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Structural Diversity of Zn(II) Based Coordination Polymers Constructed from a Flexible Carboxylate Linker and Pyridyl Co-linkers : Fluorescence Sensing of Nitro-aromatics

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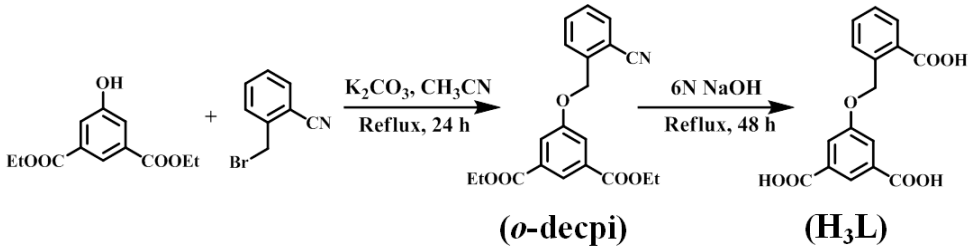
Synthesis of the ligand (H_3L)

This synthesis of ligand H_3L (**scheme 1**) and pyridyl-based co-ligand dpd was reported in our previous work[1] and was characterized by elemental analysis, ^1H and ^{13}C NMR spectroscopy, and ESI-MS analysis.



Scheme S1. The synthetic scheme for preparation of **(H_3L).**

Synthesis of diethyl 5-(2-cyanophenethyl)isophthalate (*o*-decpi)

5-Hydroxyisophthalic acid diethyl ester[2] (2 g, 8.4 mmol) and dry K_2CO_3 (1.7 g, 12.6 mmol) were mixed in a round-bottom flask under an inert atmosphere. Dry acetonitrile (10 mL) was added to it, and the mixture was stirred for 30 min at 80 °C. The mixture was treated with 2-(bromomethyl)benzonitrile (1.65 g, 8.40 mmol), and the resulting solution was refluxed for 24 h. At the end of this period, it was allowed to cool to room temperature and poured in ice-cold

water (75 mL) to obtain a white solid that was collected by filtration and dried in air. Yield: 2.8g (86%). ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.3251(s, 1H), 7.8436 (s, 2H), 7.7297 - 7.6372 (m, 3H), 7.4774 - 7.4547 (m, 1H), 5.318 (s, 2H), 4.3946 (q, J = 7.12 Hz, 4H), 1.4002 (t, J = 5.84 Hz, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz):165, 158, 139, 133, 132, 128, 124, 120, 117, 111,77, 68, 61, 14; IR (cm-1, KBr pellet): 3087 (m), 2983 (m), 2229 (m), 1713 (s), 1598(m), 1451(m), 1334(s), 1236 (s), 1128(m), 1044;(s), 957(s), 889(m), 768(s); ESI-MS: m/z $[M+H]^+$ 354.13 (100%) , $[M+H_2O]^+$ 371.16 (60%). Elemental analysis: Calcd. for $C_{20}H_{19}NO_5$ (353.37): C, 67.97; H, 5.42; N, 3.96 % Found: C, 67.39; H, 5.51; N, 3.75 %.

Synthesis of 5-(2-Carboxybenzyloxy)isophthalic acid (H_3L).

Compound *o*-dmcbi obtained as above (2 g, 5.17 mmol) was hydrolyzed by refluxing it with 6(N) NaOH solution (20 mL) for 24 h. After cooling to 5 °C, the resulting solution was acidified with 6(N) HCl solution to obtain a white precipitate. It was collected by filtration, washed thoroughly with water, and dried in air. Yield: 1.3 g (80%). It has been characterized by ^{1}H NMR (DMSO-d_6, 400 MHz), Mass Spectrometry, IR spectroscopy, elemental analysis. ^{1}H-NMR (DMSO-d_6, 400 MHz): 8.0537 (s, 1H), 7.9117 - 7.8920 (m, 1H), 7.6685 - 7.6380 (m, 3H), 7.5694 (t, J = 7.76 Hz, 1H), 7.4205 (t, J = 7.28 Hz, 1H), 5.5069 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): 169, 167, 159, 138, 131, 128, 123, 119, 100, 69, 40; IR (cm-1, KBr pellet): 3403(broad), 3201(broad), 2625 (m), 1711(m), 1594(m), 1472(m), 1395(m), 1271(m), 1152(m), 1044(m), 953(m), 871(m), 759(s); ESI-MS: m/z $[M]^+$ 316.06 (20%) , $[M-H]^+$ 315.05(100%). Elemental analysis: Calcd. for $C_{16}H_{12}O_7$ (316.26): C, 60.76; H, 3.82% Found: C, 59.97; H, 3.75%.

Materials and measurements.

Materials

Reagent-grade 5-hydroxyisophthalic acid, 2 (bromomethyl)benzonitrile, 4-aminopyridine, sodium hypochlorite solution, N,N-diethylformamide (DEF), 1,3-di(4-pyridyl)propane (1,3-dpp), 1,2-di(4-pyridyl)ethane (1,2-dpe), 1,2-di(4-pyridyl)ethylene (dpe) and $Zn(NO_3)_2 \cdot 6H_2O$ were acquired from Aldrich and used as received. All solvents, HCl, NaOH and K_2CO_3 were procured from S. D. Fine Chemicals, India. The solvents were purified prior to use following standard methods.

Physical Measurement

Infrared spectra were recorded on Perkin-Elmer Model 1320 spectrometer (KBr disk, 400–4000 cm^{-1}). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL-ECX 500 FT (500 MHz and 125 MHz respectively) instrument in$CDCl_3$ and DMSO-d_6 with Me_4Si as the internal standard. ESI-mass spectra were recorded on a WATERS Q-TOF Premier mass spectrometer. Thermogravimetric analyses (TGA) were recorded on Mettler Toledo Star System (heating rate of 5°C/min). Microanalyses for the compounds were obtained using a CE-440 elemental analyzer (Exeter Analytical Inc.). The solid-state emission spectra were recorded using a Jobin Yvon Horiba Fluorolog-3 spectrofluorimeter at room temperature (RT). The UV-vis spectra were recorded on a Shimadzu 2450 UV-vis spectrophotometer at RT. The steady-state emission spectra of the complexes dispersed in solvents were obtained using a Agilent Cary eclipse fluorescence spectrophotometer at RT. Powder X-ray diffraction (Cu K_α radiation, scan rate 3°/min, 293 K) was performed on a Bruker D8 Advance Series 2 powder X-ray diffractometer.

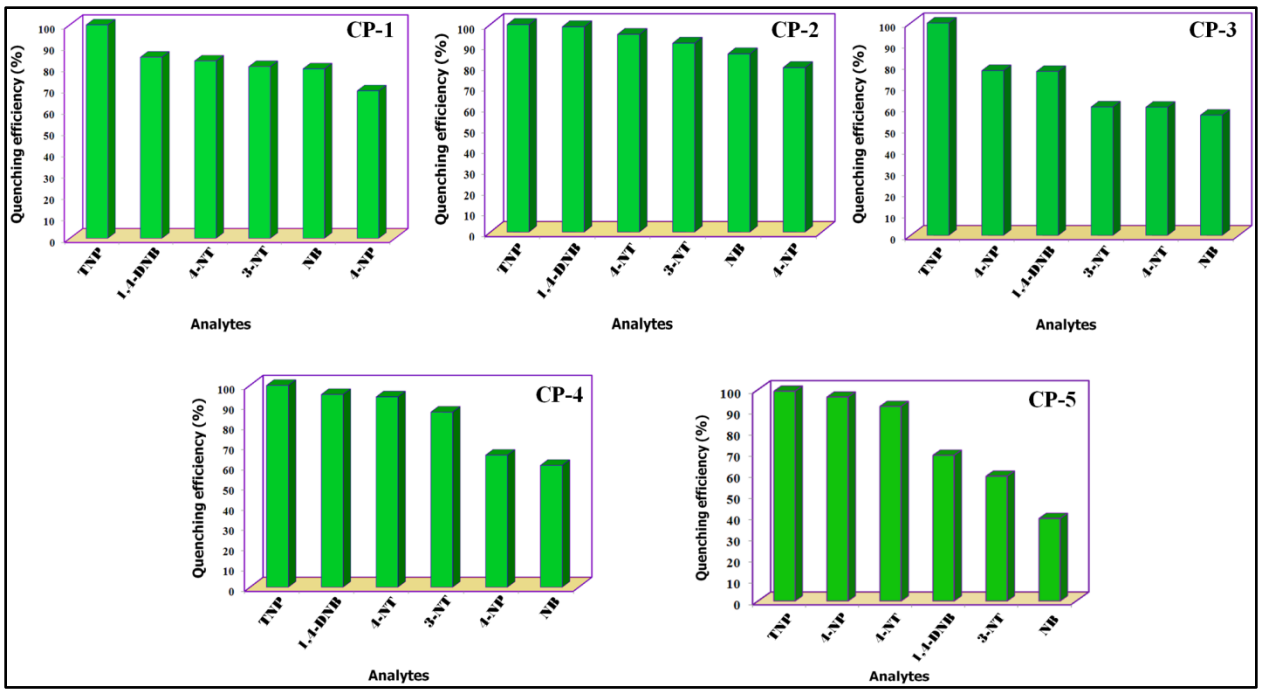


Fig. S1 showing Quenching-efficiency plot (bar diagram) obtained for different nitro-armatic analytes in **CPs 1-5** at room temperature.

Elemental analysis and IR of CP 1-5

CP-1: Block shaped. colorless. Yield = 57%. Anal. Calcd for $C_{28}H_{21}Zn_2N_2O_9$: C, 50.93; H, 3.21; N, 4.24%. Found: C, 50.63; H, 3.37; N, 4.11%. IR (cm^{-1}): 3485 (broad), 3063 (m), 1613 (s), 1578 (s), 1454 (m), 1407 (s), 1355 (s), 1260 (m), 1127 (m), 1098 (m), 1022 (s), 967 (m), 926 (m), 888 (m), 828 (s), 776 (s), 757 (s), 673 (m).

CP-2: Niddle shaped. Colorless. Yield = 51%. Anal. Calcd for $C_{34}H_{29}ZnN_3O_8$: C, 60.68; H, 4.34; N, 6.24%. Found: C, 60.17; H, 3.13; N, 6.41%. IR (cm^{-1}): 3492 (broad), 3069 (m), 1618 (s), 1571 (s), 1504 (m), 1448 (m), 1399 (s), 1325 (m), 1261 (m), 1127 (m), 1043 (s), 926 (m), 822 (m), 798 (s), 780 (s), 750 (s), 686 (m).

CP-3: Block shaped. Orange color. Yield = 63%. Anal. Calcd for $C_{62}H_{50}Zn_2N_{12}O_{17}$: C, 54.51; H, 3.69; N, 12.31%. Found: C, 54.93; H, 3.81; N, 12.07%. IR (cm^{-1}): 3483 (broad), 3100 (m), 3067 (m), 1664 (s), 1615 (s), 1587 (s), 1494 (m), 1456 (m), 1420 (s), 1380 (s), 1355 (s), 1260 (m), 1223 (m), 1154 (m), 1128 (m), 1057 (m), 1022 (s), 995 (m), 927 (m), 880 (m), 847 (s), 776 (s), 758 (s), 673 (m).

CP-4: Block shaped. Pale yellow color. Yield = 47%. Anal. Calcd for $C_{29}H_{24}ZnN_2O_7$: C, 60.27; H, 4.19; N, 4.85%. Found: C, 60.81; H, 4.36; N, 4.49%. IR (cm^{-1}): 3407 (broad), 3063 (m), 2933 (m), 1706 (s), 1621 (s), 1585 (s), 1554 (s), 1434 (s), 1382 (s), 1266 (m), 1193 (m), 1128 (m), 1070 (m), 1033 (s),917 (m), 816 (m), 781 (m), 765 (s), 681 (m).

CP-5: Block shaped. Colorless. Yield = 39%. Anal. Calcd for $C_{76}H_{68}Zn_5N_2O_{38}$: C, 46.94; H, 3.52; N, 1.44%. Found: C, 45.31; H, 3.93; N, 1.32%. IR (cm^{-1}): 3432 (broad), 2930 (m), 1617 (s), 1589 (s), 1569 (s), 1501(m), 1446 (s), 1402(s), 1359 (m), 1259 (m), 1128 (m), 1044 (s), 899 (m), 823 (m), 779 (s), 729(m), 687 (m).

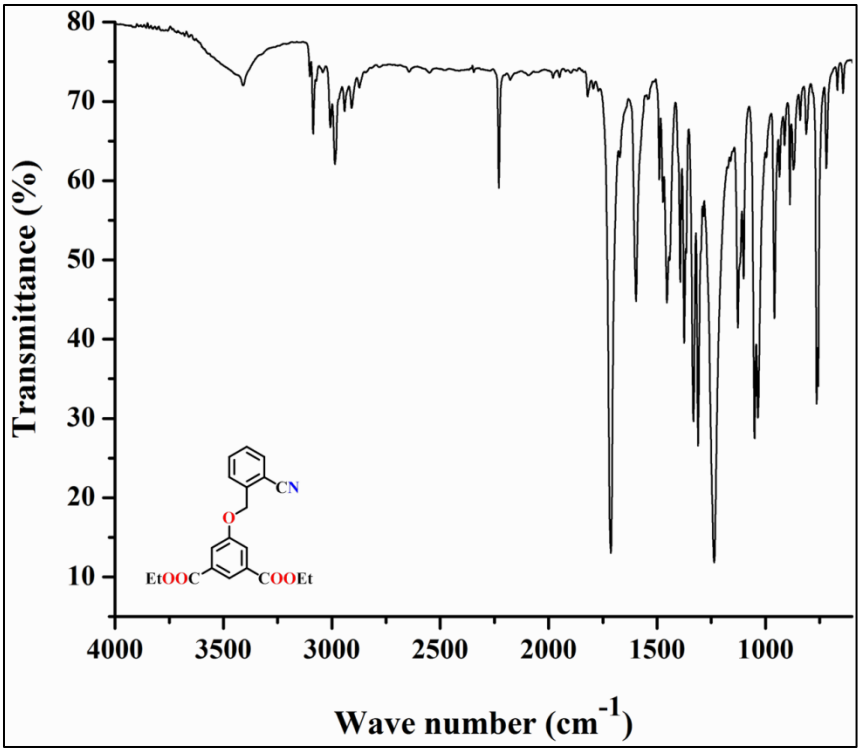


Fig. S2 IR Spectrum of *o*-decpi.

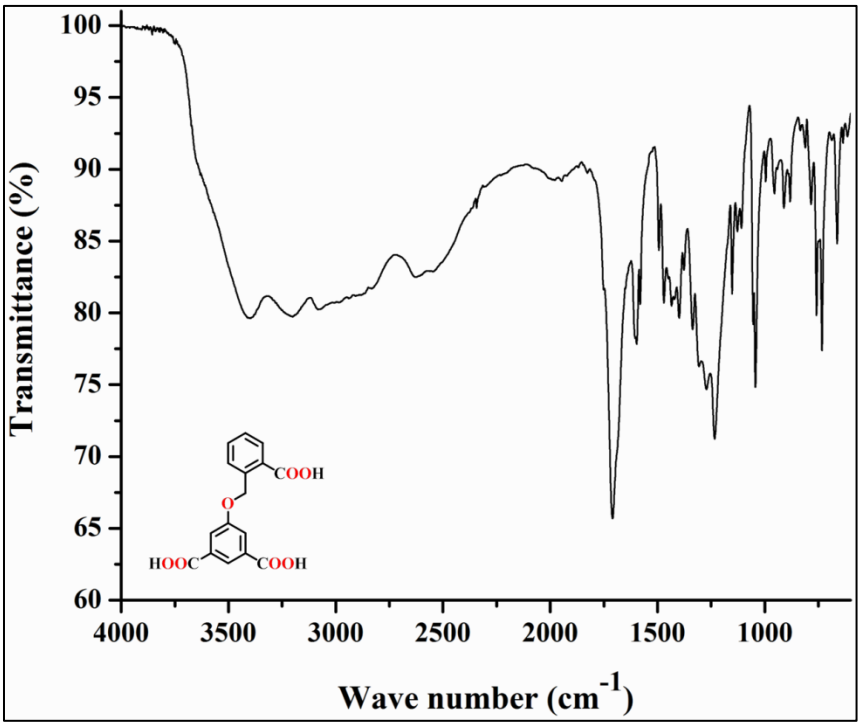


Fig. S3 IR Spectrum of H_3L.

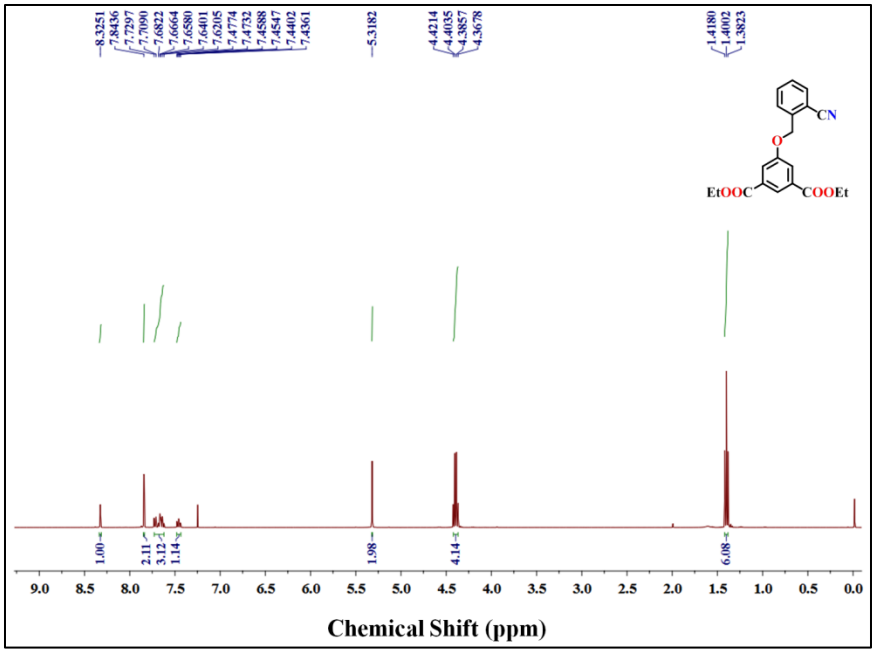


Fig. S4 ^{1}H NMR spectrum of *o*-decpi.

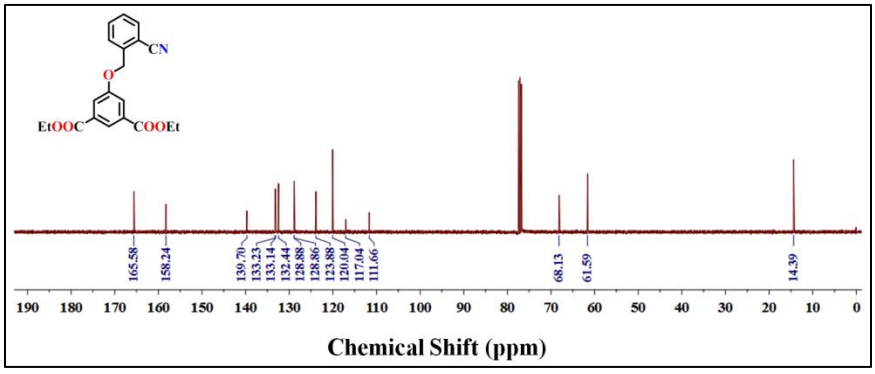


Fig. S5 ^{13}C NMR spectrum of *o*-decpi.

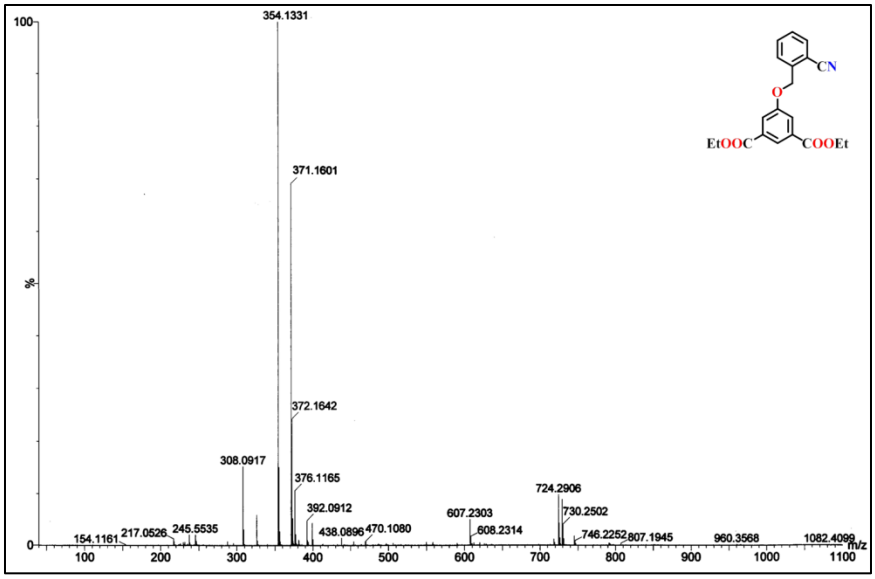


Fig. S6 ESI-MS spectrum of *o*-decpi.

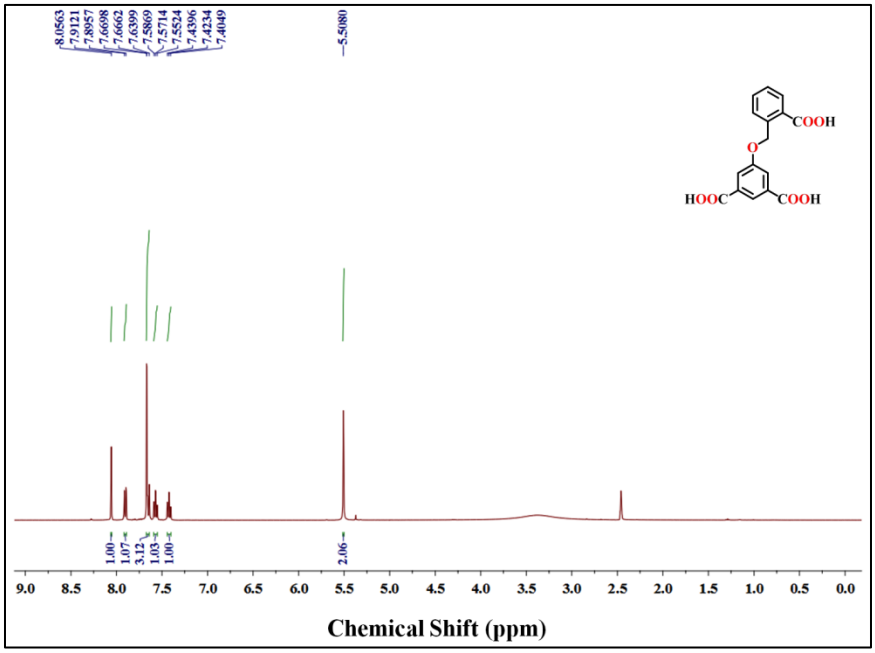


Fig. S7 ^{1}H NMR spectrum of H_3L.

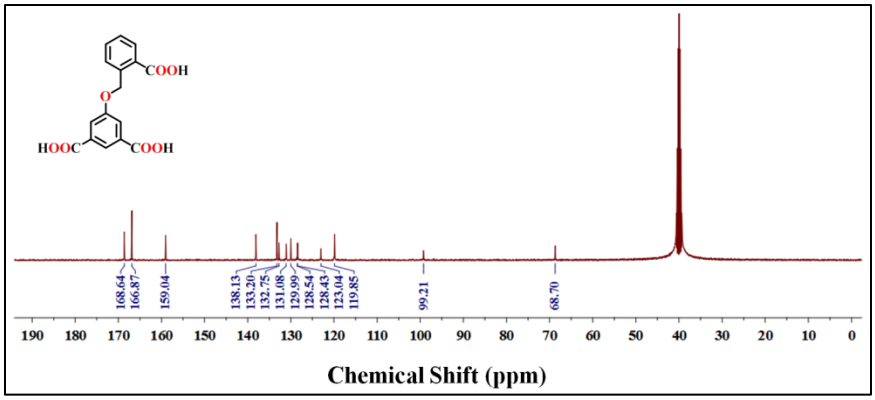


Fig. S8 ^{13}C NMR spectrum of H_3L.

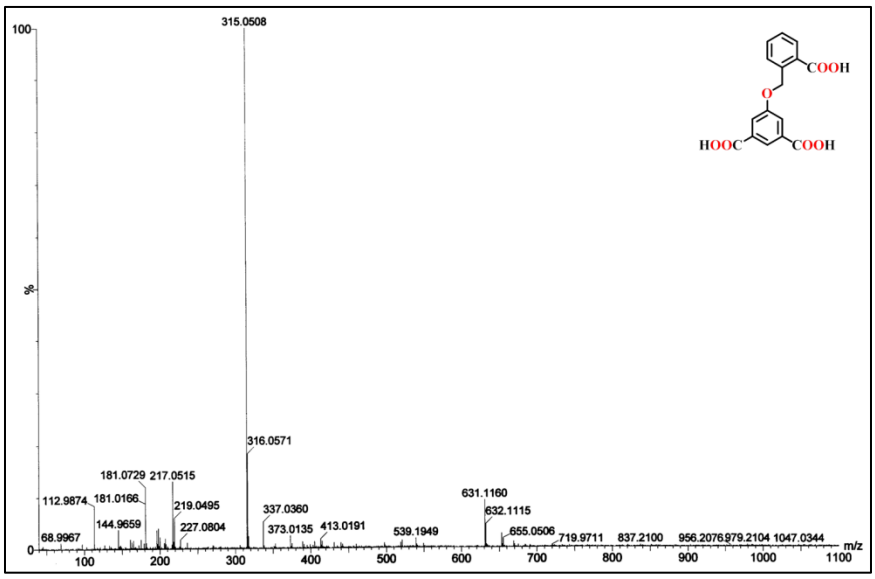


Fig. S9 ESI-MS spectrum of H_3L.

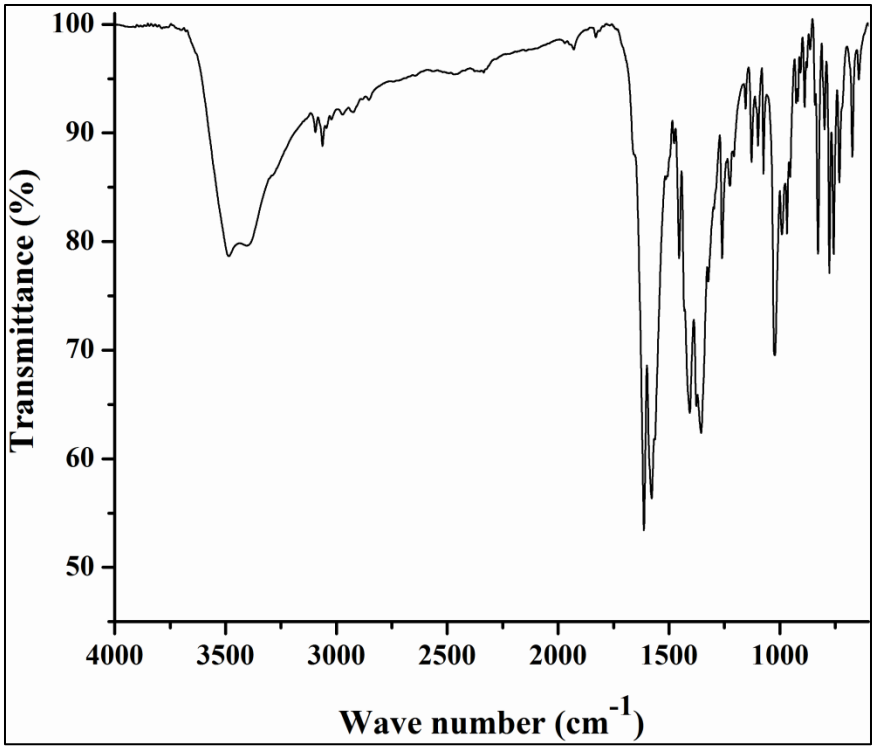


Fig. S10 IR spectrum of CP **1.**

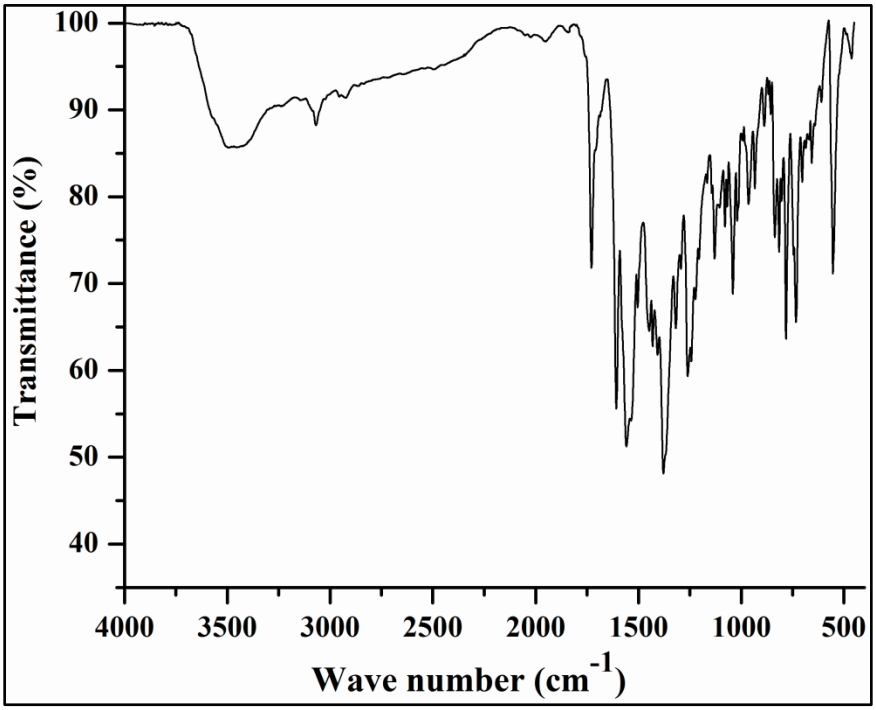


Fig. S11 IR spectrum of CP **2.**

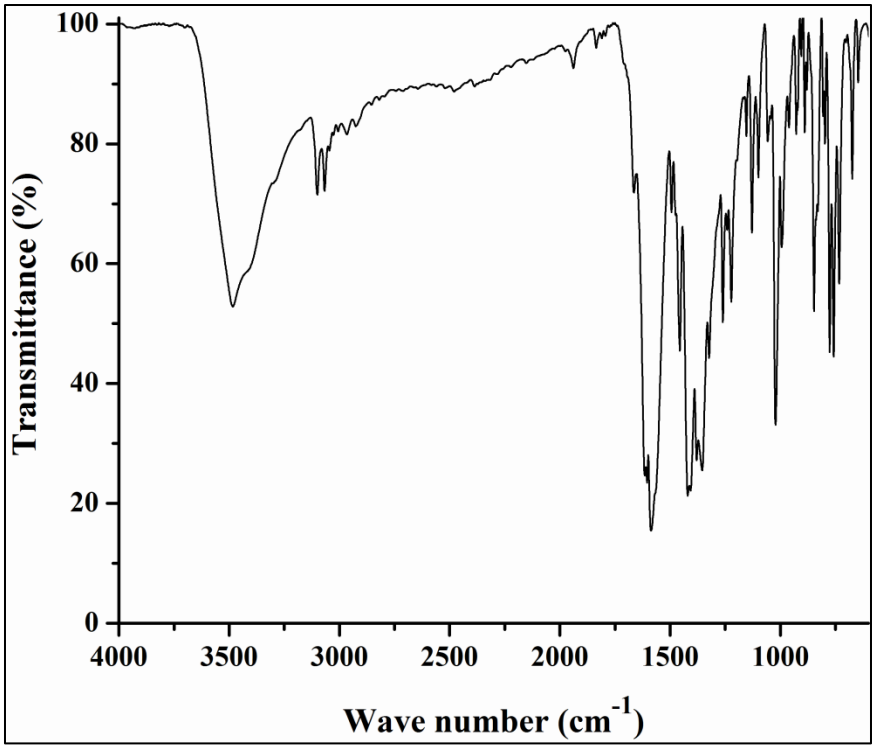


Fig. S12 IR spectrum of CP **3.**

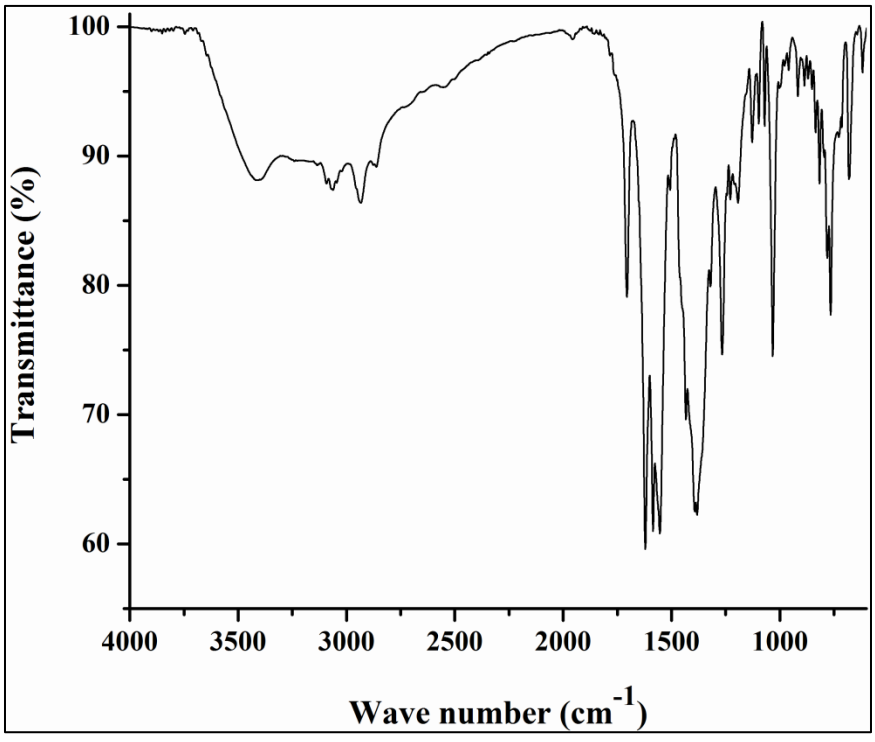


Fig. S13 IR spectrum of CP **4.**

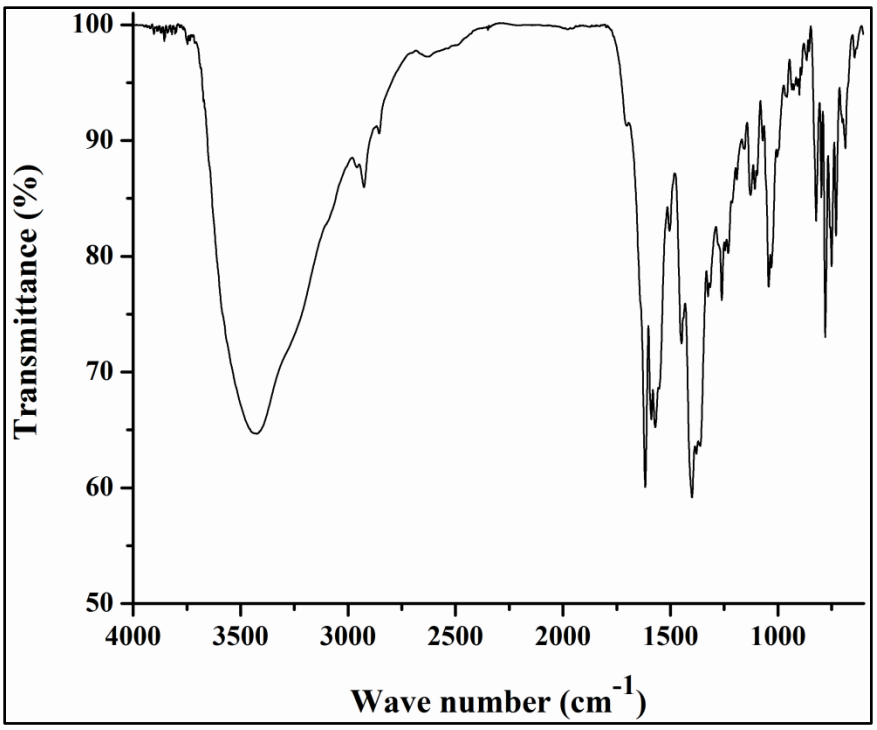


Fig. S14 IR spectrum of CP **5.**

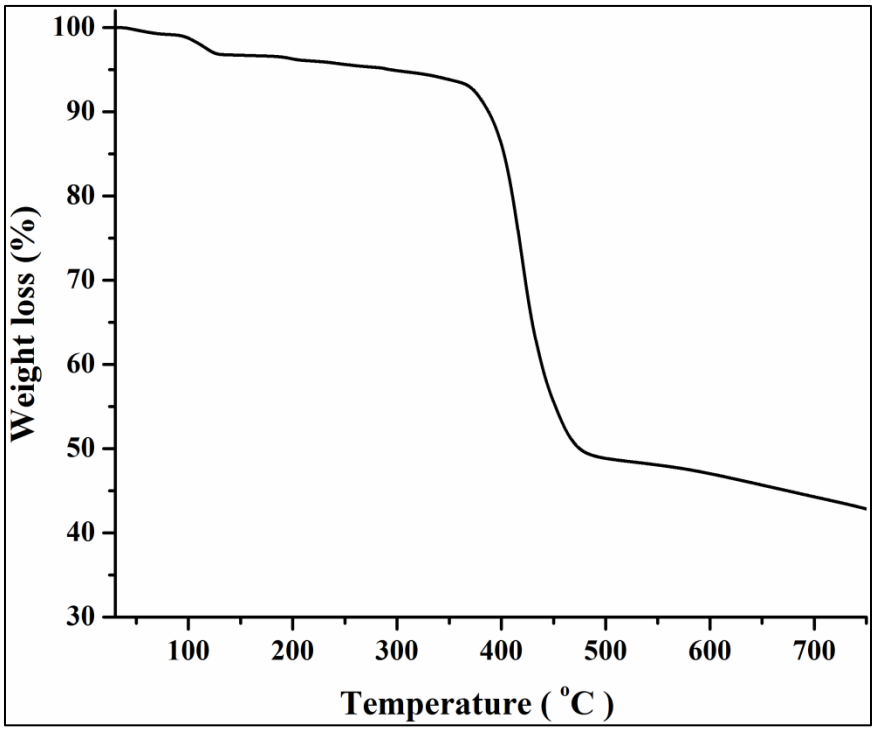


Fig. S15 TGA of CP **1.**

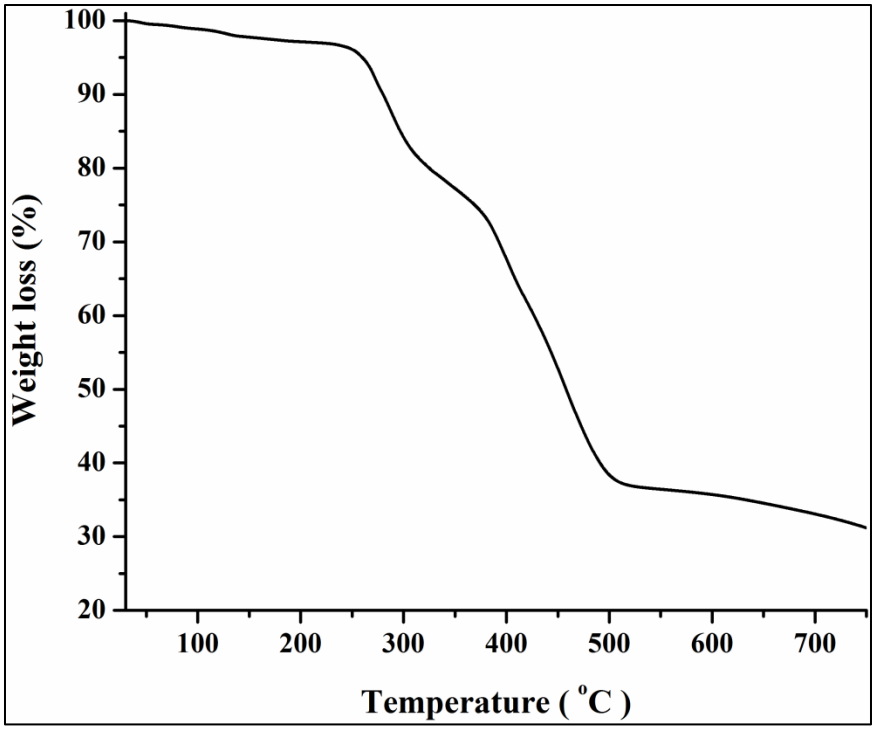


Fig. S16 TGA of CP **2.**

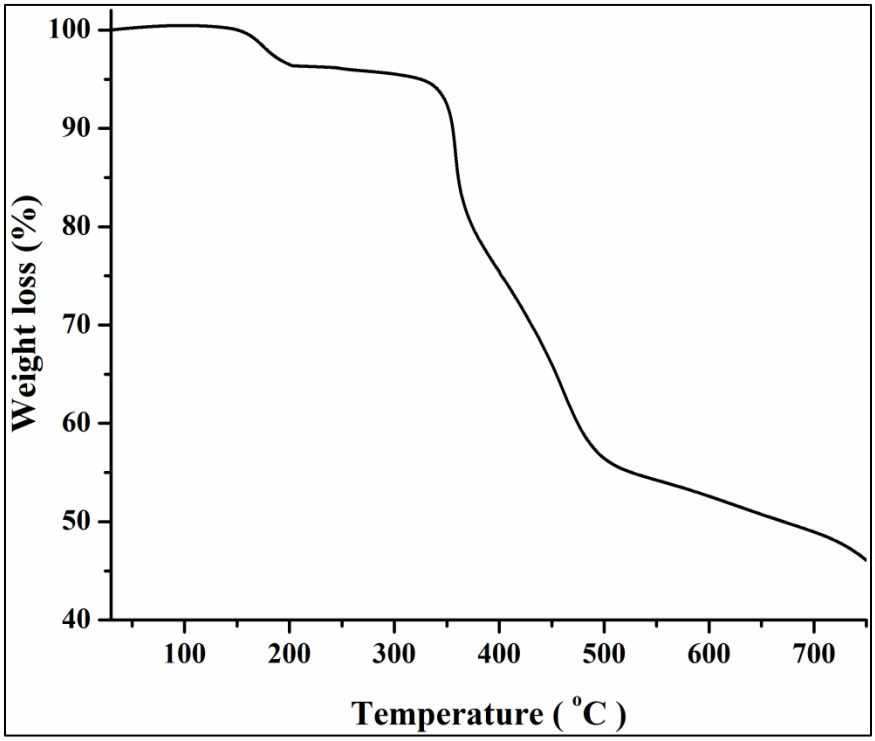


Fig. S17 TGA of CP **3.**

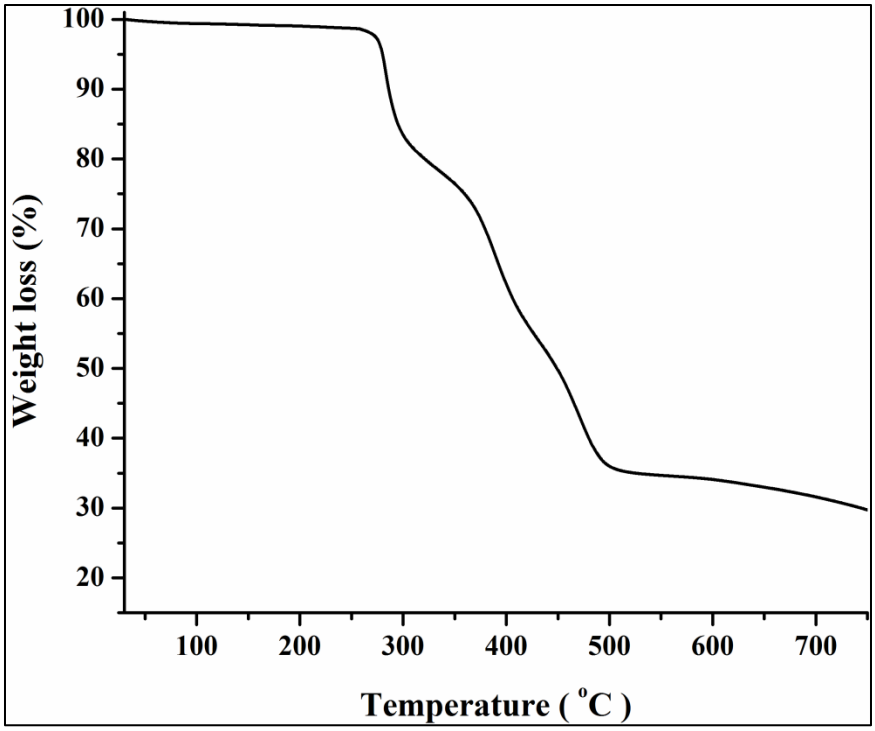


Fig. S18 TGA of CP **4.**

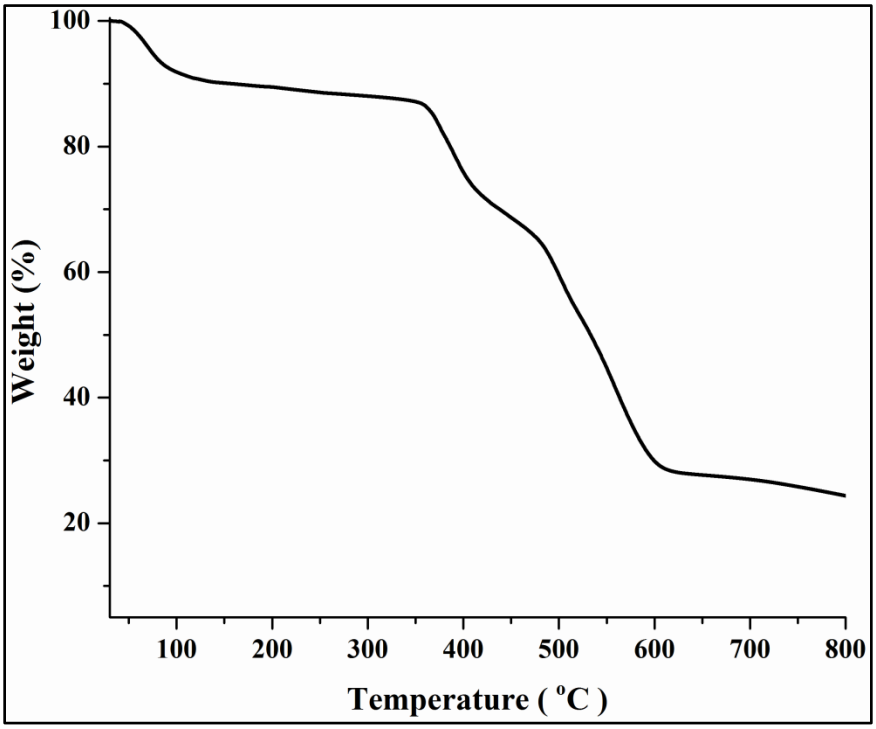


Fig. S19 TGA of CP **5.**

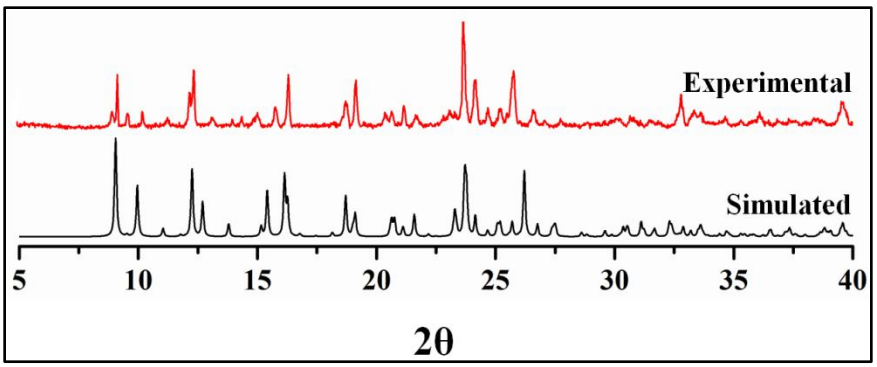


Fig. S20 PXRD of CP **1.**

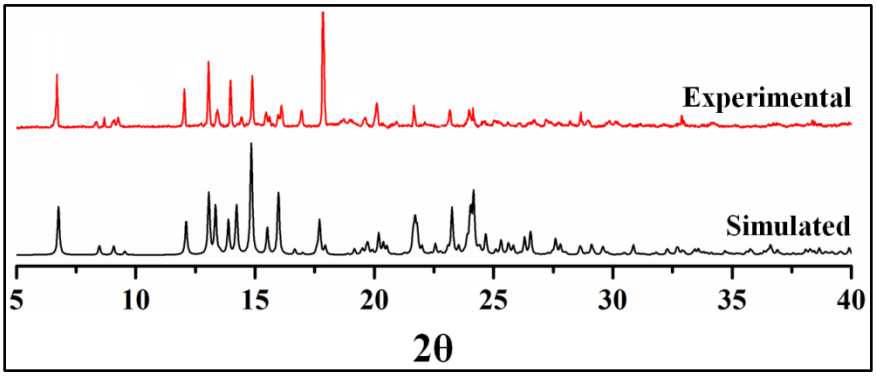


Fig. S21 PXRD of CP **2.**

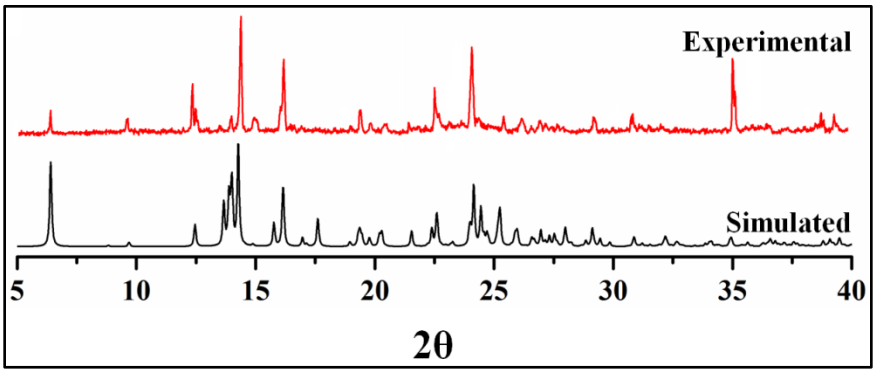


Fig. S22 PXRD of CP **3.**

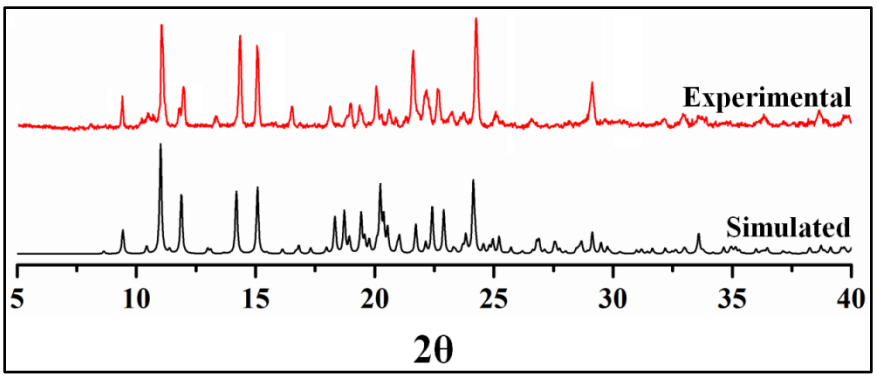


Fig. S23 PXRD of CP **4.**

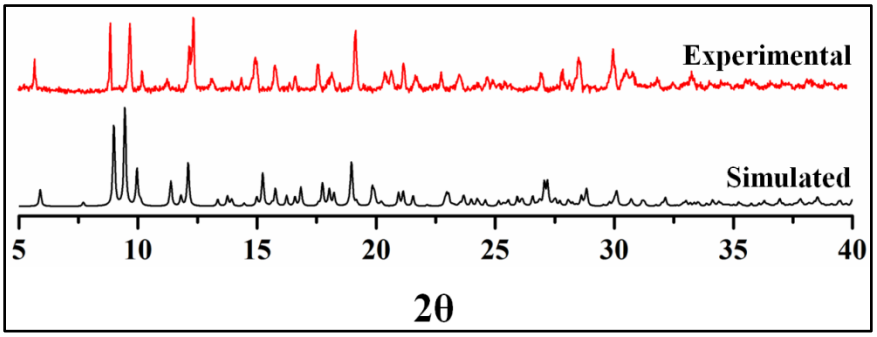


Fig. S24 PXRD of CP **5.**

Table S1. Crystal and Structure Refinement Data for CP 1–5.

Parameters	**CP-1**	**CP-2**	**CP-3**
Empirical formula	$C_{28}H_{21}Zn_2N_2O_9$	$C_{34}H_{29}ZnN_3O_8$	$C_{62}H_{44}Zn_2N_{12}O_{17}$
Formula wt.	660.25	672.99	1359.87
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$

a, Å	11.612(5)	13.8409(6)	14.513(5)
b, Å	18.565(5)	14.6035(6)	14.200(5)
c, Å	11.650(5)	15.7700(7)	14.873(5)
α (deg)	90	90	90
β (deg)	99.506(5)	109.2860(10)	108.193(5)
γ (deg)	90	90	90
U, Å^3	2477.0(16)	3008.6(2)	2911.9(17)
Z	4	4	2
ρ_{calc} g/cm^3	1.770	1.486	1.551
μ, mm^{-1}	2.000	0.876	0.910
Temperature (ºK)	100	100	100
θ_{max}	25.488	28.331	25.496
F(000)	1340	1392	1392
Refl. collected	20234	30020	23636
Independent refl.	4599	7495	5407
GOOF	1.155	1.038	1.021

Final R indices [I > 2σ(I)]	R1 = 0.0372 wR2 = 0.0923	R1 = 0.0827 wR2 = 0.1869	R1 = 0.0548 wR2 = 0.1146
R indices (all data)	R1 = 0.0587 wR2 = 0.1201	R1 = 0.1429 wR2 = 0.2241	R1 = 0.0852 wR2 = 0.1284

Parameters	**CP-4**	**CP-5**
Empirical formula	$C_{29}\,H_{24}\,Zn\,N_2\,O_7$	$C_{76}\,H_{60}\,Zn_5\,N_2\,O_{37}$
Formula wt.	577.89	1920.21
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P -1
a, Å	11.800(5)	10.2889(7)
b, Å	15.524(5)	11.9148(8)
c, Å	13.684(5)	15.1141(11)
α (deg)	90	91.109(2)
β (deg)	95.835(5)	96.935(2)
γ (deg)	90	105.482(2)
U, Å^3	2493.7(16)	1770.0(2)

Z	4	1
ρ_{calc} g/cm^3	1.539	1.801
μ, mm^{-1}	1.039	1.777
Temperature (ºK)	100	100
θ_{max}	25.500	28.361
F(000)	1192	976
Refl. collected	20282	27341
Independent refl.	4636	8828
GOOF	1.088	1.026
Final R indices [I > 2σ(I)]	R1 = 0.0444 wR2 = 0.09354	R1 = 0.0441 wR2 = 0.0990
R indices (all data)	R1 = 0.0731 wR2 = 0.1167	R1 = 0.0670 wR2 = 0.1085

Table S2 Selected Bond distances (Å) and angles (º)

$\{[Zn_2(L)(\mu\text{-}OH)(dpe)(H_2O)]\}_n$ (1)					
Bond Distances (Å)					
O8—Zn1	1.914(3)	O8—Zn2	1.971(3)	O3—Zn2	2.009(3)
O2W—Zn2	2.197(3)	O6—Zn1	1.981(3)	O1—Zn1	1.969(3)
O5—Zn2	2.091(3)	N1A—Zn1	2.078(3)	N2A—Zn2	2.090(3)
Bond Angles (°)					
Zn1-O8-Zn2	115.50(14)	O8-Zn1-N1A	103.85(12)	O8-Zn1-O6	111.86(12)
O8-Zn1-O1	118.19(11)	O6-Zn1-N1A	100.17(12)	O1-Zn1-N1A	107.64(12)
O1-Zn1-O6	112.94(12)	N2A-Zn2-O2W	105.80(12)	N2A-Zn2-O5	100.25(12)
O8-Zn2-N2A	93.78(12)	O8-Zn2-O3	167.75(11)	O8-Zn2-O2W	83.57(12)
O8-Zn2-O5	97.46(12)	O3-Zn2-N2A	97.19(12)	O3-Zn2-O2W	88.19(12)
O3-Zn2-O5	85.97(11)	O5-Zn2-O2W	153.82(11)		

$\{[Zn(L)(1,2\text{-}dpe)_{1.5})]\cdot H_2O\}_n$ (2)					
Bond Distances (Å)					
Zn1—O4	2.096(4)	Zn1—O1	1.992(4)	Zn1—O3	2.218(4)
Zn1—N2	2.067(4)	Zn1—N1	2.062(4)		
Bond Angles (°)					
O4-Zn1-O3	60.97(14)	O1-Zn1-O4	140.12(14)	O1-Zn1-O3	93.42(14)
O1-Zn1-N2	97.81(19)	O1-Zn1-N1	107.5(2)	N2-Zn1-O4	94.80(19)
N2-Zn1-O3	151.58(17)	N1-Zn1-O4	104.0(2)	N1-Zn1-O3	92.94(16)
N1-Zn1-N2	108.24(17)				

{[Zn(HL)(dpd)$_{1.5}$]$_2$·2(H$_2$O)}$_n$ (3)					
Bond Distances (Å)					
Zn1—O3A	2.002(3)	Zn1—N2A	2.068(3)	Zn1—O6A	2.427(4)
Zn1—N3A	2.061(3)	Zn1—O7A	2.017(3)	N4A—N5A	1.195(5)
Bond Angles (°)					
O3A-Zn1-N2A	99.93(12)	O3A-Zn1-O6A	156.45(13)	O3A-Zn1-N3A	101.20(12)
O3A-Zn1-O7A	104.50(13)	N2A-Zn1-O6A	89.19(13)	N3A-Zn1-N2A	105.52(13)
N3A-Zn1-O6A	97.13(13)	O7A-Zn1-N2A	141.17(15)	O7A-Zn1-O6A	57.73(14)
O7A-Zn1-N3A	98.83(13)				

{[Zn(HL)(1,3-dpp)]}$_n$ (4)					
Bond Distances (Å)					
Zn1—O7	2.265(3)	Zn1—O2	2.007(3)	Zn1—O6	2.067(3)
Zn1—N2	2.062(3)	Zn1—N1	2.066(3)		
Bond Angles (°)					
O2-Zn1-O7	132.80(10)	O2-Zn1-O6	105.42(11)	O2-Zn1-N2	103.32(11)
O2-Zn1-N1	94.83(11)	O6-Zn1-O7	60.45(11)	N2-Zn1-O7	86.45(11)
N2-Zn1-O6	145.87(11)	N2-Zn1-N1	100.21(11)	N1-Zn1-O7	129.25(11)
N1-Zn1-O6	95.33(11)				

{[Zn$_5$(L)$_4$(H$_2$O)]·(H$_2$O)$_8$(1,2-dpe)}$_n$ (5)					
Bond Distances (Å)					
Zn2—O12	2.199(2)	Zn2—O1	2.015(2)	Zn2—O5	2.110(2)
Zn1—O12	2.088(2)	Zn1—O6	2.004(2)	Zn1—O3	1.995(2)

Zn1—O2	1.964(2)	Zn1—O11	2.300(2)	Zn3—O9	2.020(2)
Zn3—O15	1.991(2)	Zn3—O8	2.097(2)	Zn3—O7	2.051(2)
Zn3—O10	2.022(2)	Zn3—Zn3	2.9684(7)		
Bond Angles (°)					
O12-Zn2-O12	180.0	O1-Zn2-O12	90.38(8)	O1-Zn2-O1	180.0
O1-Zn2-O5	95.50(9)	O5-Zn2-O12	92.05(8)	O5-Zn2-O5	180.00(10)
O12-Zn1-O11	59.60(8)	O6-Zn1-O12	104.59(9)	O6-Zn1-O11	92.44(9)
O3-Zn1-O12	142.69(9)	O3-Zn1-O6	104.95(9)	O3-Zn1-O11	96.86(9)
O2-Zn1-O12	101.96(9)	O2-Zn1-O6	102.04(10)	O2-Zn1-O3	93.63(9)
O2-Zn1-O11	159.30(9)	O9-Zn3-Zn3	78.10(6)	O9-Zn3-O8	88.00(9)
O9-Zn3-O7	88.12(10)	O9-Zn3-O10	158.76(9)	O15-Zn3-Zn3	168.65(8)
O15-Zn3-O9	103.12(10)	O15-Zn3-O8	98.73(10)	O15-Zn3-O7	102.12(10)
O15-Zn3-O10	98.11(10)	O8-Zn3-Zn3	69.97(6)	O7-Zn3-Zn3	89.17(7)
O7-Zn3-O8	159.13(9)	O10-Zn3-Zn3	80.95(7)	O10-Zn3-O8	88.13(10)
O10-Zn3-O7	88.10(10)	Zn1-O12-Zn2	105.31(9)		

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