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Electronic Supplementary Information

Solvothermal Synthesis of Coordination Polymers at Different Temperatures and Their Luminescence Studies

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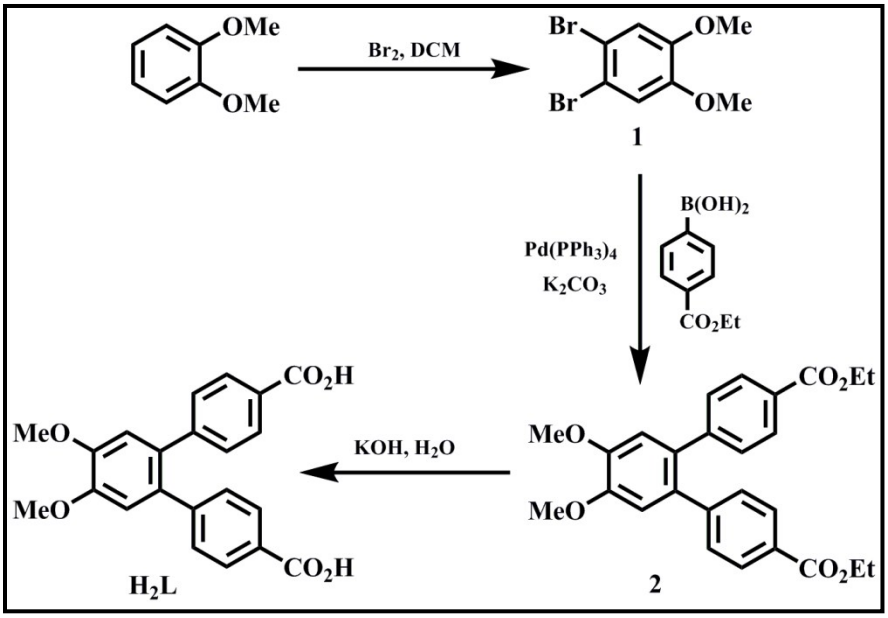
Synthesis of Ligand (H_2L):



Scheme S1. Synthetic route of **H_2L**

1,2-dibromo-4,5-dimethoxybenzene (1):

It was prepared by following the reported procedure.[1] 1,2-Dimethoxybenzene (6 g, 43 mmol) and iodine (0.22 g, 0.8 mmol) were added to dichloromethane (100 mL) with stirring. Bromine (5.6 mL, 17.4g, 108 mmol) was added drop wise with constant stirring. After complete addition of the Br_2, the reaction was stirred an additional 3 hours. Excess Br_2 was removed by adding KOH solution into the reaction mixture and the organic layer was washed with brine, Dried over Na_2SO_4 and concentrated followed by recrystallisation with EtOH. It was isolated by filtration and dried to produce colorless needles. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.05 (s, 2H), 3.85 (s, 6H).

[1,1':2',1''-Terphenyl]-4',5'-dimethoxy-4,4''-ethyldicarboxylate (2):

5 g (17 mmol) 1,2-dibromo-4,5-dimethoxybenzene, 7 g (36 mmol) 4-ethoxyarbonylphenylboronic acid and 12 g (85 mmol) K_2CO_3 were added to a mixture of 40 mL toluene, 20 mL EtOH and 20 mL water in 250 mL round bottom flask. It was degassed under N_2 using Schlenk line at 80 °C for 15 minutes. Then 200 mg, (0.02 mmol) freshly prepared [$Pd(PPh_3)_4$] was added to the solution. Then the mixture was refluxed at 100 °C for 24 hours with constant stirring under constant flow of nitrogen. The reaction mixture was allowed to cool and organic solvents were evaporated. Then it was extracted from EtOAc and washed with brine

and dried over Na_2SO_4. Chromatographic purification of the crude material on silica gel column using 4% EtOAc in hexane afforded compound **2** as white powder.

Yield: 6 g (82%). ^{1}H-NMR ($CDCl_3$, 500 MHz), δ (ppm): 1.37 (t, *J* = 7.4 Hz, 6H); 3.95 (s, 6H); 4.35 (q, *J* = 7.4 Hz, 4H); 6.92 (s, 2H); 7.17 (d, *J* = 8.5 Hz, 4H); 7.87 (d, *J* = 8 Hz, 4H) (Fig. S1); ^{13}C-NMR ($CDCl_3$), δ (ppm): 14.42, 56.23, 61.08, 113.48, 128.58, 129.43, 129.98, 132.23, 145.83, 148.82, 166.60(Fig. S2); Elemental analysis: Calcd. for $C_{26}H_{26}O_6$ (434.46): C, 71.88; H, 6.03 %; Found: C, 71.67; H, 5.99%; ESI-MS: *m/z* (100%) 452.2066 [M+NH_4^+] (Fig. S3).

[1,1':2',1''-Terphenyl]-4',5'-dimethoxy-4,4''-dicarboxylic acid (H_2L):

Compound **2** (5 g, 11.5 mmol) was hydrolyzed by refluxing with 6(N) NaOH solution (50 mL) for 24 h. Finally, the resulting solution was carefully acidified in cold condition, with dropwise addition of 6(N) HCl to obtain a white precipitate. Keeping flask overnight in the freezer, the white solid was collected by filtration, washed thoroughly with water and dried at 80 ^{o}C under vacuo.

Yield: 4 g (92%). Melting point: 155 $^\circ$C (uncorrected). ^{1}H-NMR (DMSO-d_6, 400 MHz), δ (ppm): 3.81 (s, 6H); 6.98 (s, 2H); 7.17 (d, *J* = 8.5 Hz, 4H); 7.74 (d, *J* = 8.2 Hz, 4H) (Fig. S4); ^{13}C-NMR (DMSO-d_6), δ (ppm): 56.28, 114.43, 129.45, 129.56, 130.43, 131.95, 145.73, 149.11, 167.70 (Fig. S5); Elemental analysis: Calcd. for $C_{22}H_{18}O_6$ (378.35): C, 69.84; H, 4.79 %; Found: C, 69.09; H, 4.01%; ESI-MS: *m/z* (100%) 377.1006 [M-1]$^+$ (Fig. S6).

Table S1. Crystal and Structure Refinement Data for CP 1-6.

Complexes	1	2	3	4
Empirical formula	$C_{27}H_{21}N_2O_{6.5}Zn$	$C_{57}H_{50}N_5O_{14.5}Zn_2$	$C_{35}H_{33}N_5O_7Zn$	$C_{30}H_{29}CdN_3O_8$
Formula wt	542.85	1167.81	701.3	671.96
Crystal system	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	*P-1*	*P-1*	*Pbca*	*P-1*
a, Å	9.415(5)	11.106(5)	10.972(5)	9.502(5)
b, Å	10.117(5)	15.856(5)	16.101(5)	11.646(5)
c, Å	14.657(5)	17.853(5)	37.978(5)	13.277(5)
α (°)	85.815(5)	82.222(5)	90	84.836(5)
β (°)	74.704(5)	88.158(5)	90	73.449(5)
γ (°)	70.067(5)	88.201(5)	90	84.180(5)
U, Å^3	1265.8(10)	3112.2(19)	6709(4)	1398.2(11)
Z	2	4	8	2
ρ_{calc} g/cm^3	1.401	1.139	1.388	1.596
μ, mm^{-1}	1.014	0.825	0.788	0.838
F(000)	548	1096	2912	684
Reflns collected	6817	21992	33524	7529
R_{int}	0.0263	0.0440	0.1464	0.0236
Independent reflns	4576	11448	6223	5030
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
GOF	1.073	1.048	1.014	1.078
Final R indices [I>2σ(I)]	R1 = 0.0505 wR2 = 0.1169	R1 = 0.0601 wR2 = 0.1561	R1 = 0.0729 wR2 = 0.1775	R1 = 0.0385 wR2 = 0.0948
R indices (all data)	R1 = 0.0629 wR2 = 0.1315	R1 = 0.0743 wR2 = 0.1613	R1 = 0.1210 wR2 = 0.2160	R1 = 0.0434 wR2 = 0.1016

Complexes	**5**	**6**
Empirical formula	$C_{27}H_{24}CoN_2O_8$	$C_{84}H_{112}Co_3N_{14}O_{30}$
Formula wt	563.42	1974.66
Crystal system	Monoclinic	Monoclinic
Space group	*C2/*m	*P21/c*
a, Å	9.5536(11)	13.1143(6)
b, Å	28.335(4)	18.2637(8)
c, Å	10.1074(12)	18.1148(9)
α (°)	90	90
β (°)	107.415(3)	91.9710(10)
γ (°)	90	90
U, Å^3	2610.7(5)	4336.2(3)
Z	4	2
ρ_{calc} g/cm^3	1.342	1.091
μ, mm^{-1}	0.700	0.626
F(000)	1084	1946
Reflns collected	16311	35554
R_{int}	0.0357	0.0670
Independent reflns	2481	8036
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
GOF	1.051	1.005
Final R indices [I>2σ(I)]	R1 = 0.0500 wR2 = 0.1346	R1 = 0.0579 wR2 = 0.1423
R indices (all data)	R1 = 0.0539 wR2 = 0.1377	R1 = 0.0908 wR2 = 0.1528

Table S2. Selected Bond Distances (Å) and Bond Angles (°) in **1-6.**

CP	Bond lengths		Bond angles	
1				
	Zn(1)-O(1)	2.033(3)	O(1)-Zn(1)-O(2)	160.36(11)
	Zn(1)-O(2)	2.034(3)	O(1) -Zn(1)-O(4)	87.53(12)
	Zn(1)-O(4)	2.038(3)	O(2)-Zn(1)-O(4)	87.09(12)
	Zn(1)-O(3)	2.044(3)	O(1)-Zn(1)-O(3)	90.81(11)
	Zn(1)-N(1)	2.047(3)	O(2)-Zn(1)-O(3)	88.14(12)
			O(4)-Zn(1)-O(3)	160.90(11)
			O(1)-Zn(1)-N(1)	99.22(12)
			O(2)-Zn(1)-N(1)	100.37(12)
			O(4)-Zn(1)-N(1)	101.91(12)
			O(3)-Zn(1)-N(1)	97.13(12)
2				
	Zn(1)-N(1)	2.020(3)	N(1)-Zn(1)-O(9)	102.73(13)
	Zn(1)-O(9)	2.032(3)	N(1)-Zn(1)-O(12)	98.46(12)
	Zn(1)-O(12)	2.034(3)	O(9)-Zn(1)-O(12)	87.82(13)
	Zn(1)-O(11)	2.037(3)	N(1)-Zn(1)-O(11)	100.53(12)
	Zn(1)-O(10)	2.039(3)	O(9)-Zn(1)-O(11)	87.63(13)
	Zn(2)-O(6)	2.028(3)	O(12)-Zn(1)-O(11)	161.00(11)
	Zn(2)-O(5)	2.028(3)	N(1)-Zn(1)-O(10)	96.19(13)
	Zn(2)-O(4)	2.044(3)	O(9)-Zn(1)-O(10)	160.96(12)
	Zn(2)-N(4)	2.052(3)	O(12)-Zn(1)-O(10)	87.34(14)
	Zn(2)-O(3)	2.070(3)	O(11)-Zn(1)-O(10)	90.99(14)
			O(6)-Zn(2)-O(5)	158.66(12)
			O(6)-Zn(2)-O(4)	87.53(12)
			O(5)-Zn(2)-O(4)	87.51(12)
			O(6)-Zn(2)-N(4)	105.07(12)
			O(5)-Zn(2)-N(4)	96.14(12)
			O(4)-Zn(2)-N(4)	109.75(12)
			O(6)-Zn(2)-O(3)	90.24(12)
			O(5)-Zn(2)-O(3)	87.14(13)
			O(4)-Zn(2)-O(3)	159.34(11)
			N(4)-Zn(2)-O(3)	90.67(12)
3				
	Zn(1)-O(1)	1.943(4)	O(4) Zn(1) O(1)	99.34(15)
	Zn(1)-(O4)	1.915(3)	O(4) Zn(1) N(4)	105.36(16)
	Zn(1)-N(4)	2.003(4)	O(1) Zn(1) N(4)	125.96(15)
	Zn(1)-N(1)	2.014(5)	O(4) Zn(1) N(1)	120.42(16)
			O(1) Zn(1) N(1)	100.43(17)
			N(4) Zn(1) N(1)	106.74(17)

4	N(2)-Cd(1) 2.348(3) O(2)-Cd(1) 2.223(3) O(1W)-Cd(1) 2.287(3) O(3)-Cd(1) 2.255(3) O(7)-Cd(1) 2.347(3) O(1)-Cd(1) 2.694(3) O(4)-Cd(1) 2.735(3)	O(2)-Cd(1)-O(3) 137.44(10) O(2)-Cd(1)-O(1W) 95.73(11) O(3)-Cd(1)-O(1W) 104.03(11) O(2)-Cd(1)-O(7) 78.42(11) O(3)-Cd(1)-O(7) 86.36(12) O(1W)-Cd(1)-O(7) 169.02(12) O(2)-Cd(1)-N(2) 134.64(10) O(3)-Cd(1)-N(2) 83.65(10) O(1W)-Cd(1)-N(2) 89.03(11) O(7)-Cd(1)-N(2) 88.61(11)
5	Co(01)-O(1) 2.020(3) Co(01)-O(2) 2.029(3) Co(01)-N(1) 2.075(4)	O(1)-Co(01)-O(1) 87.43(17) O(1)-Co(01)-O(2) 166.38(11) O(1)-Co(01)-O(2) 89.28(13) O(2)-Co(01)-O(2) 90.84(17) O(1)-Co(01)-N(1) 98.52(12) O(2)-Co(01)-N(1) 95.03(12)
6	Co(1)-O(6A) 2.082(3) Co(1)-O(6A) 2.082(3) Co(1)-O(4A) 2.091(3) Co(1)-O(1F) 2.126(4) Co(2)-O(3A) 2.041(4) Co(2)-O(5A) 2.054(4) Co(2)-N(4B) 2.157(5)	O(6A)-Co(1)-O(6A) 180.000(1) O(6A)-Co(1)-O(4A) 91.75(14) O(6A)-Co(1)-O(4A) 88.25(14) O(4A)-Co(1)-O(4A) 180.00(7) O(6A)-Co(1)-O(1F) 89.46(14) O(6A)-Co(1)-O(1F) 90.54(14) O(4A)-Co(1)-O(1F) 94.51(14) O(4A)-Co(1)-O(1F) 85.49(14) O(6A)-Co(1)-O(1F) 90.54(14) O(6A)-Co(1)-O(1F) 89.46(14) O(4A)-Co(1)-O(1F) 85.49(14) O(4A)-Co(1)-O(1F) 94.51(14) O(1F)-Co(1)-O(1F) 180.000(1) O(3A)-Co(2)-O(5A) 91.88(16) O(3A)-Co(2)-O(1W) 173.15(16) O(5A)-Co(2)-O(1W) 90.56(15) O(3A)-Co(2)-N(1B) 88.38(17) O(5A)-Co(2)-N(1B) 176.32(17) O(1W)-Co(2)-N(1B) 89.59(16) O(3A)-Co(2)-O(1F) 95.62(14) O(5A)-Co(2)-O(1F) 89.42(14) O(1W)-Co(2)-O(1F) 90.80(15) N(1B)-Co(2)-O(1F) 86.91(16) O(3A)-Co(2)-N(4B) 84.85(16) O(5A)-Co(2)-N(4B) 91.97(16)

		O(1W)-Co(2)-N(4B) N(1B)-Co(2)-N(4B) O(1F)-Co(2)-N(4B)	88.67(17) 91.71(18) 178.52(16)

Table S3. Selected non-covalent interactions. *

Complexes	C-H···π interactions (Å)	Hydrogen bonding interactions
1	i) C27-H27A···centroid distance =3.461(9) ii) C26-H26A···centroid distance =3.435(1) iii) C27-H27C···centroid distance =3.838(2) iv) C26-H26C···centroid distance =3.751(2)	
2	i) C32-H32A···centroid distance =3.905(8) ii) C32-H32B···centroid distance =3.636(10) iii) C54-H54A···centroid distance =3.903(9) iv) C54-H54C···centroid distance =3.478(9) v) C31-H31B···centroid distance =3.713(1)	
3	i) C15A-H15A···centroid distance =3.597(9)	i) H2B···O2 = 2.160(3) Å, N2-H2B···O2 = 170.86(5)º ii) H3C···O3 = 2.031(3) Å, N3-H3C···O3 = 169.09(2)º
4	C27-H15C···centroid distance = 2.459(7)	i) H1W···O1= 2.031(6) Å, O1W-H1W···O1= 162.39(3)º ii) H2W···O4 = 2.003(7) Å, O1W-H2W···O4=174.92(5)º
5	i) C11A-H11A···centroid distance=3.447(4)	

* For complex **1** and **2** see Fig S16 c, d.

Table S4. List of N-N, N=N bond lengths and C-N-N-C torsion angle.

Complexes	**N=N bond length** (Å)	**N-N bond length** (Å)	**C-N-N-C torsion angle** (°)
1	N1=N1 = 1.182(8)		C3-N2-N2-C3=180.00(38)
2	N2=N2 = 1.238(7) N3=N3 = 1.229(7)		C8-N2-N2-C8=180.00(33) C1-N3-N3-C1=180(33)
3		N2-N3 = 1.388(5)	C3-N2-N3-C6=106.22(65)
4	N3=N3 = 1.249(6)		C3-N3-N3-C3=180.00(29)
5	N2=N2 =1.024(17)		C3B-N2-N2-C3B=180.00(75)
6		N2B-N3B = 1.369(4)	C3B-N2B-N3B-C6B=85.50(48)

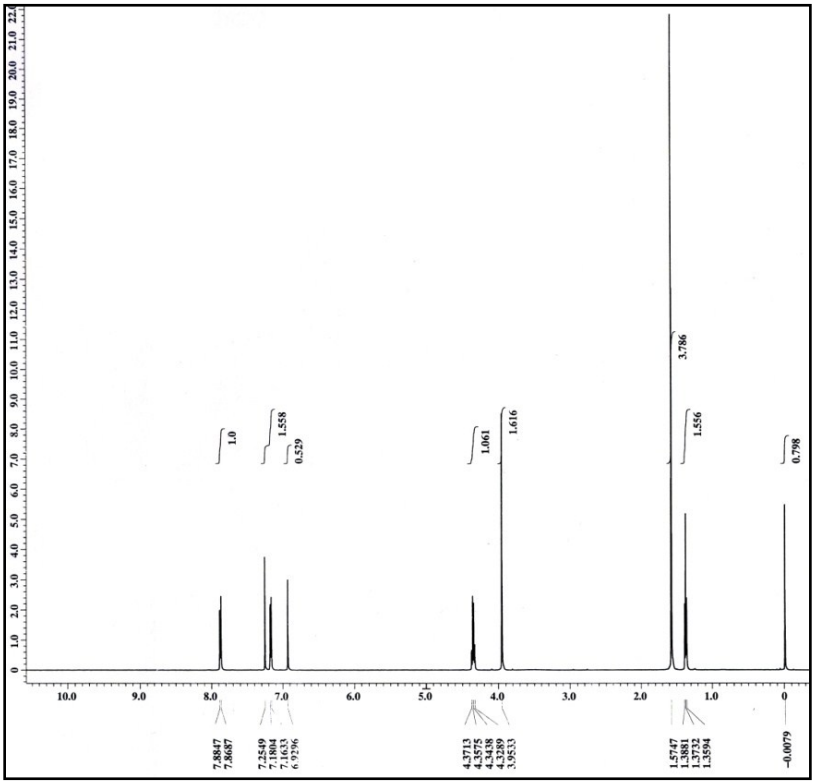


Fig. S1 ^{1}H NMR spectrum of **2.**

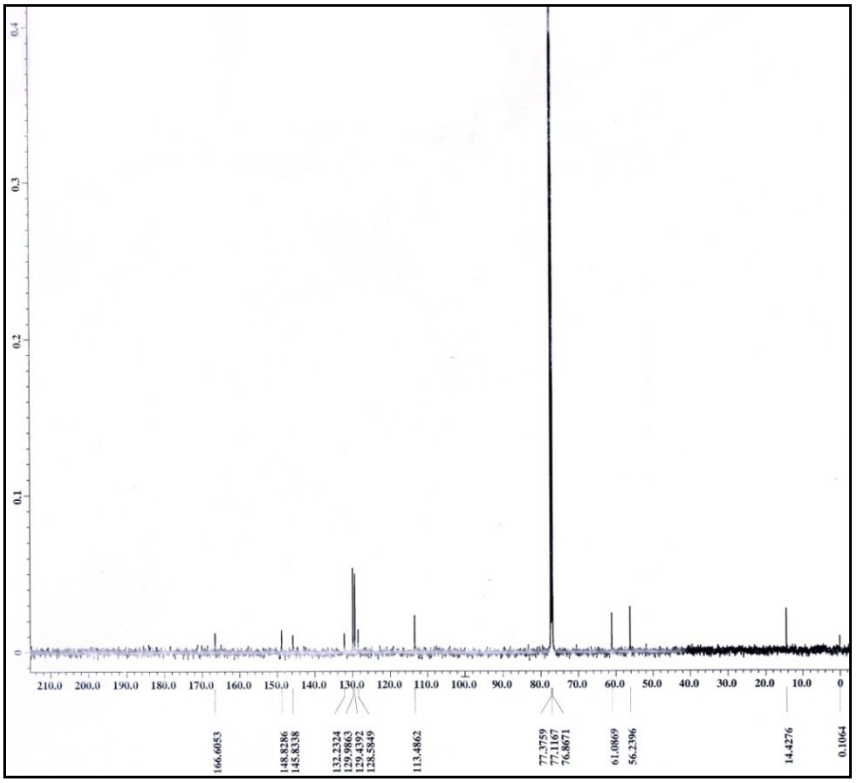


Fig. S2 ^{13}C NMR spectrum of **2.**

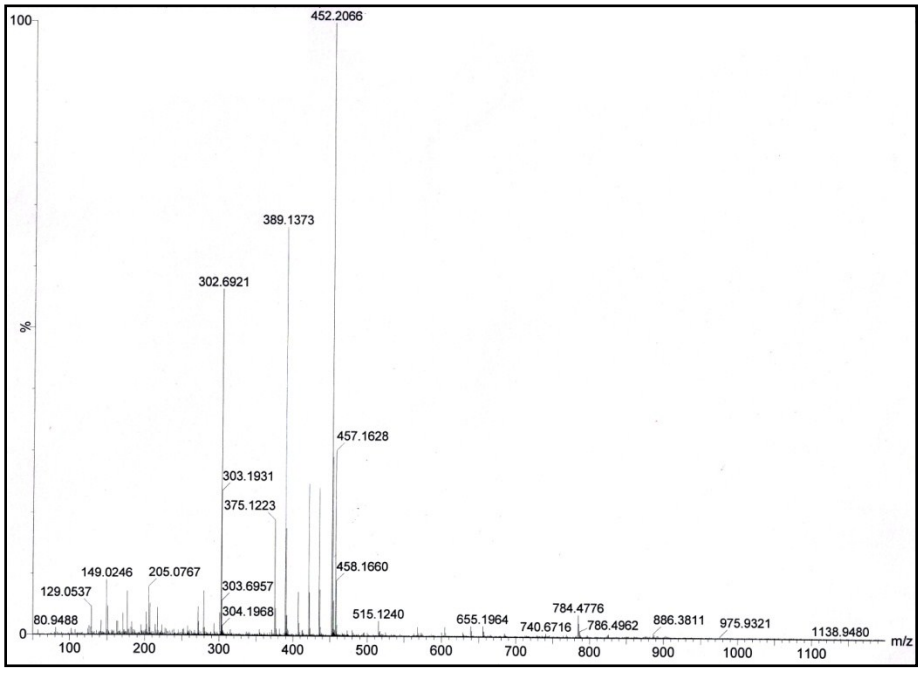


Fig. S3 ESI-MS spectrum of **2.**

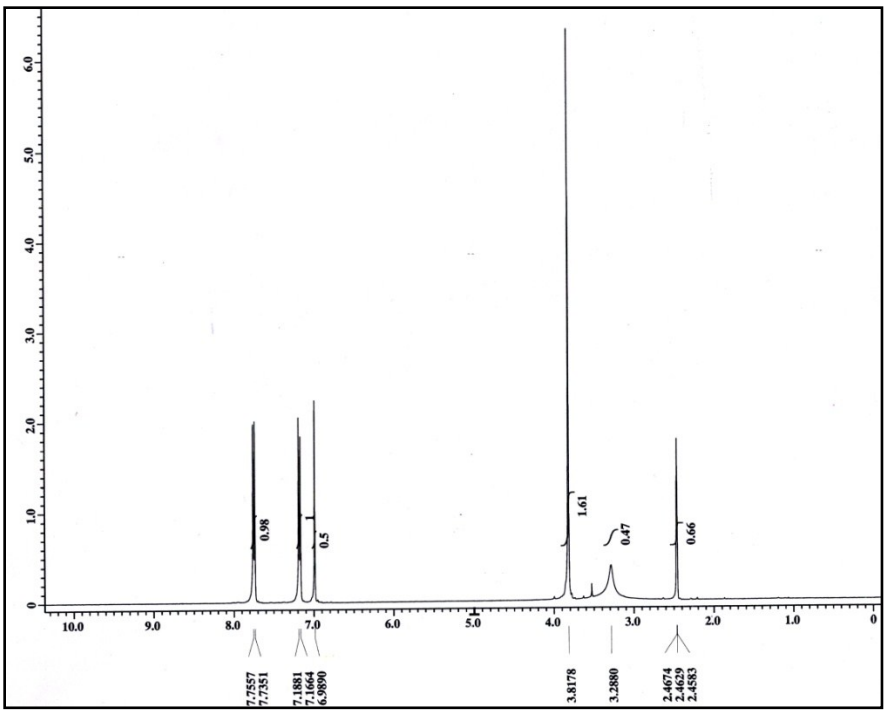


Fig. S4 ^{1}H NMR spectrum of **H_2L.**

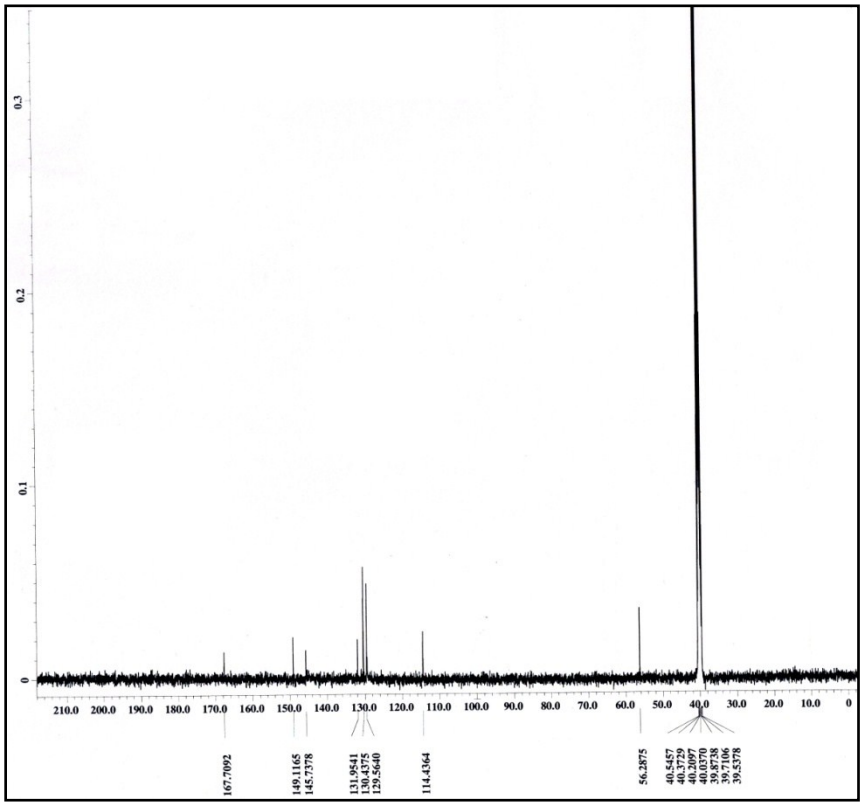


Fig. S5 ^{13}C NMR spectrum of **H_2L.**

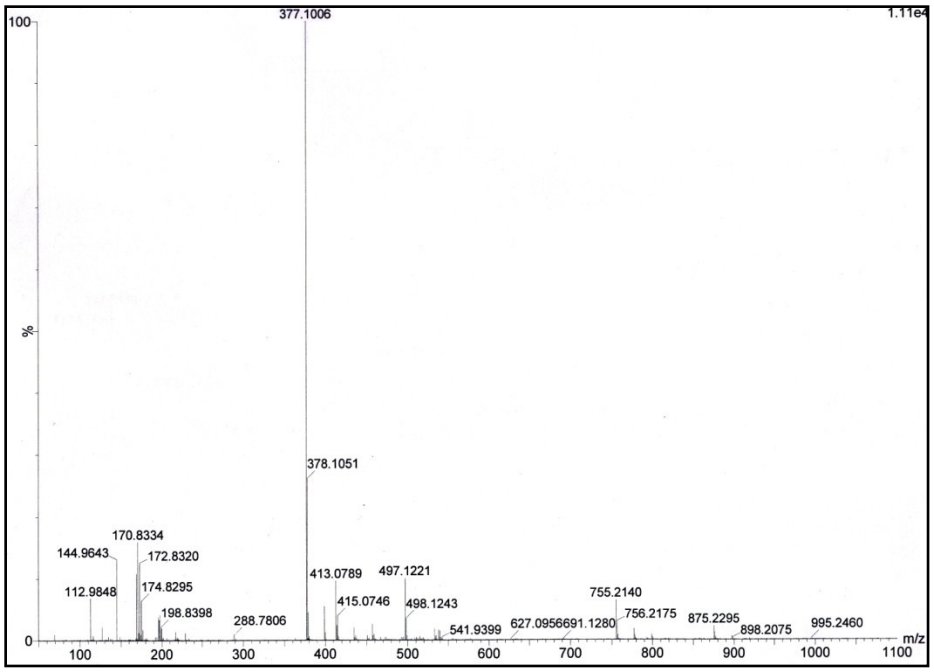


Fig. S6 ESI-MS spectrum of **H_2L.**

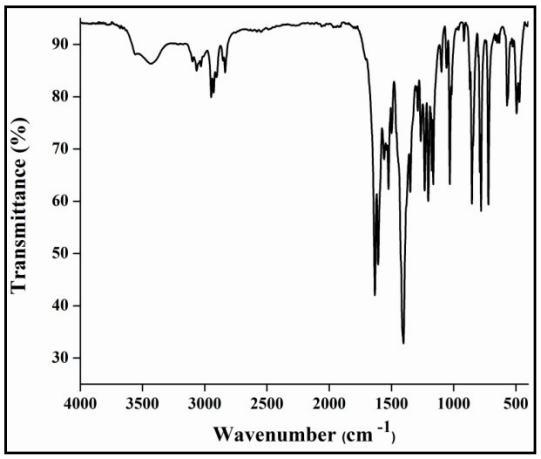


Fig. S7 IR spectrum of CP **1.**

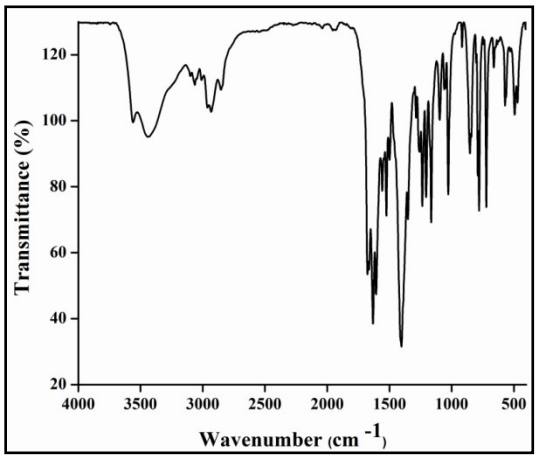


Fig. S8 IR spectrum of CP **2.**

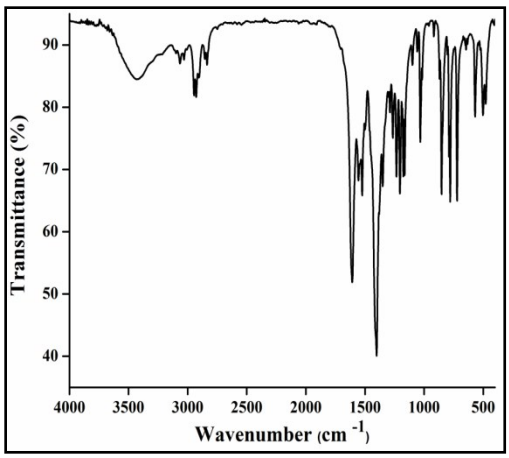


Fig. S9 IR spectrum of CP **3.**

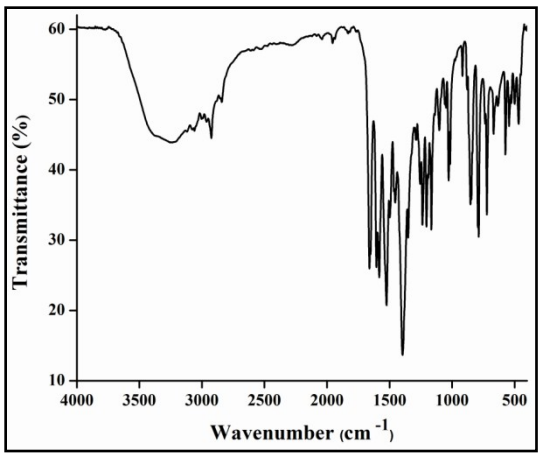


Fig. S10 IR spectrum of CP **4.**

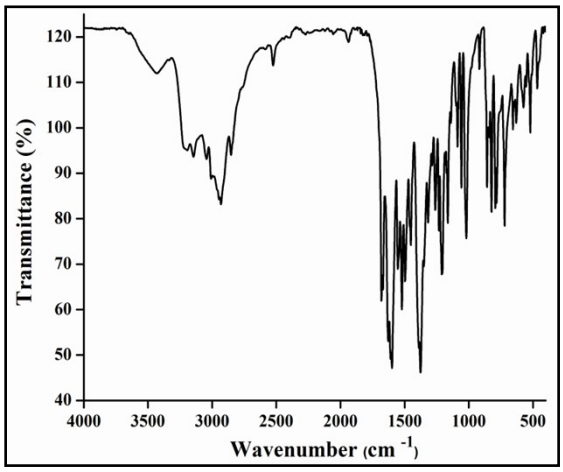


Fig. S11 IR spectrum of CP **5.**

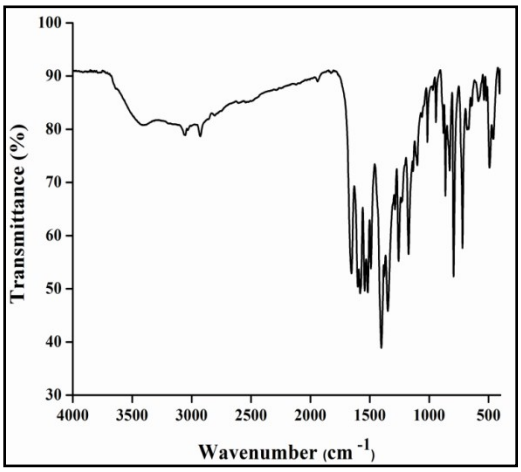


Fig. S12 IR spectrum of CP **6.**

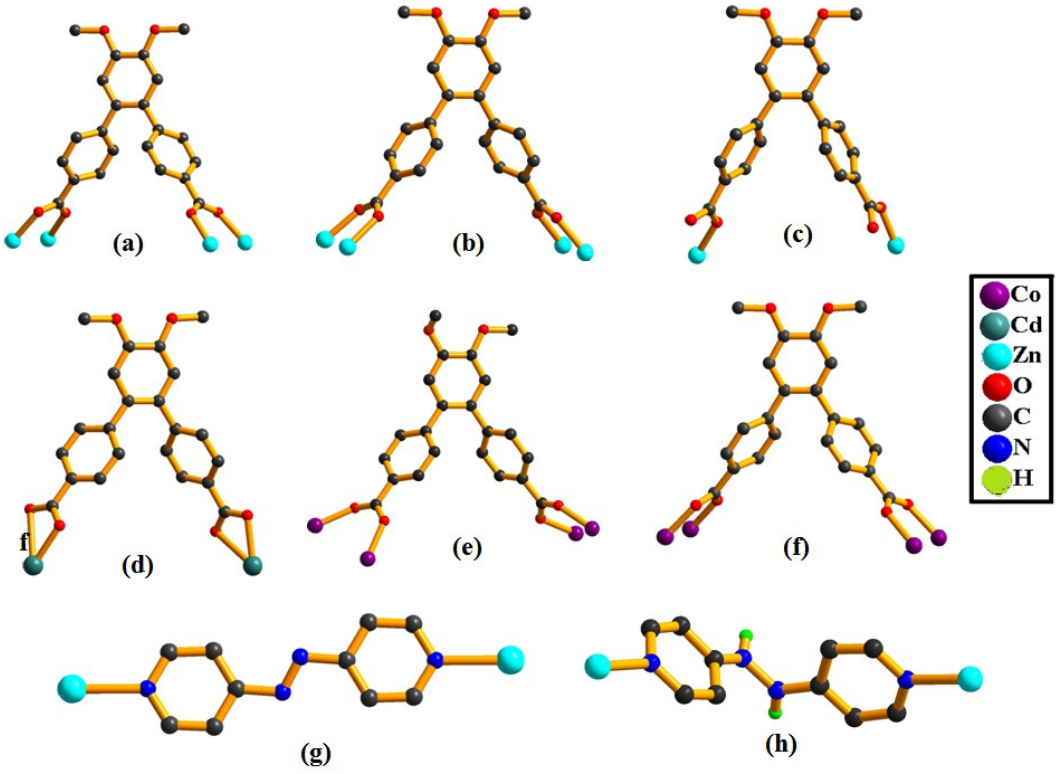


Fig. S13 (a-f) Coordination mode of ***L*** in complex **1**-**6**, (g) Common binding mode of **azpy** in **1**,**2**,**4** and **5** (here shown with Zn(II)), (h) Common binding mode of **bphy** in **3** and **6** (here shown with Zn(II)) (hydrogen atoms are omitted for clarity).

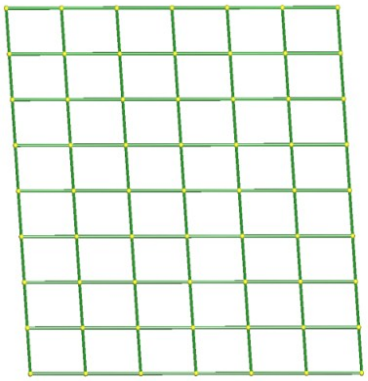


Fig. S14 Topological view of CP **1.**

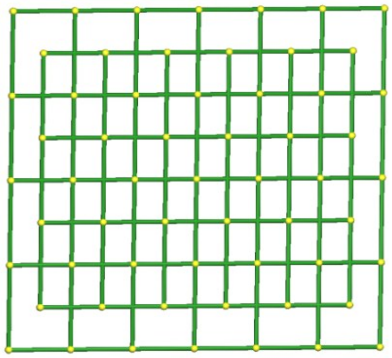


Fig. S15 Topological view of CP **2.**

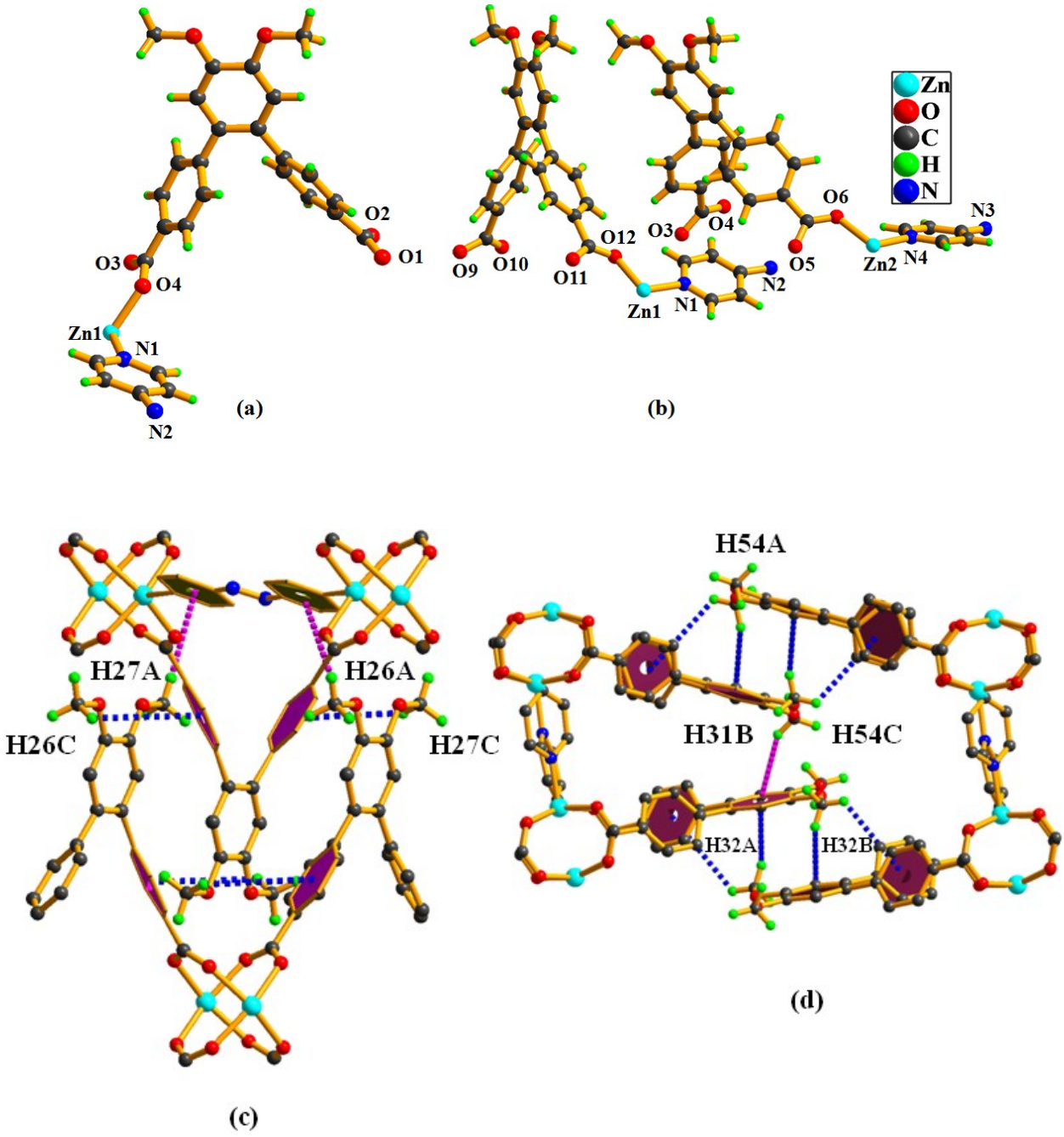


Fig. S16 (a) Asymmetric units of CP **1,** (b) asymmetric units of CP **2**, (c) the perspective view of the C–H•••π interactions in **1** and (d) the perspective view of the C–H•••π interactions in **2**.

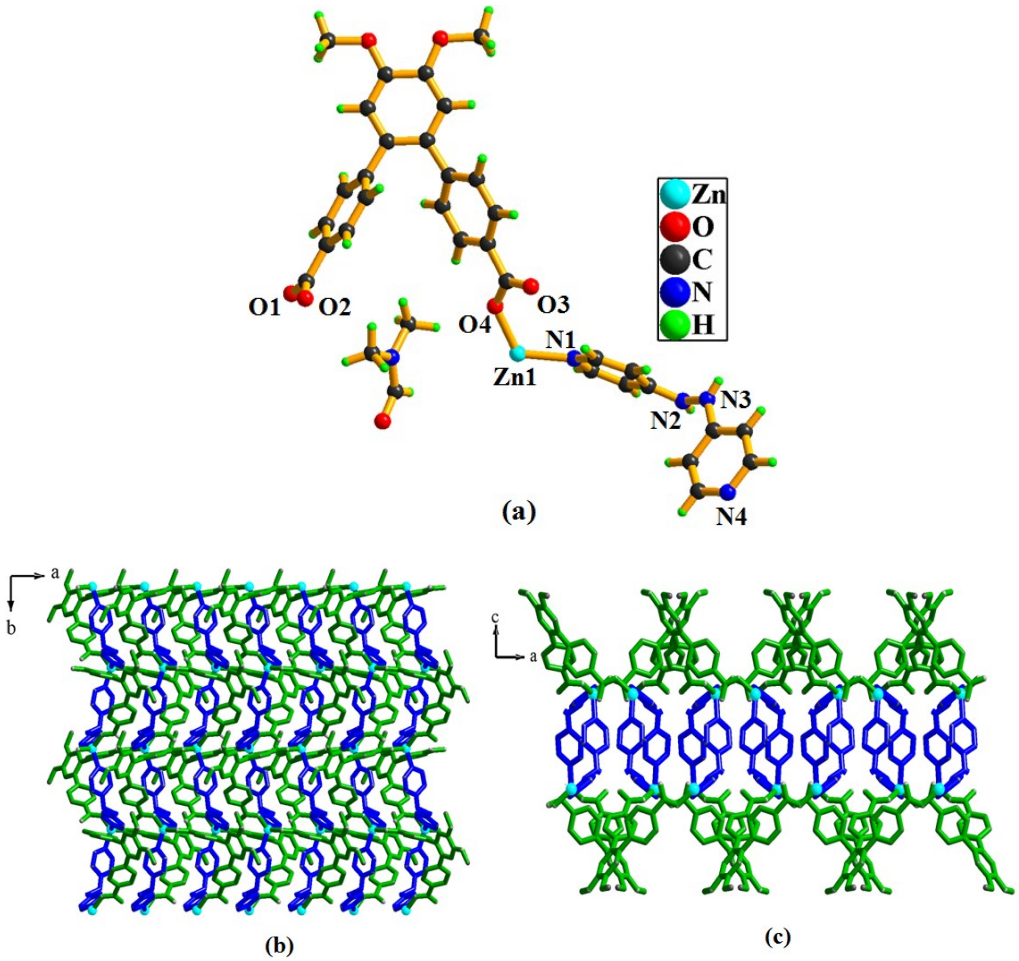


Fig. S17 (a) Asymmetric unit of CP **3** (b) 2D layer of **3** as viewed along c-axis and (c) along b axis.

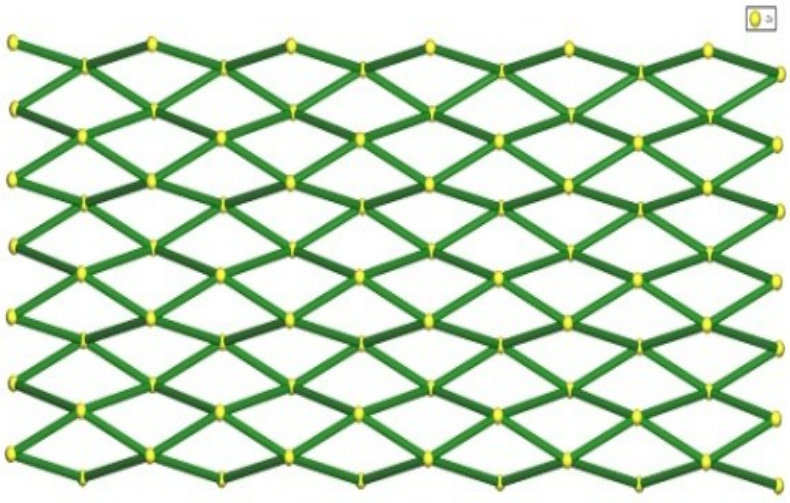


Fig. S18 Topological view of CP **3.**

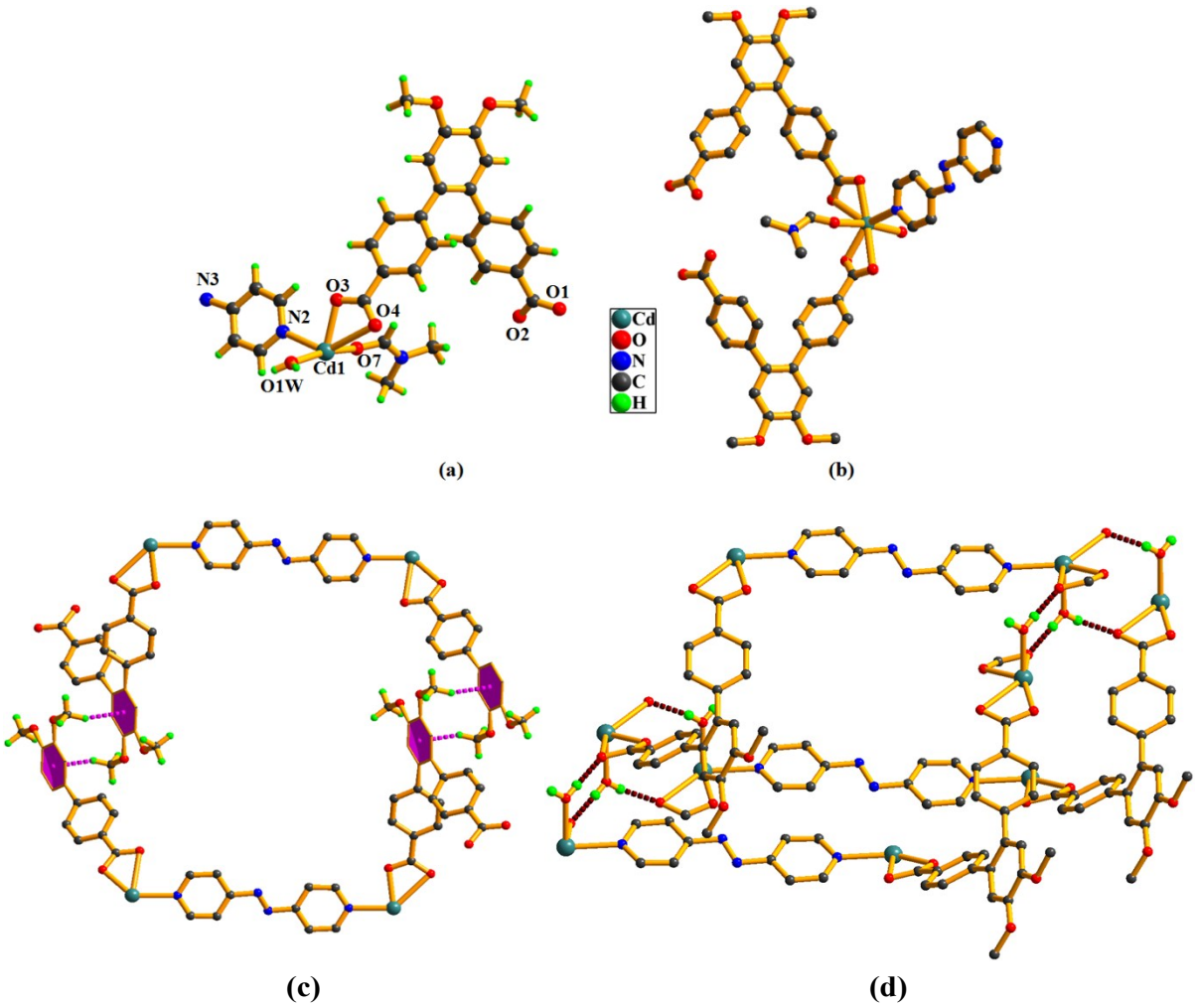


Fig. S19 (a) Asymmetric unit of CP **4**, (b) Coordination environment around Cd(II) center, (c) the presence of C–H•••π interactions and (d) hydrogen bonding interactions in **4**.

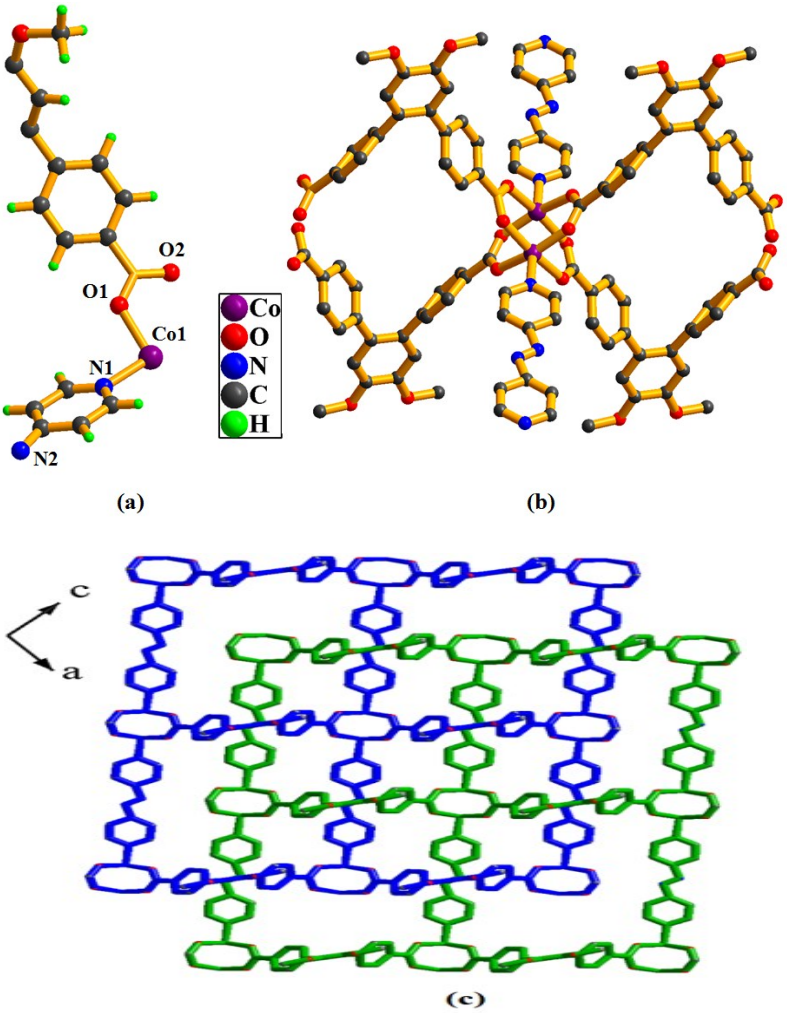


Fig. S20 (a) Asymmetric unit of CP **5**, (b) Coordination environment around Co(II) ions, (c) view of doubly interpenetrated 2D layers in **5** as viewed along b axis.

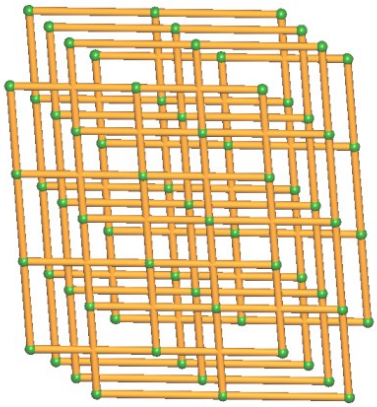


Fig. S21 Topological view of CP **5.**

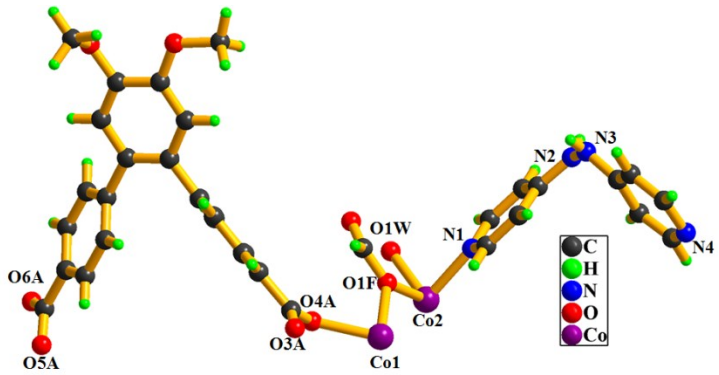


Fig. S22 Asymmetric unit of CP **6**.

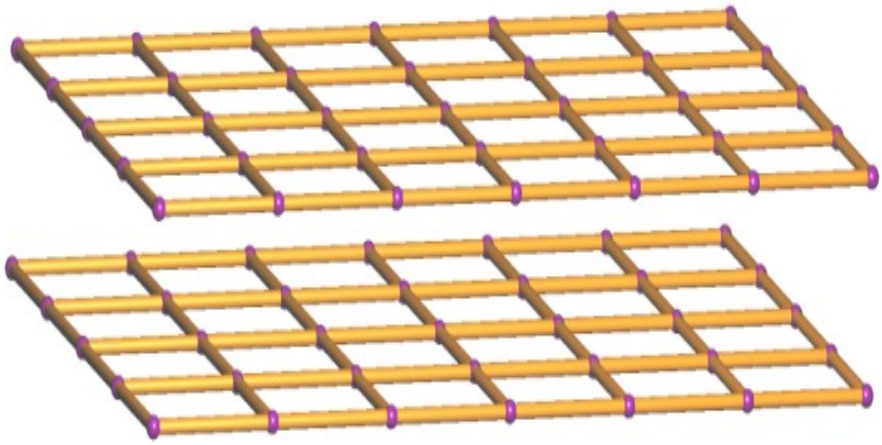


Fig. S23 Topological view of CP **6.**

PXRD Pattern at room temperature (Bottom to top, simulated (red) and as-synthesized (black))

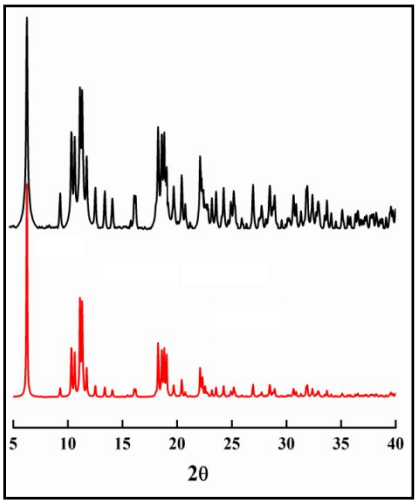


Fig. S24 PXRD of CP **1.**

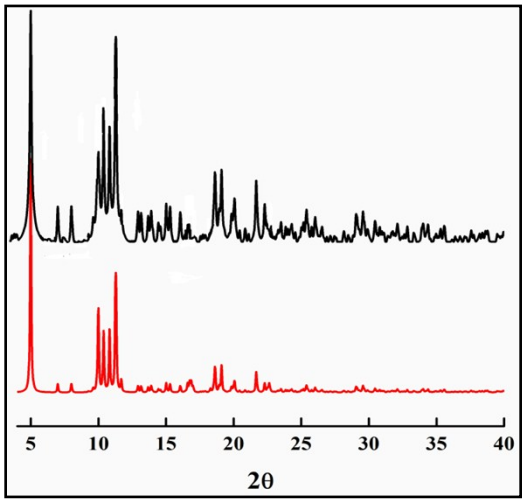


Fig. S25 PXRD of CP **2.**

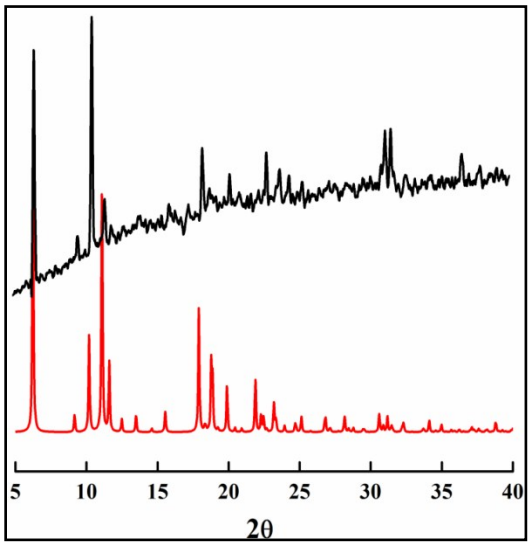


Fig. S26 PXRD of CP **3.**

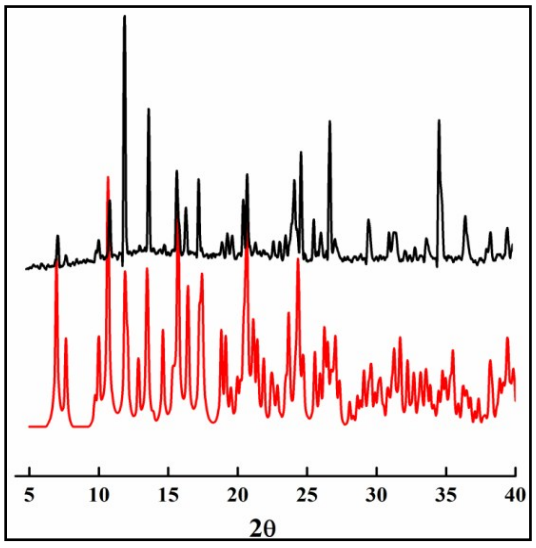


Fig. S27 PXRD of CP **4.**

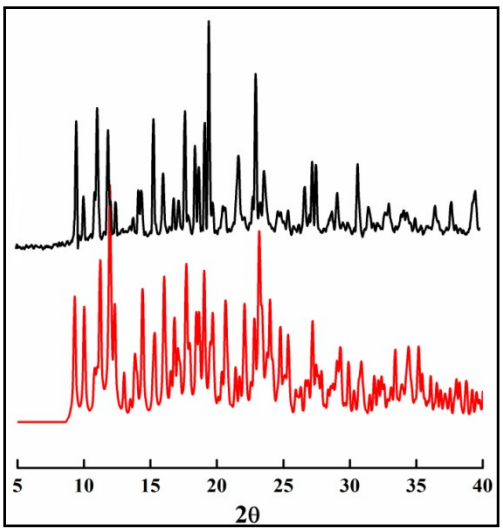


Fig. S28 PXRD of CP **5.**

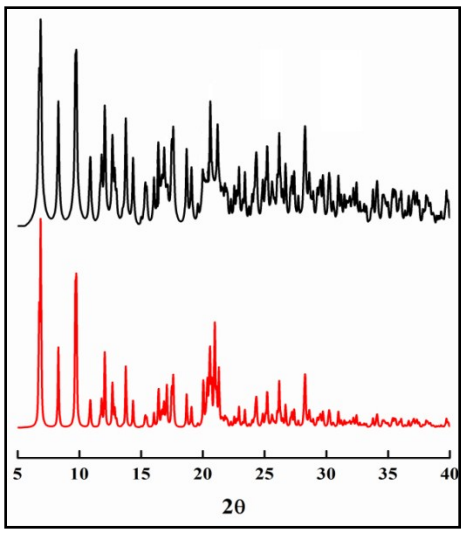


Fig. S29 PXRD of CP **6.**

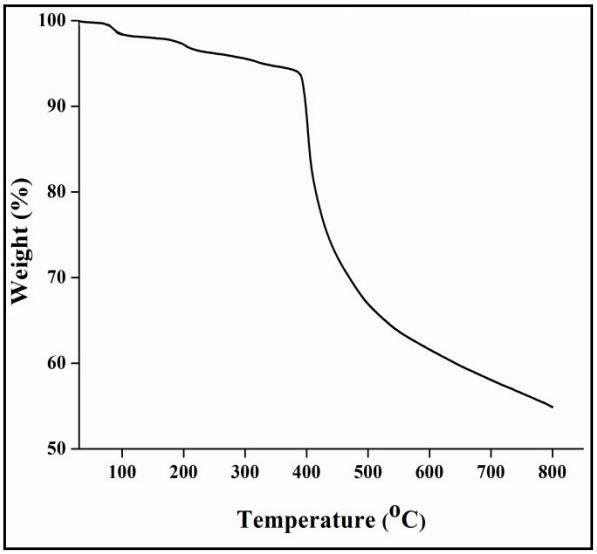


Fig. S30 Thermogram of CP **1.**

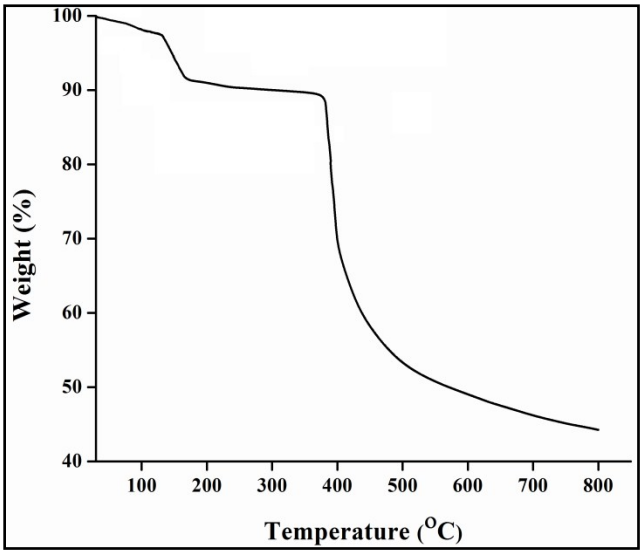


Fig. S31 Thermogram of CP **2.**

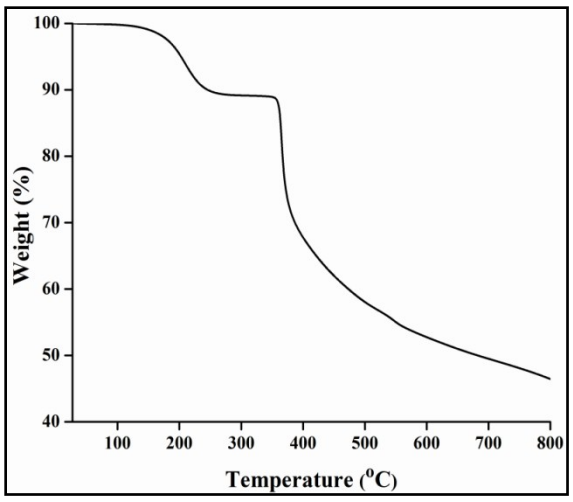


Fig. S32 Thermogram of CP **3.**

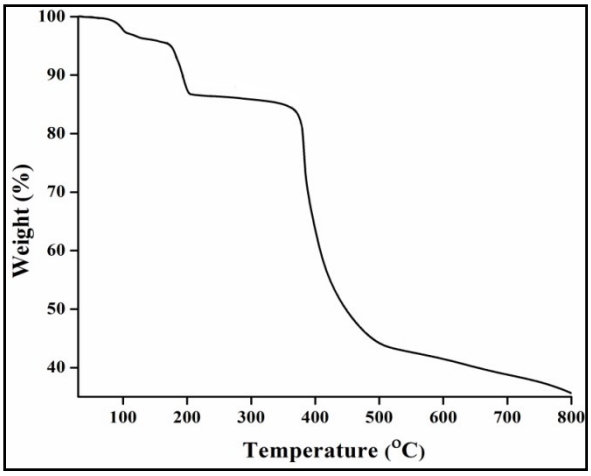


Fig. S33 Thermogram of CP **4.**

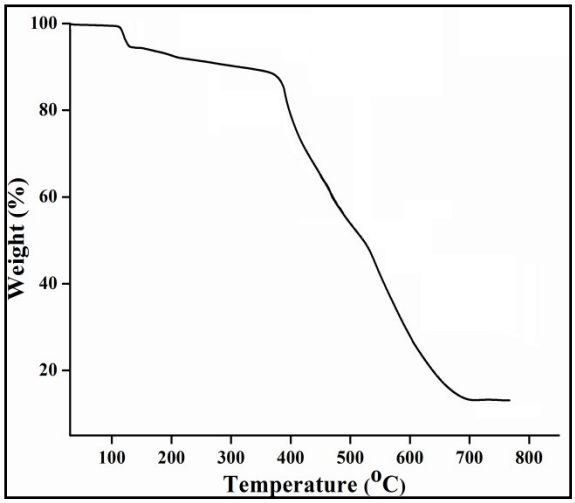


Fig. S34 Thermogram of CP **5.**

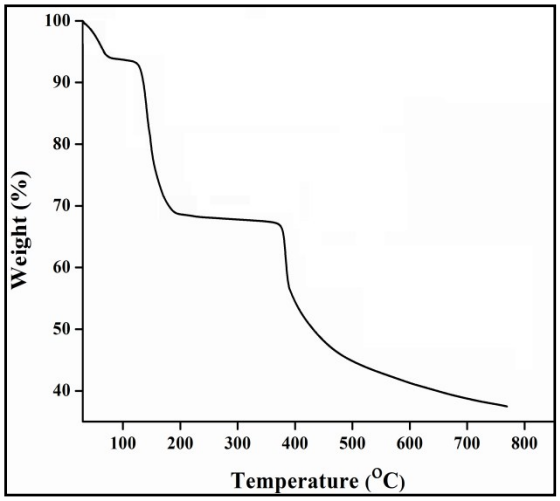


Fig. S35 Thermogram of CP **6.**

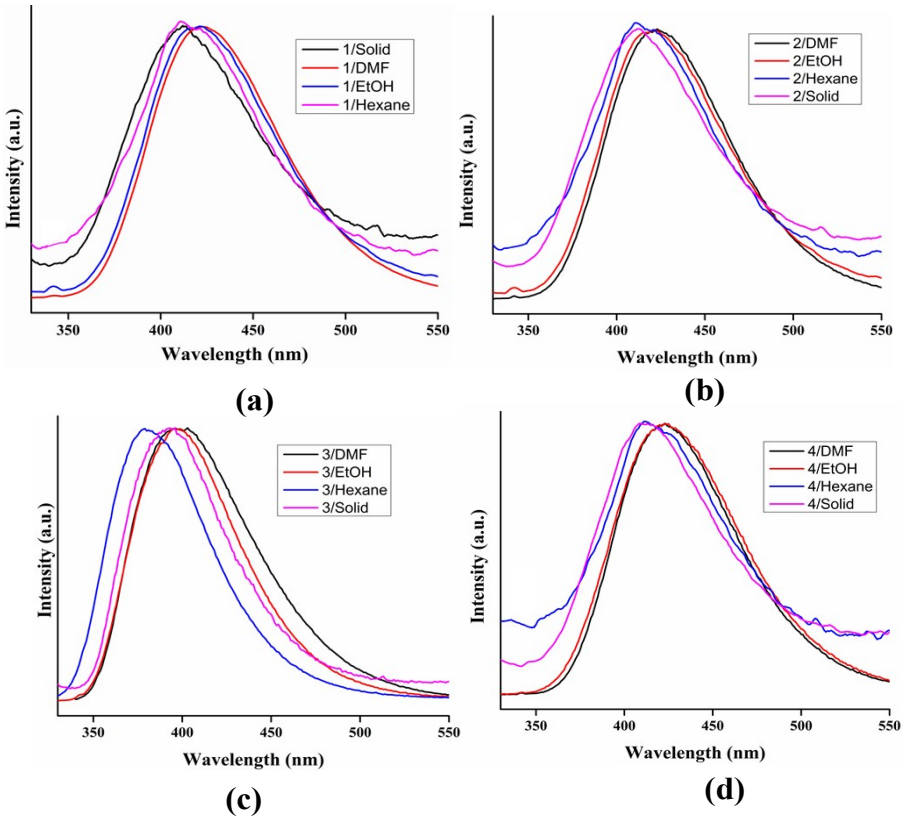


Fig. S36 Comparison of emission spectra of complex **1-4** in solid state as well as in solution phase of varying solvent polarity (DMF, ethanol and hexane) under dispersed condition.

Reference

(1) T. Wenderski, K. M. Light, D. Ogrin, S. G. Bott and C. J. Harlan, *Tetrahedron Letters*, 2004, **45,** 6851-6853.