150.98(6)
N2-Zn1-O2a	89.67(7)	N2a-Zn1-O2	89.67(7)

\*Symmetry operation (a): -x, y, 0.5-z.

<b>4</b>					
Cd1-N1	2.288(4)	Cd1-O4	2.308(3)	Cd1-N2	2.326(4)
Cd1-O3	2.329(4)	Cd1-O5	2.335(3)	Cd1-O2	2.460(4)
Cd1-O4a	2.620(3)				

N1-Cd1-O4	89.18(13)	N1-Cd1-N2	174.35(13)
O4-Cd1-N2	88.33(14)	N1-Cd1-O3	96.61(16)
O4-Cd1-O3	143.28(12)	N2-Cd1-O3	88.40(16)
N1-Cd1-O5	90.84(13)	O4-Cd1-O5	129.43(11)
N2-Cd1-O5	86.84(14)	O3-Cd1-O5	86.85(12)
N1-Cd1-O2	97.60(14)	O4-Cd1-O2	89.15(12)
N2-Cd1-O2	87.43(14)	O3-Cd1-O2	54.17(12)
O5-Cd1-O2	140.73(11)	N1-Cd1-O4a	85.86(12)
O4-Cd1-O4a	77.17(12)	N2-Cd1-O4a	88.65(12)
O3-Cd1-O4a	139.27(12)	O5-Cd1-O4a	52.43(10)
O2-Cd1-O4a	165.87(12)		

\*Atom O4a is related to O4 by the symmetry operation, 1-x, -y, 2-z.

5					
Cd1-N4	2.295(3)	Cd1-O2	2.305(3)	Cd1-O4	2.321(3)
Cd1-O1	2.329(2)	Cd1-N3	2.331(3)	Cd1-O3	2.443(3)
Cd1-O2a	2.637(3)				

N4-Cd1-O2	88.91(10)	N4-Cd1-O4	95.83(11)
O2-Cd1-O4	143.79(9)	N4-Cd1-O1	91.33(10)
O2-Cd1-O1	129.05(9)	O4-Cd1-O1	86.82(9)
N4-Cd1-N3	174.51(11)	O2-Cd1-N3	88.13(10)
O4-Cd1-N3	89.29(11)	O1-Cd1-N3	86.95(10)
N4-Cd1-O3	96.78(10)	O2-Cd1-O3	89.18(9)
O4-Cd1-O3	54.62(9)	O1-Cd1-O3	141.14(9)
N3-Cd1-O3	87.80(10)	N4-Cd1-O2a	86.12(10)
O2-Cd1-O2a	77.01(9)	O4-Cd1-O2a	139.04(9)
O1-Cd1-O2a	52.22(8)	N3-Cd1-O2a	88.71(10)
O3-Cd1-O2a	165.85(8)		

\*Atom O2a is related to O2 by the symmetry operation, 2-x, -y, 1-z.

6					
Cd1-N2	2.290(5)	Cd1-O2	2.313(4)	Cd1-N1	2.317(5)
Cd1-O1	2.323(4)	Cd1-O3	2.347(4)	Cd1-O4	2.444(4)
Cd1-O2a	2.643(4)				

N2-Cd1-O2	88.46(16)	N2-Cd1-N1	174.05(17)
O2-Cd1-N1	87.18(16)	N2-Cd1-O1	90.65(16)
O2-Cd1-O1	128.24(14)	N1-Cd1-O1	88.87(16)
N2-Cd1-O3	101.25(18)	O2-Cd1-O3	143.69(14)
N1-Cd1-O3	84.66(19)	O1-Cd1-O3	86.95(14)
N2-Cd1-O4	93.73(16)	O2-Cd1-O4	90.23(14)
N1-Cd1-O4	90.34(16)	O1-Cd1-O4	141.41(14)
O3-Cd1-O4	54.59(14)	N2-Cd1-O2a	85.03(15)
O2-Cd1-O2a	76.27(14)	N1-Cd1-O2a	90.00(15)
O1-Cd1-O2a	52.13(13)	O3-Cd1-O2a	138.87(14)
O4-Cd1-O2a	166.46(13)		

\*Atom O2a is related to O2 by the symmetry operation, -x, -y, 1-z.

7					
Cu1–N4	2.293(7)	Cu1–O2	2.301(6)	Cu1–O4	2.338(6)
Cu1–O1	2.345(6)	Cu1–N3	2.352(8)	Cu1–O3	2.481(6)
Cu1–O2a	2.608(6)				

N4–Cu1–O2	89.3(2)	N4–Cu1–O4	96.3(3)
O2–Cu1–O4	144.0(2)	N4–Cu1–O1	90.6(2)
O2–Cu1–O1	129.1(2)	O4–Cu1–O1	86.5(2)
N4–Cu1–N3	174.9(2)	O2–Cu1–N3	89.0(2)
O4–Cu1–N3	87.8(3)	O1–Cu1–N3	86.7(2)
O2–Cu1–O2a	76.5(2)	O1–Cu1–O2a	52.8(2)
O3–Cu1–O2a	165.3(2)	O4–Cu1–O2a	139.3(2)
N3–Cu1–O2a	88.7(2)	N4–Cu1–O2a	86.2(2)

\*Atom O2a is related to O2 by the symmetry operation, 2-x, 2-y, 1-z.

**Table S2:** Symmetric stretching ( $\nu_s$ ), asymmetric stretching ( $\nu_{as}$ ), their differences ( $\Delta\nu$ ) and the binding mode of the carboxylate groups of CPs 1–7

Compound	$\nu_{as}$	$\nu_s$	$\Delta\nu$	Binding mode
CP1	1585, 1528	1410	175, 118	Bidentate bridging, chelate
CP2	1590, 1555	1412	178, 143	Bidentate bridging, chelate
CP3	1580	1430	150	Chelate
CP4	1628, 1540	1402	226, 138	Unidentate, chelate
CP5	1597, 1542	1399	198, 143	Unidentate, chelate
CP6	1595, 1539	1394	201, 145	Unidentate, chelate
CP7	1597, 1502	1387	210, 115	Unidentate, chelate

The carboxylate group has versatile coordination behaviour. It can be ionic, monodentate, bidentate chelating or bidentate bridging. One method to determine the mode of the carboxylate binding is the infrared spectroscopy (IR). The frequency of the asymmetric carboxylate vibration in the IR spectra,  $\nu_{as}(\text{COO}^-)$ , symmetric carboxylate vibration,  $\nu_s(\text{COO}^-)$  and the magnitude of the separation between the carboxylate stretches,  $\Delta\nu = \nu_{as}(\text{COO}^-) - \nu_s(\text{COO}^-)$ , are often used as spectroscopic criteria to determine the mode of the carboxylate binding.<sup>1</sup> These criteria are applied to assign the type of the carboxylate coordination in inorganic complexes<sup>2</sup> and biomolecules as well.<sup>3</sup> It was shown that frequencies of the asymmetric carboxylate stretches of



alkali-metal halogenobenzoates and the values of  $\Delta\nu$  correlate with the ionic potential of metals and halogens as substituents.<sup>4</sup> Generally, the following order is proposed for divalent metal carboxylates:<sup>2a</sup>

$\Delta\nu$  (chelating) <  $\Delta\nu$  (bridging) <  $\Delta\nu$  (ionic) <  $\Delta\nu$  (monodentate).

Symmetric stretching ( $\nu_s$ ), asymmetric stretching ( $\nu_{as}$ ), their differences ( $\Delta\nu$ ) and the binding mode of the carboxylate groups of CPs **1–7** are tabulated above. The differences ( $\Delta\nu$ ) between  $\nu_{as}(\text{COO}^-)$  and  $\nu_s(\text{COO}^-)$  vibrations in the FTIR spectra of CP 1 are  $175\text{ cm}^{-1}$  and  $118\text{ cm}^{-1}$  which are attributed to the bidentate bridging ( $\mu_2\text{-}\eta^1\text{:}\eta^1$ ) coordination of carboxylate and the bidentate chelating coordination of carboxylate groups. In the similar way,  $\Delta\nu$  values for the other CPs have also been calculated as listed in Table above and the corresponding binding modes have been assigned as well which shows the similar trend  $\Delta\nu$  (chelating) <  $\Delta\nu$  (bridging) <  $\Delta\nu$  (monodentate) for our study.

**Table S3.** Non-bonding interactions in CP **1 - 7**.

Complex-1			
D-H...A	d(H...A) (Å)	D(D...A) (Å)	$\angle$ DHA ( $^\circ$ )
C23 – H23...O1	2.568(2)	3.492(4)	173.44(2)
C17 – H17...O4	2.391(2)	2.953(3)	118.72(2)

Complex-2			
D-H...A	d(H...A) (Å)	D(D...A) (Å)	$\angle$ DHA ( $^\circ$ )
C19–H19...O6	2.506(2)	3.365 (2)	153.59(5)
C18–H18...O1	2.621(4)	3.481 (7)	154.01(3)
C23–H23...O2	2.286(4)	3.190(7)	164.09(3)
C6–H6...O6	2.764(1)	3.408(1)	127.25(4)
C13–H13...O3	2.32(3)	3.24(6)	170.52(3)
C24–H24...N2	2.996(5)	3.700(8)	133.8(3)

Complex-3			
D-H...A	d(H...A) (Å)	D(D...A) (Å)	$\angle$ DHA ( $^\circ$ )
C13 – H13...O2	2.399(2)	3.233(3)	149.24(1)
C3 – H3...O2	2.679(2)	3.207(3)	116.80(1)
C5 – H5...N1	2.882(2)	3.794(3)	166.74(1)

Complex-4			

D-H...A	d(H...A) (Å)	D(D...A) (Å)	∠ DHA (°)
C23-H23...O6	2.545(7)	3.435(9)	160.41(4)
C16-H16...O3	2.195(5)	3.111(8)	167.89(4)
C13-H13...O2	2.322(4)	3.251(6)	175.18(3)
C25-H25...O1	2.973(5)	3.731(8)	139.61(4)
C22-H22...O1	2.506(4)	3.368(7)	154.197(4)
C20-H20...O5	2.535(3)	3.175(6)	126.37(3)
C17-H17...N4	3.03(5)	3.614(7)	122.02(3)

Complex-5			
D-H...A	d(H...A) (Å)	D(D...A) (Å)	∠ DHA (°)
C18 - H18...O6	2.401(6)	3.290(8)	159.75(3)
C13 - H13...O6	2.660(4)	3.263(6)	123.20(3)
C17 - H17...O5	2.573(3)	3.423(5)	152.24(3)
C22 - H22...O1	2.545(3)	3.207(5)	128.43(3)
C24 - H24...O4	2.200(3)	3.116(5)	168.12(3)
C7 - H7...O3	2.352(3)	3.280(5)	174.92(2)
C28 - H28A...O3	2.865(3)	3.813(7)	165.56(3)
C28 - H28B...O6	2.859(5)	3.594(7)	133.26(3)
C23 - H23...N1	3.013(3)	3.618(5)	125.48(2)

Complex-6			
D-H...A	d(H...A) (Å)	D(D...A) (Å)	∠ DHA (°)
C19 - H19...O6	2.464(9)	3.313(1)	151.91(5)
C30 - H30C...O4	2.627(5)	3.512(1)	153.20(6)
C20 - H20...O5	2.521(4)	3.384(8)	154.53(4)
C24 - H24...O3	2.191(5)	3.073(9)	158.09(4)
C7 - H7...O4	2.310(5)	3.236(8)	173.69(5)
C22 - H22...O1	2.567(4)	3.205(8)	126.22(4)
C30 - H30B...O6	2.799(8)	3.693(1)	155.26(6)

Complex-7			
D-H...A	d(H...A) (Å)	D(D...A) (Å)	∠ DHA (°)
C22-H22...O5	2.501(7)	3.361(1)	153.81(7)
C7-H7...O3	2.319(7)	3.247(1)	175.56(6)
C27-H27B...O7	2.879(3)	3.798(4)	160.32(1)
C17-H17...O4	2.140(8)	3.059(1)	169.26(6)
C24-H24...O1	2.526(6)	3.175(1)	127.14(6)
C28-H28B...O3	2.200(8)	2.811(5)	120.68(2)

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