Cd(II) Coordination Polymers Built with a Flexible Carboxylate Linker and Pyridyl Co-linkers: Variation in Network Topologies and Photoluminescence Properties

*Anoop K. Gupta, Kapil Tomar and Parimal K. Bharadwaj**

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India.

Email: pkb@iitk.ac.in

EXPERIMENTAL SECTION

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), 4,4′-bipyridyl (4,4′-bpy) and $Cd(NO_3)_2 \cdot 4H_2O$ 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.

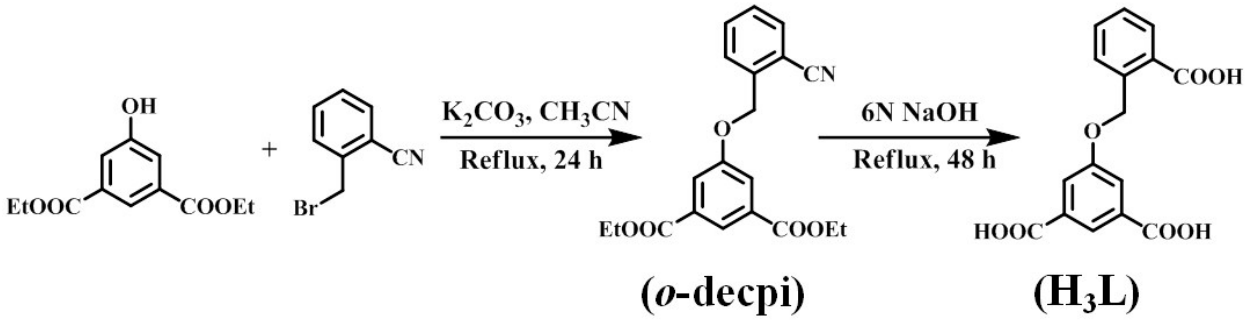
Physical Measurement. Infrared spectra were recorded on Perkin-Elmer Model 1320 spectrometer (KBr disk, 400–4000 cm^{-1}). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL-ECX 500 FT (500 MHz and 125 MHz respectively) instrument in$CDCl_3$ and DMSO-d_6 with Me_4Si as the internal standard. ESI-mass 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.

X-ray Structural Studies. The details of single-crystal X-ray analysis were carried out as described earlier.[1] The calculations to solve the structures and to refine the model proposed were carried out with the programs SHELXS[2] and SHELXL2014.[3] All non-hydrogen atoms in **1–6** were refined anisotropically. In compound **2** atoms C29 and C30 are non-positive definite. The H-atoms attached to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters. For **2**, squeeze refinement was performed using PLATON[4] and the molecular formula was assigned using elemental data, TGA and squeeze details. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center and CCDC numbers: 1527973-1527978. Lattice parameters of the **1–6**, data collection and refinement parameters are summarized in Table S1 and selected bond distances and bond angles are given in Table S2.

Synthesis of the ligand (H_3L)

This reported ligand H_3L (scheme 1) was synthesized by following a previously reported procedure[5] with a slight modification in the reactant, and the pyridyl-based ligand dpd was synthesized according to the literature procedure[6] 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 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%.

Elemental analysis and IR of compound 1-6

Compound **1** Anal. Calcd for $C_{32}H_{42}Cd_3O_{26}$: C, 32.57; H, 3.58%. Found: C, 32.42; H, 3.63%. IR (cm^{-1}): 3445(broad), 2926(m), 1610(s), 1580(s), 1555(m), 1449(m), 1384(sh), 1265(s), 1104(sh), 1058(m), 994(m), 775(sh), 736(sh), 475(m).

Compound **2** Anal. Calcd for $C_{62.5}H_{55.5}Cd_3N_{6.5}O_{18.5}$: C, 49.82; H, 3.60; N, 5.86%. Found: C, 49.67; H, 3.73; N, 5.79%. IR (cm^{-1}): 3407(broad), 2906(m), 2486(m), 1617(s), 1559(s), 1448(m), 1378(s), 1261(m), 1129(m), 1079(m), 1041(m), 964(m), 836(m), 782(s), 733(s), 548(s).

Compound **3** Anal. Calcd for $C_{44}H_{36}Cd_2N_2O_{17}$: C, 48.50; H, 3.33; N, 2.57%. Found: C, 48.66; H, 3.26; N, 2.48%. IR (cm^{-1}): 3407(broad), 3084(m), 1729(s), 1608(s), 1559(s), 1504(m), 1448(m), 1378(s), 1261(m), 1129(m), 1079(m), 1041(m), 964(m), 836(m), 782(s), 733(s).

Compound **4** Anal. Calcd for $C_{21}H_{16}CdN_2O_8$: C, 46.98; H, 3.01; N, 5.22%. Found: C, 46.61; H, 3.14; N, 5.11%. IR (cm^{-1}): 3407(broad), 3083(m), 1727(s), 1605(m), 1559(s), 1492(m), 1449(m), 1377(s), 1260(s), 1129(m), 1039(s), 933(m), 856(s), 781(s), 733(s).

Compound **5** Anal. Calcd for $C_{22}H_{16}CdNO_7$: C, 50.93; H, 3.11; N, 2.70%. Found: C, 51.07; H, 3.26; N, 2.81%. IR (cm^{-1}): 3071(m), 2929(m), 1703(m), 1671(m) 1604(m), 1548(s), 1450(m), 1369(s), 1241(m), 1145(m), 1053(s), 930(m), 885(m), 830(m), 798(s), 726(s).

Compound **6** Anal. Calcd for $C_{58}H_{52}Cd_3N_4O_{17}$: C, 49.25; H, 3.70; N, 3.96%. Found: C, 48.87; H, 3.38; N, 4.17%. IR (cm^{-1}): 3496(broad), 3072(m), 2927(m), 1961(s), 1816(s), 1567(s), 1504(m), 1447(m), 1405(s), 1367(s), 1323(m), 1230(m), 1152(m), 1040(s), 994(m), 801(s), 775(s,) 724(s).

Result and Discussion

The compounds **1–6** were easily synthesized adopting the solvothermal technique at 130 °C for 48 h. Once isolated, all the compounds were found to be stable in air and insoluble in common organic solvents and water. All the compounds were formulated by single-crystal X-ray diffraction and further corroborated by TGA and elemental analysis. The phase purity of **1–6** were confirmed by comparing the experimental and simulated powder X-ray diffraction patterns. The IR spectra (Fig. S9–S14) of the compounds except **5** show a broad peak in the range of 3230–3560 cm^{-1}, indicating the presence of lattice and coordinated water molecules[7] while in **5** no such band is observed. Besides, strong absorption bands observed between 1400–1600 cm^{-1} in **1-6** are diagnostic of coordinated carboxylate groups.[8] In **2**, sharp peaks between 1610 and 1650 cm^{-1} are indicative of the presence of DEF molecules.[9] In **3**, **4**, and **5**, a band in the region 1690–1730 cm^{-1} suggests the presence of a protonated carboxylate group.[10] The peak in the range of 1604–1629 cm^{-1} corresponds to the presence of –N=N– in **4**.[11]

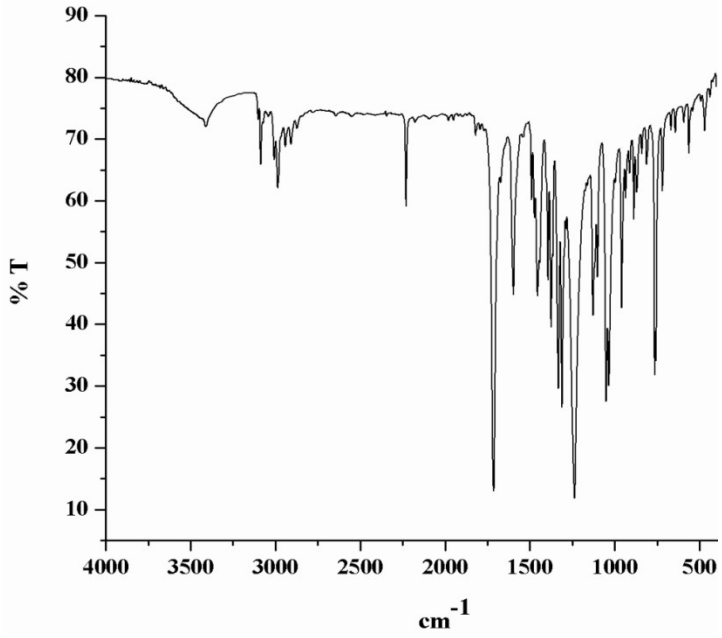


Fig. S1 IR Spectrum of *o*-decpi.

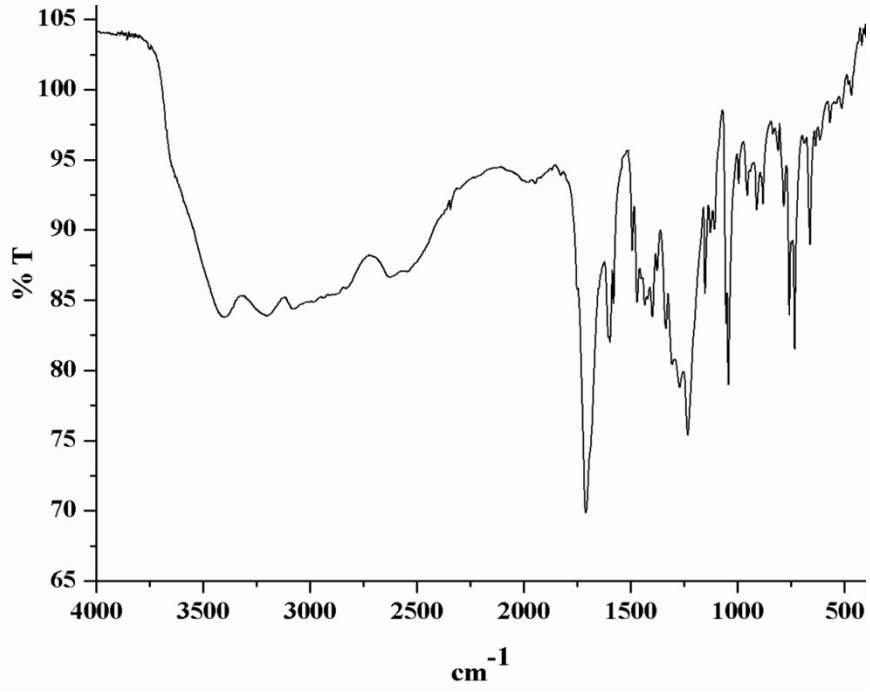


Fig. S2 IR Spectrum of H_3L.

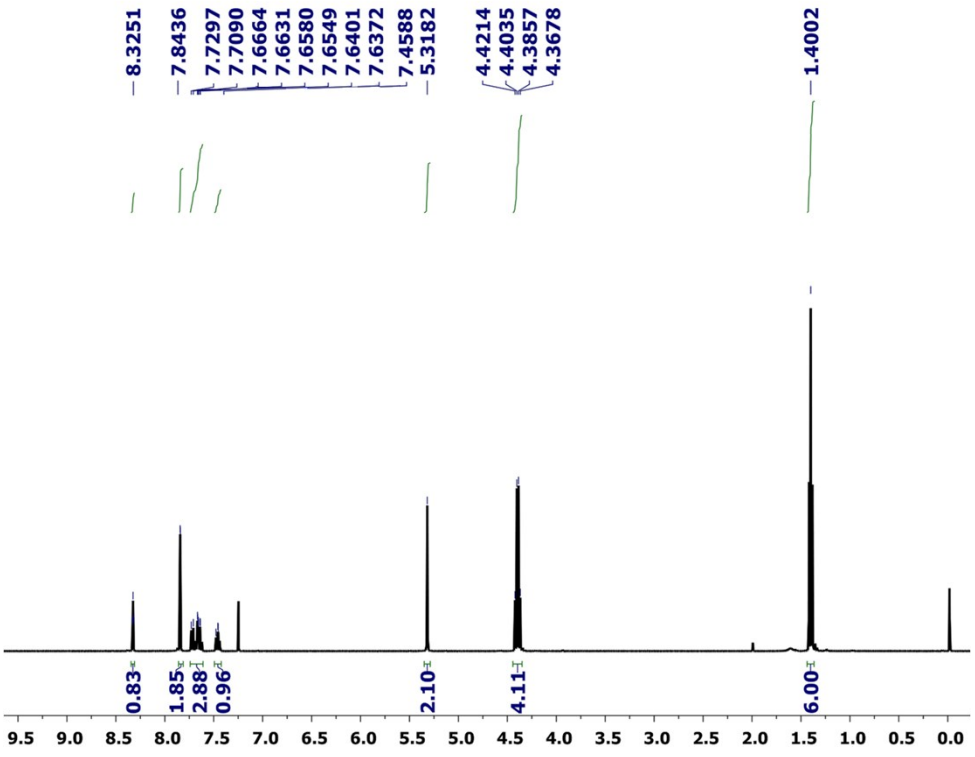


Fig. S3 ^{1}H NMR spectrum of *o*-decpi.

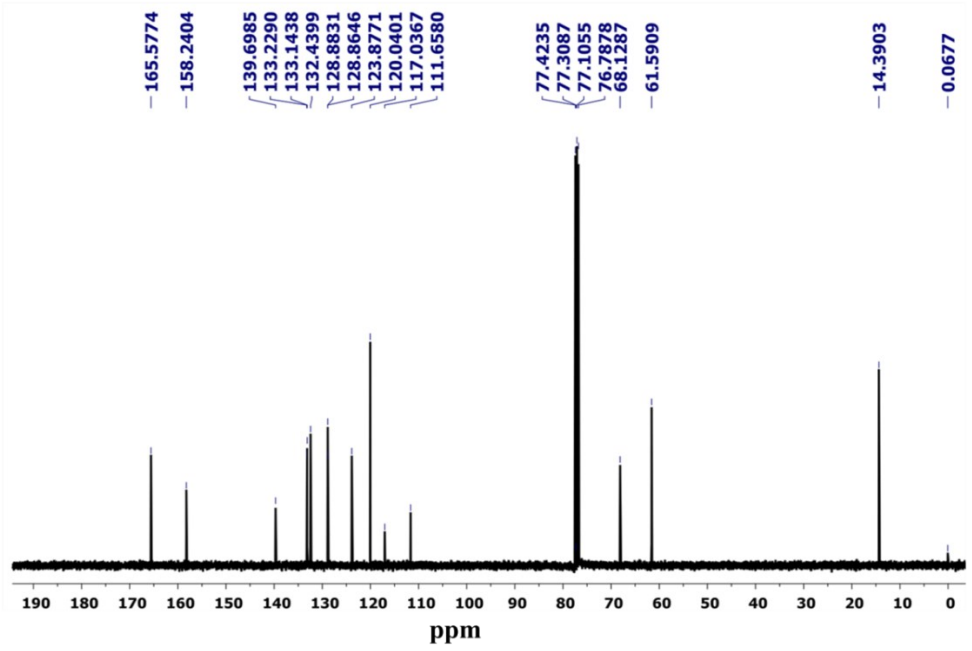


Fig. S4 ^{13}C NMR spectrum of *o*-decpi.

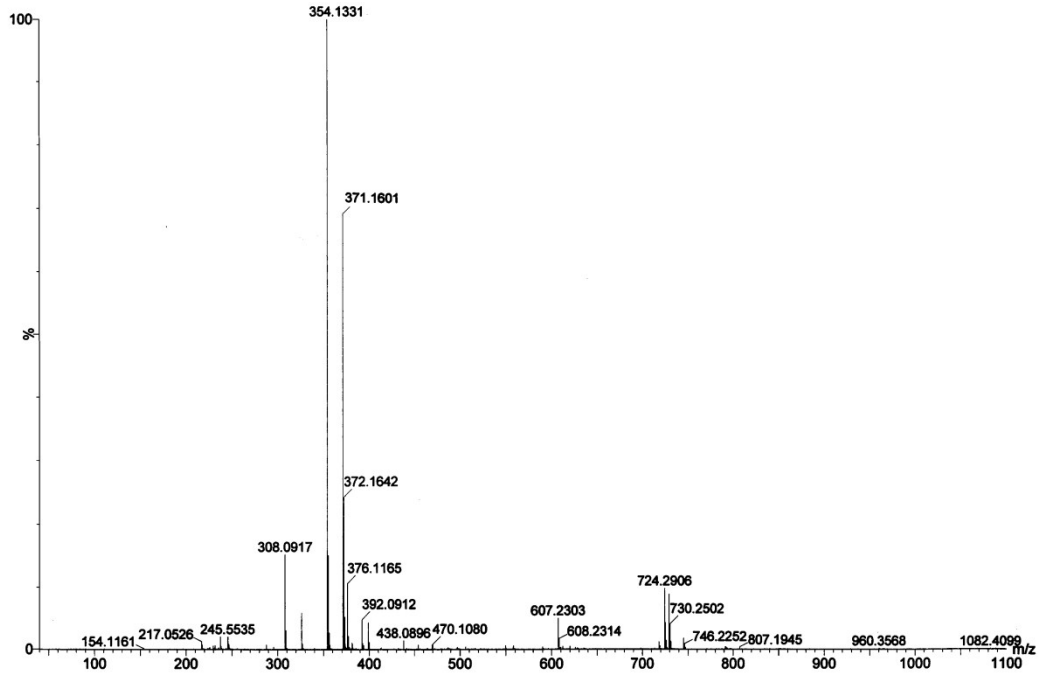


Fig. S5 ESI-MS spectrum of *o*-decpi.

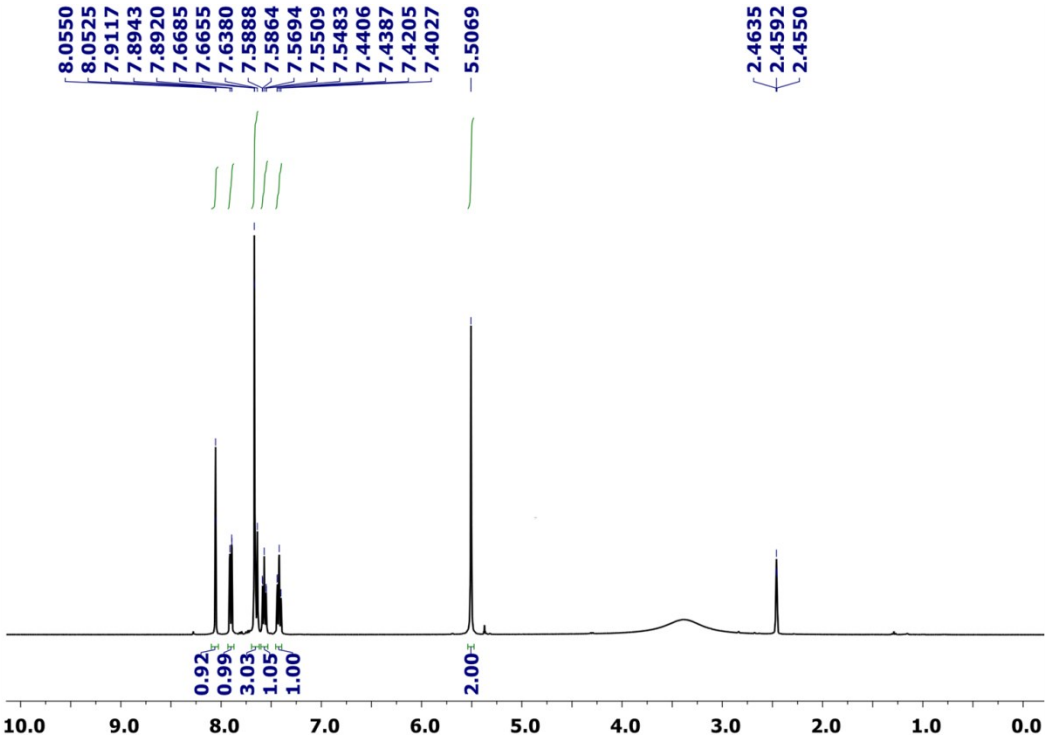


Fig. S6 ^{1}H NMR spectrum of H_3L.

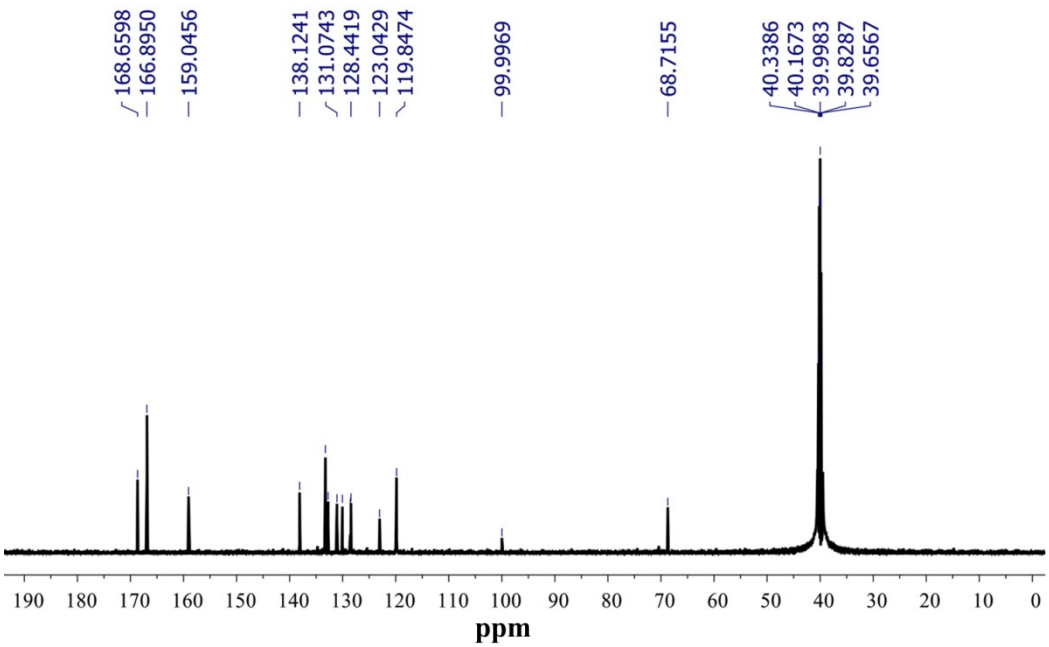


Fig. S7 ^{13}C NMR spectrum of H_3L.

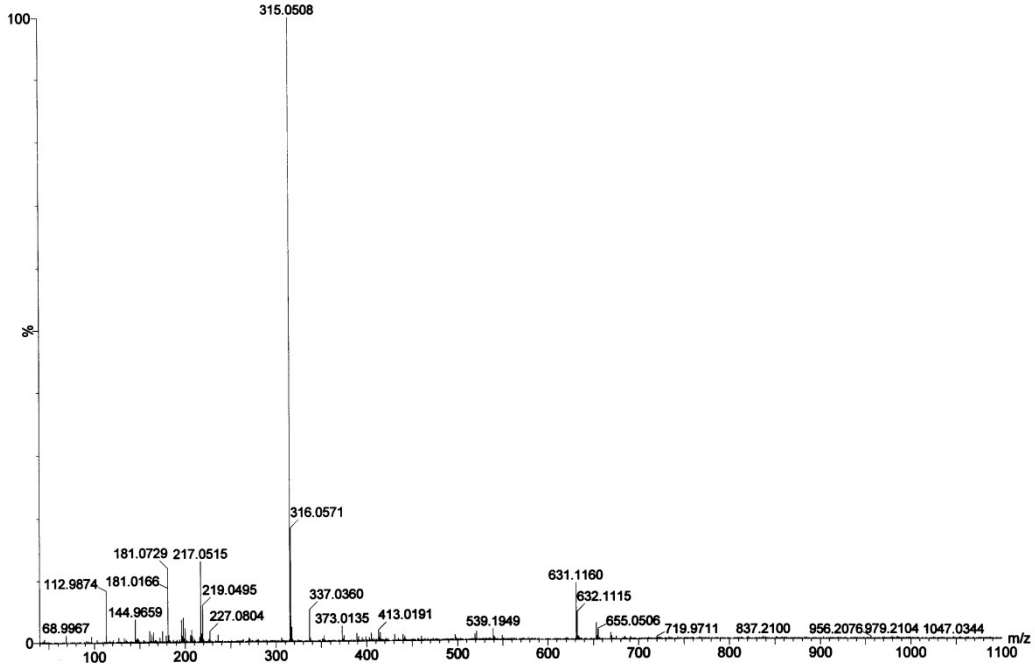


Fig. S8 ESI-MS spectrum of H_3L.

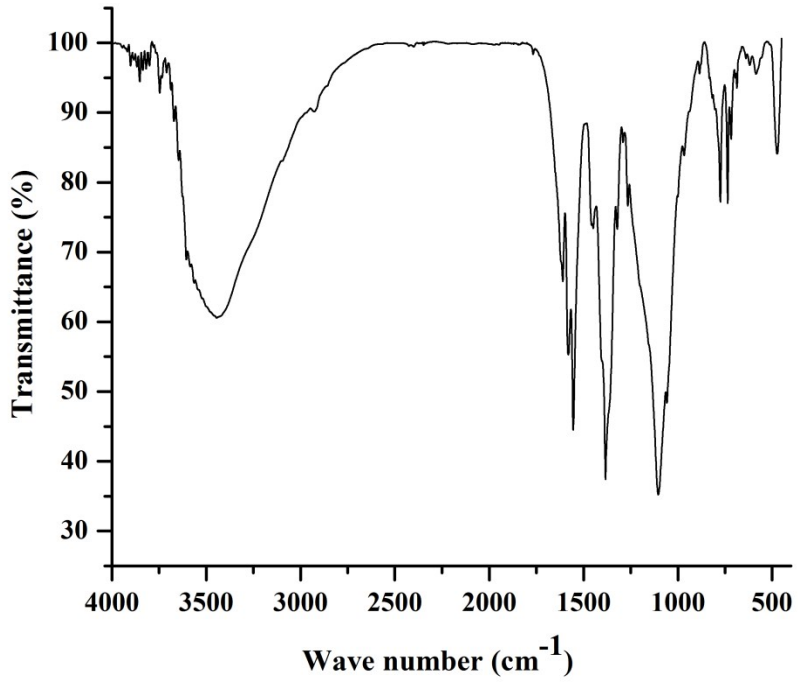


Fig. S9 IR spectrum of **1.**

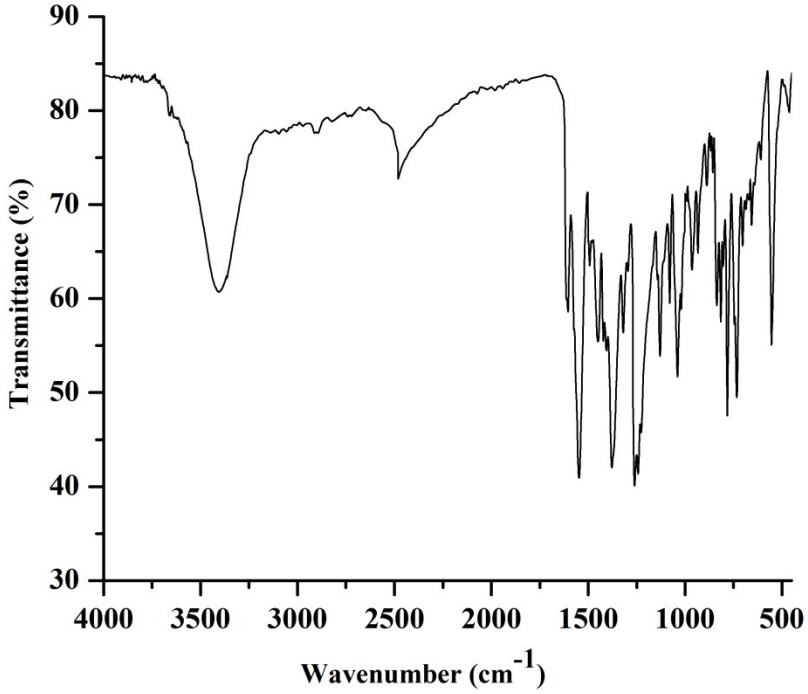


Fig. S10 IR spectrum of **2.**

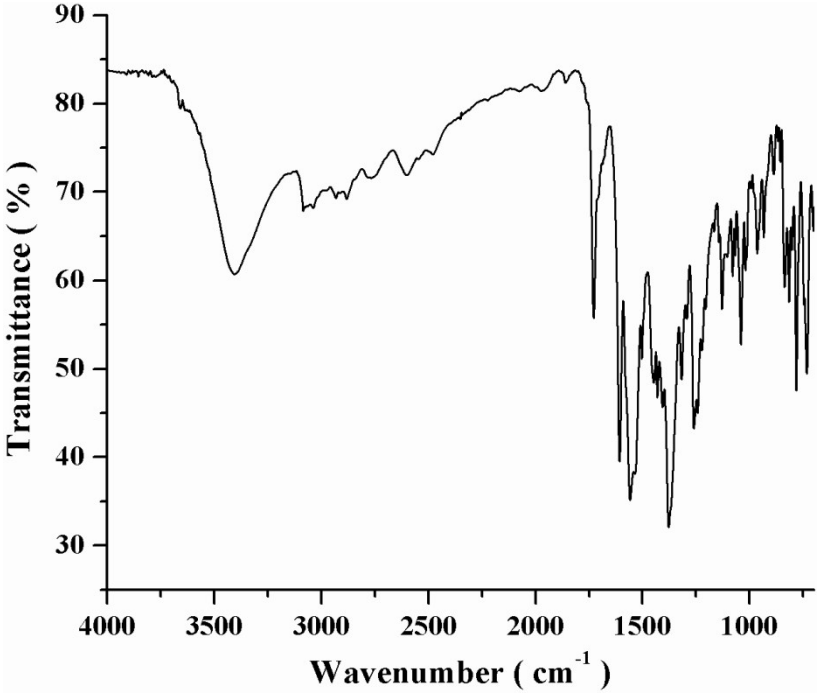


Fig. S11 IR spectrum of **3.**

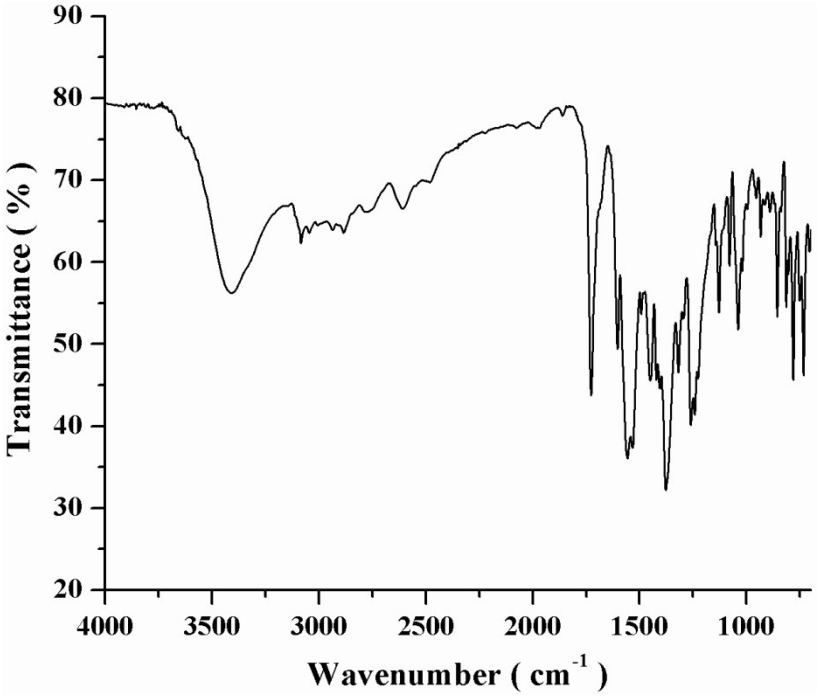


Fig. S12 IR spectrum of **4.**

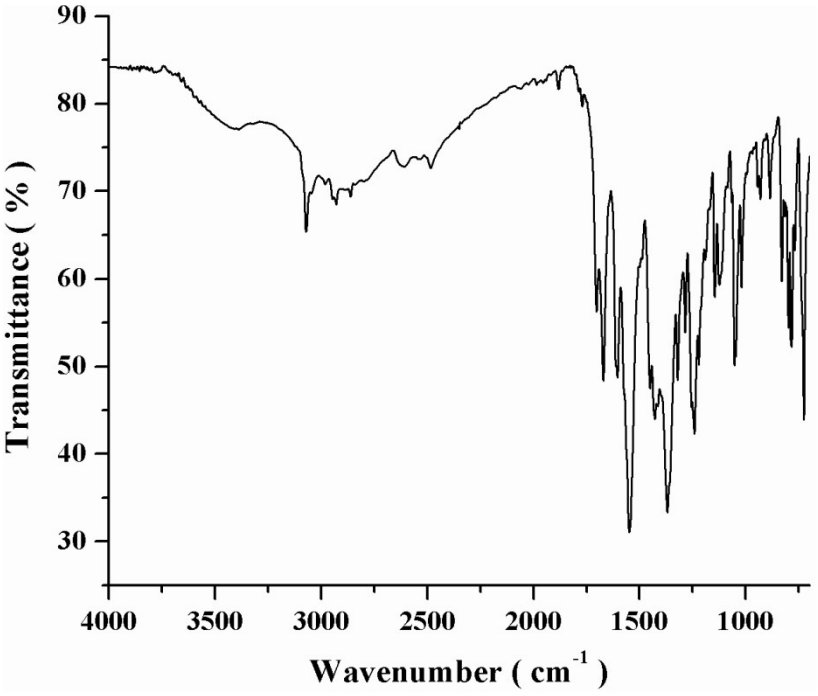


Fig. S13 IR spectrum of **5.**

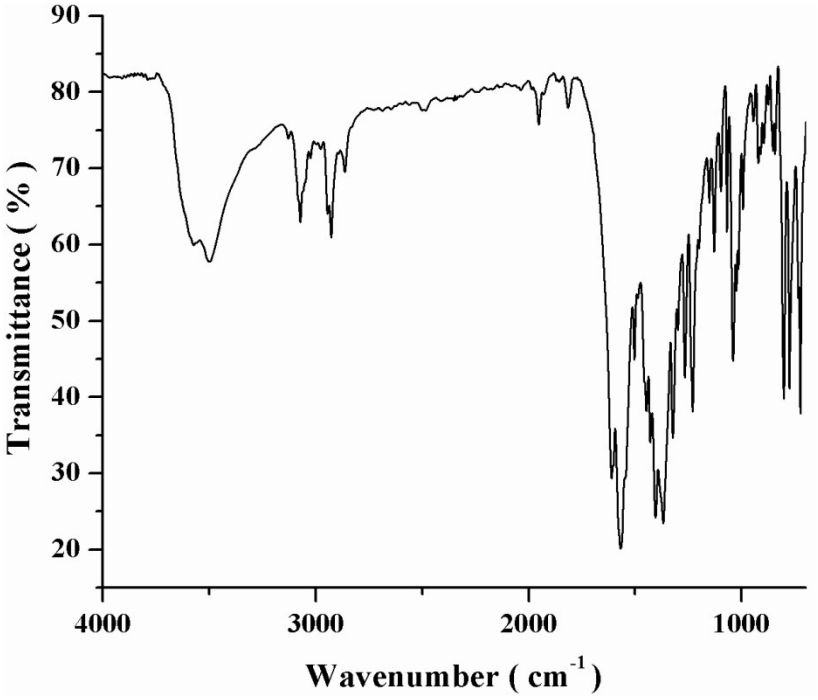


Fig. S14 IR spectrum of **6.**

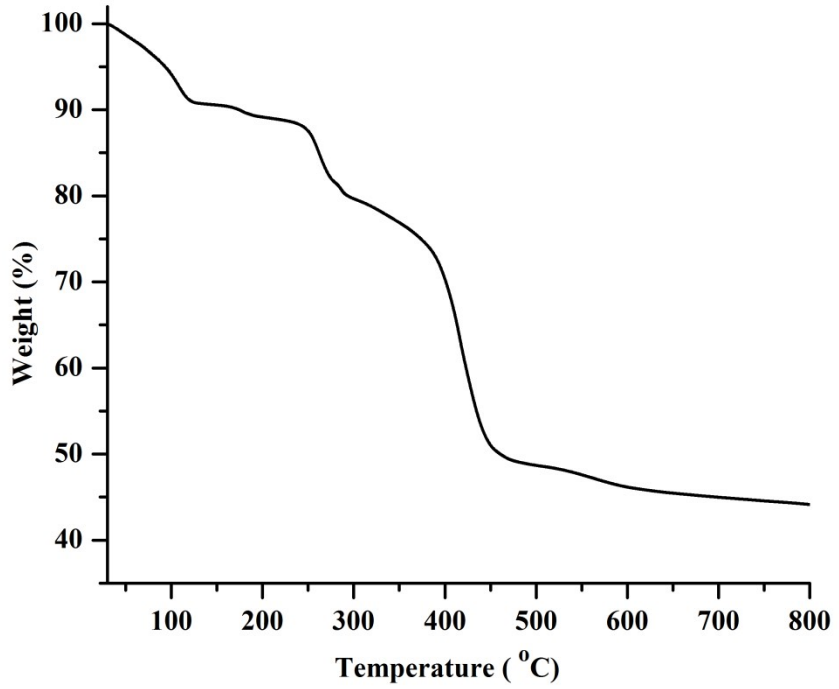


Fig. S15 TGA of **1.**

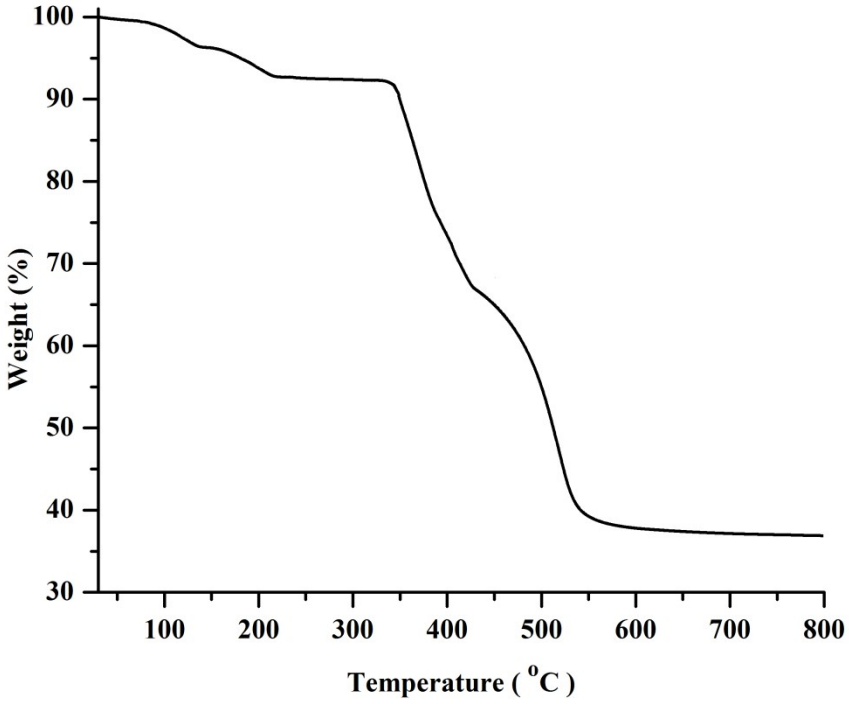


Fig. S16 TGA of **2.**

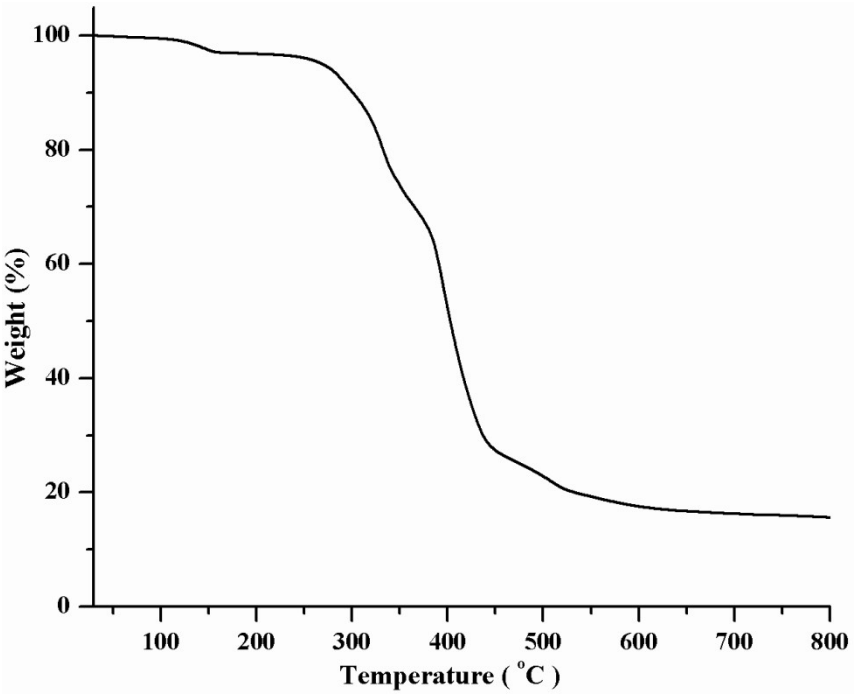


Fig. S17 TGA of **3.**

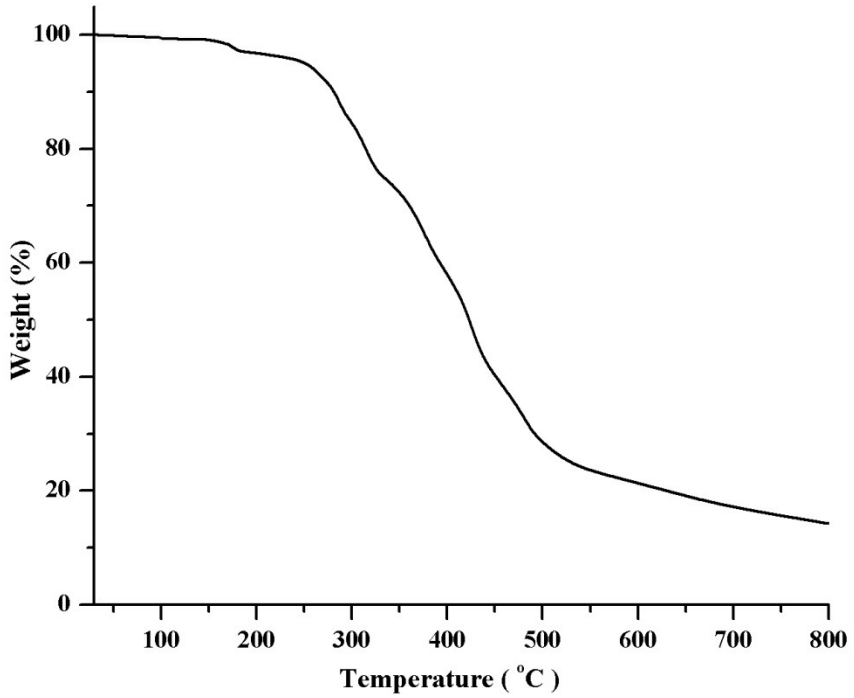


Fig. S18 TGA of **4.**

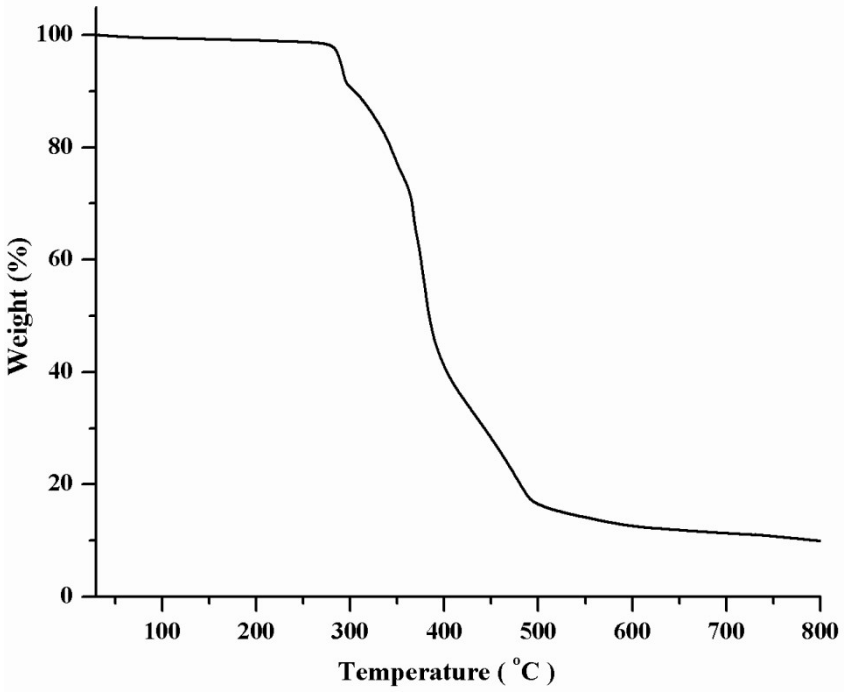


Fig. S19 TGA of **5.**

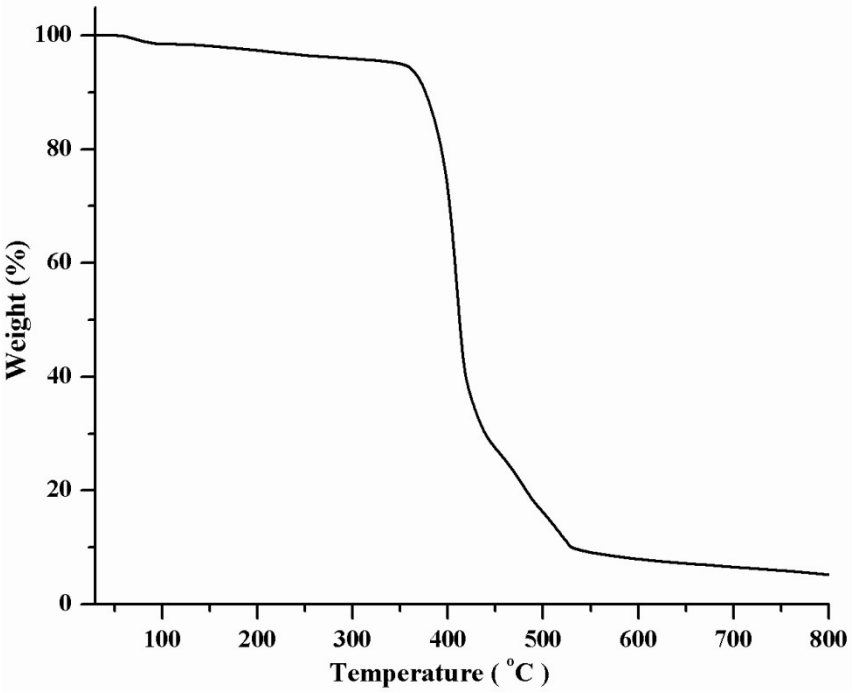


Fig. S20 TGA of **6.**

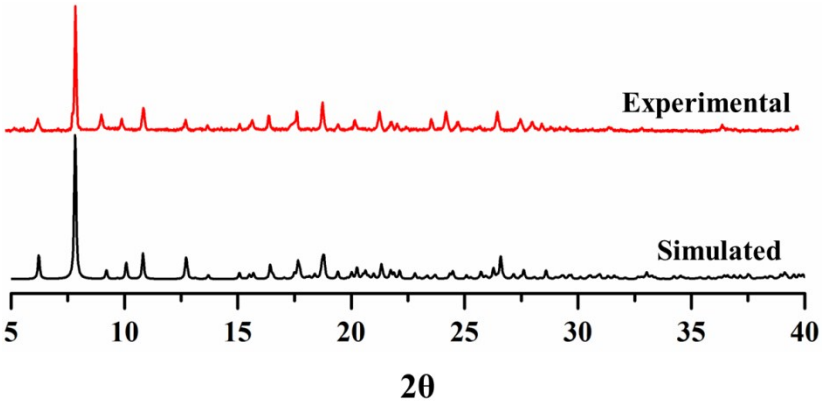


Fig. S21 PXRD of **1.**

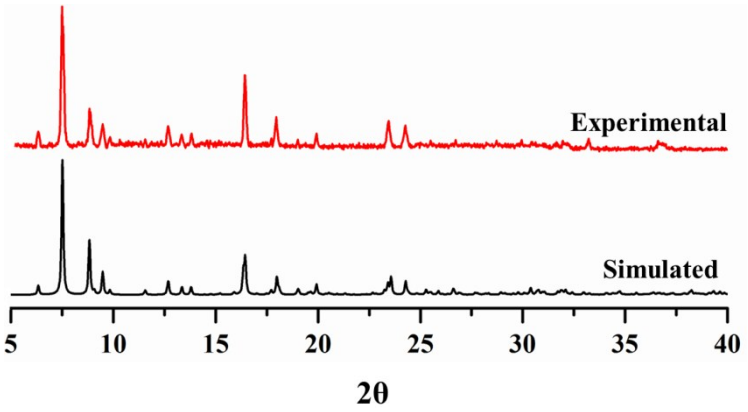


Fig. S22 PXRD of **2.**

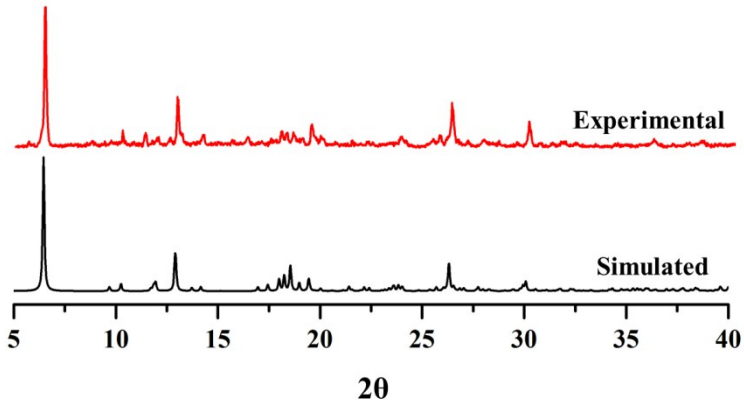


Fig. S23 PXRD of **3.**

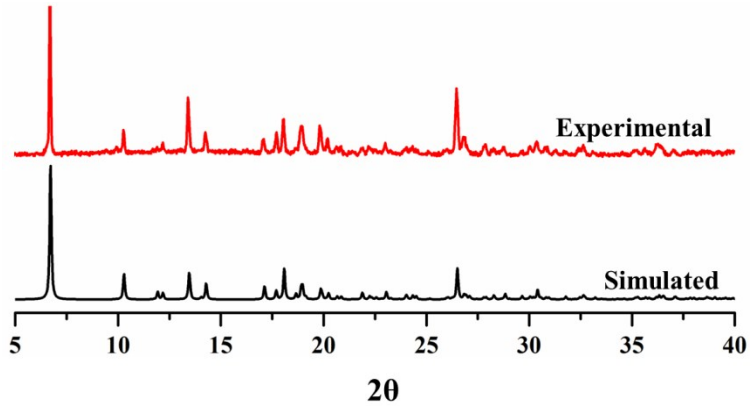


Fig. S24 PXRD of **4.**

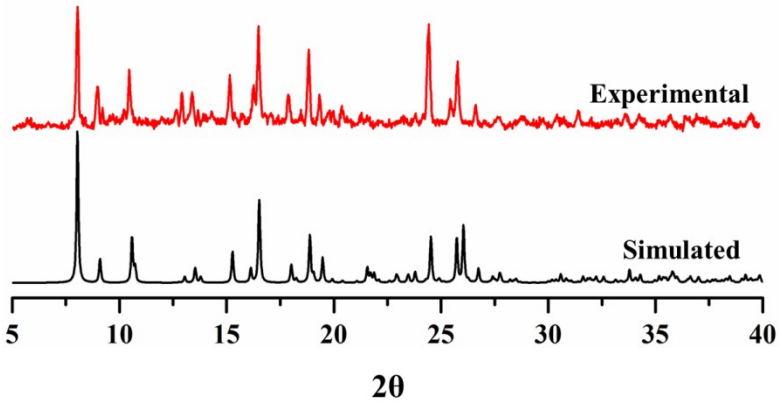


Fig. S25 PXRD of **5.**

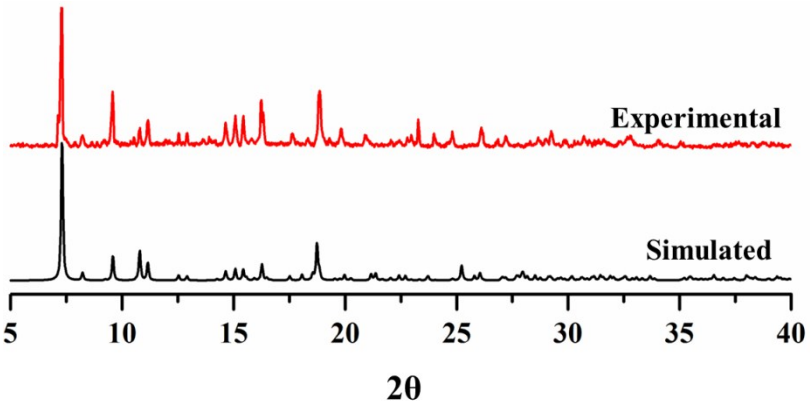


Fig. S26 PXRD of **6.**

Table S1. Crystal and Structure Refinement Data for 1–6.

Parameters	**Compound 1**	**Compound 2**	**Compound 3**
Empirical formula	$C_{32}H_{40}Cd_3O_{26}$	$C_{62}H_{46}Cd_3N_6O_{16}$	$C_{44}H_{34}Cd_2N_2O_{17}$
Formula wt.	1177.87	1468.28	1087.55
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_12_12_1$	$P2/c$	P-1
a, Å	9.995(5)	16.164(5)	8.363(9)
b, Å	18.248(5)	11.755(5)	10.188(11)
c, Å	22.570(5)	20.199(4)	14.322(15)
α (deg)	90	90	98.845(15)
β (deg)	90	120.402(17)	100.165(14)
γ (deg)	90	90	112.564(12)
U, Å^3	4117(3)	3310.2(19)	1076(2)
Z	4	2	1
ρ_{calc} g/cm^3	1.900	1.473	1.678
μ, mm^{-1}	1.630	1.022	1.064
Temperature (ºK)	100	100	100

θ_{max}	25.50	25.50	25.11
F(000)	2336	1464	544
Refl. collected	32964	24013	5434
Independent refl.	7661	6170	3831
GOOF	1.080	1.007	1.148
Final R indices [I > 2σ(I)]	R1 = 0.0388 wR2 = 0.0900	R1 = 0.0593 wR2 = 0.1532	R1 = 0.0467 wR2 = 0.1106
R indices (all data)	R1 = 0.0511 wR2 = 0.0972	R1 = 0.0961 wR2 = 0.1683	R1 = 0.0640 wR2 = 0.1441
Parameters	**Compound 4**	**Compound 5**	**Compound 6**
Empirical formula	$C_{21}H_{16}CdN_2O_8$	$C_{22}H_{16}CdNO_7$	$C_{58}H_{52}Cd_3N_4O_{17}$
Formula wt.	536.77	518.77	1414.27
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
a, Å	8.322(5)	8.418(5)	9.904(5)
b, Å	10.111(5)	10.214(5)	11.945(5)

c, Å	14.048(5)	11.382(5)	13.078(5)
α (deg)	99.667(5)	75.111(5)	69.194(5)
β (deg)	102.545(5)	83.956(5)	75.412(5)
γ (deg)	113.317(5)	78.582(5)	70.291(5)
U, Å^3	1016.2(9)	925.5(8)	1346.1(10)
Z	2	2	1
ρ_{calc} g/cm^3	1.754	1.862	1.745
μ, mm^{-1}	1.128	1.230	1.253
Temperature (ºK)	100	100	100
θ_{max}	25.49	26	25
F(000)	536	518	708
Refl. collected	9809	12020	16441
Independent refl.	3778	3641	4723
GOOF	1.071	1.053	1.028
Final R indices [I > 2σ(I)]	R1 = 0.0642 wR2 = 0.1858	R1 = 0.0360 wR2 = 0.0843	R1 = 0.0466 wR2 = 0.0899

R indices (all data)	R1 = 0.0838 wR2 = 0.2000	R1 = 0.0448 wR2 = 0.0888	R1 = 0.0871 wR2 = 0.1021

Table S2 Bond distances and angles

$\{[Cd_3(L)_2(H_2O)_5(\mu\text{-}H_2O)]\cdot 6H_2O\}_n$ **(1)**					
Bond Distances (Å)					
Cd1—O23	2.264(5)	Cd1—O24	2.268(4)	Cd1—O9	2.314(5)
Cd1—O27	2.361(4)	Cd1—O10^{i}	2.363(4)	Cd1—O11^{i}	2.388(4)
Cd1—O8	2.510(4)	Cd2—O20	2.273(5)	Cd2—O22	2.278(5)
Cd2—O21	2.291(4)	Cd2—O18	2.340(5)	Cd2—O16^{ii}	2.359(4)
Cd2—O17^{ii}	2.496(5)	Cd2—O19	2.566(4)	Cd3—O8^{iii}	2.252(4)
Cd3—O12	2.252(4)	Cd3—O15	2.289(5)	Cd3—O19^{iv}	2.304(4)
Cd3—O14	2.397(4)	Cd3—O13	2.547(5)	Cd3—O27^{iii}	2.612(5)
Bond Angles (°)					
O23-Cd1-O24	175.34(17)	O24-Cd1-O10^{i}	88.40(16)	O10^{i}-Cd1-O11^{i}	54.89(15)
O23-Cd1-O9	93.34(19)	O9-Cd1-O10^{i}	88.05(16)	O23-Cd1-O8	85.25(17)
O24-Cd1-O9	90.72(17)	O27-Cd1-O10^{i}	144.84(16)	O24-Cd1-O8	99.01(15)
O23-Cd1-O27	95.51(18)	O23-Cd1-O11^{i}	91.03(17)	O9-Cd1-O8	54.19(15)
O24-Cd1-O27	83.93(16)	O24-Cd1-O11^{i}	84.34(16)	O27-Cd1-O8	73.85(15)

O9-Cd1-O27	126.19(16)	O9-Cd1-O11^{i}	142.65(15)	O10^{i}-Cd1-O8	141.32(15)
O23-Cd1-O10^{i}	89.44(18)	O27-Cd1-O11^{i}	90.15(16)	O11^{i}-Cd1-O8	163.10(15)
O20-Cd2-O22	176.93(17)	O22-Cd2-O16^{ii}	88.82(16)	O16^{ii}-Cd2-O17^{ii}	53.71(16)
O20-Cd2-O21	92.76(17)	O21-Cd2-O16^{ii}	137.22(17)	O20-Cd2-O19	90.74(16)
O22-Cd2-O21	88.96(16)	O18-Cd2-O16^{ii}	89.44(16)	O22-Cd2-O19	87.02(15)
O20-Cd2-O18	85.24(18)	O20-Cd2-O17^{ii}	96.04(17)	O21-Cd2-O19	80.72(15)
O22-Cd2-O18	91.73(17)	O22-Cd2-O17^{ii}	86.68(16)	O18-Cd2-O19	52.75(14)
O21-Cd2-O18	133.33(16)	O21-Cd2-O17^{ii}	83.51(16)	O16^{ii}-Cd2-O19	141.75(15)
O20-Cd2-O16^{ii}	91.64(17)	O18-Cd2-O17^{ii}	143.12(15)	O17^{ii}-Cd2-O19	163.11(15)
O8^{iii}-Cd3-O12	89.54(17)	O15-Cd3-O14	55.57(16)	O8^{iii}-Cd3-O27^{iii}	73.63(15)
O8^{iii}-Cd3-O15	105.65(19)	O19^{iv}-Cd3-O14	83.74(16)	O12-Cd3-O27^{iii}	73.11(15)
O8^{iii}-Cd3-O19^{iv}	157.63(17)	O8^{iii}-Cd3-O13	83.73(16)	O15-Cd3-O27^{iii}	78.06(16)
O12-Cd3-O19^{iv}	89.61(16)	O12-Cd3-O13	54.76(15)	O19^{iv}-Cd3-O27^{iii}	127.20(15)
O15-Cd3-O19^{iv}	88.48(18)	O15-Cd3-O13	158.93(16)	O14-Cd3-O27^{iii}	124.55(15)
O8^{iii}-Cd3-O14	90.02(16)	O19^{iv}-Cd3-O13	77.58(15)	O13-Cd3-O27^{iii}	122.97(14)
O12-Cd3-O14	161.26(15)	O14-Cd3-O13	106.59(15)	O12-Cd3-O15	141.99(17)
Cd1-O27-Cd3^{iv}	100.38(17)	Cd3^{iii}-O19-Cd2	129.71(19)	Cd3^{iv}-O8-Cd1	106.71(17)

Symmetry Code :

(i) 2-x, 0.5+y, 1.5-z; (ii) -1-x, -0.5+y, 1.5-z; (iii) -1+x, y, z; (iv) 1+x, y, z; (v) 2-x, -0.5+y, 1.5-z; (vi) -1-x, 0.5+y, 1.5-z.

$\{[Cd_3(L)_2(4,4'\text{-bpy})_3(H_2O)_2]\cdot 4(H_2O)\cdot(DEF)\}_n$ **(2)**					
Bond Distances (Å)					
Cd1—N1^{iii}	2.363(6)	Cd1—N2	2.340(6)	Cd1—O1^{ii}	2.427(5)
Cd1—O2^{ii}	2.310(4)	Cd1—O3	2.279(5)	Cd1—O4^{i}	2.270(5)

Cd2—N3	2.318(7)	N4—Cd2^{iii}	2.385(8)	Cd2—O1W	2.367(5)
Cd2—O5^{iv}	2.296(4)				
Bond Angles (°)					
O4^{i}-Cd1-O3	125.27(16)	O2^{ii}-Cd1-N2	91.18(17)	O4^{i}-Cd1-O1^{ii}	83.27(16)
O4^{i}-Cd1-O2^{ii}	134.44(17)	O4^{i}-Cd1-N1^{iii}	84.84(18)	O3-Cd1-O1^{ii}	151.44(15)
O3-Cd1-O2^{ii}	97.64(17)	O3-Cd1-N1^{iii}	82.00(18)	O2^{ii}-Cd1-O1^{ii}	55.62(15)
O4^{i}-Cd1-N2	104.04(18)	O2^{ii}-Cd1-N1^{iii}	87.04(17)	N2-Cd1-O1^{ii}	83.71(18)
O3-Cd1-N2	87.43(19)	N2-Cd1-N1^{iii}	168.9(2)	N1^{iii}-Cd1-O1^{ii}	104.13(17)
O5-Cd2-O5^{iv}	179.3(3)	N3-Cd2-O1W	93.11(12)	O5-Cd2-N4^{v}	90.33(13)
O5-Cd2-N3	89.67(13)	O5-Cd2-O1W^{iv}	87.98(17)	O5^{iv}-Cd2-N4^{v}	90.33(13)
O5^{iv}-Cd2-N3	89.67(13)	O5^{iv}-Cd2-O1W^{iv}	92.06(17)	N3-Cd2-N4^{v}	180.000(3)
O5-Cd2-O1W	92.06(17)	N3-Cd2-O1W^{iv}	93.11(12)	O1W-Cd2-N4^{v}	86.89(12)
O5^{iv}-Cd2-O1W	87.98(17)	O1W-Cd2-O1W^{iv}	173.8(2)	O1W^{iv}-Cd2-N4^{v}	86.89(12)

Symmetry Code :

(i) -x, -y, 2-z; (ii) -x, y, 1.5-z; (iii) x, -1+y, z; (iv) 1-x, y, 1.5-z; (v) x, 1+y, z.

$\{[Cd(HL)(dpe)_{0.5}(H_2O)]_2 \cdot (H_2O)\}_n$ **(3)**					
Bond Distances (Å)					
Cd1—N1	2.279(6)	Cd1—O1^{i}	2.358(5)	Cd1—O2	2.346(6)
Cd1—O3^{ii}	2.363(5)	Cd1—O4^{ii}	2.435(5)	Cd1—O8	2.404(5)
Bond Angles (°)					
O2-Cd1-N1	128.38(19)	N1-Cd1-O1^{i}	90.24(18)	N1-Cd1-O3^{ii}	90.90(17)
N1-Cd1-O4^{ii}	145.51(17)	N1-Cd1-O8	85.00(19)	O2-Cd1-O1^{i}	100.39(17)
O1^{i}-Cd1-O3^{ii}	101.50(17)	O1^{i}-Cd1-O4^{ii}	92.06(16)	O1^{i}-Cd1-O8	175.17(16)
O2-Cd1-O3^{ii}	134.49(17)	O2-Cd1-O4^{ii}	84.94(18)	O2-Cd1-O8	83.25(18)

$O3^{ii}$-Cd1-$O4^{ii}$	54.95(16)	$O3^{ii}$-Cd1-O8	77.84(18)	O8-Cd1-$O4^{ii}$	91.43(17)

Symmetry Code :

(i) -x, -y, 1-z; (ii) x, -1+y, z; (iii) x, 1+y, z; (iv) -x, -y, 2-z.

$\{[Cd(HL)(dpd)_{0.5}(H_2O)]\}_n$ **(4)**					
Bond Distances (Å)					
Cd1—N1	2.279(6)	Cd1—O1	2.230(5)	Cd1—$O2^{i}$	2.346(6)
Cd1—$O3^{ii}$	2.348(6)	Cd1—$O4^{ii}$	2.417(6)	Cd1—O8	2.403(6)
N2—$N2^{iv}$	1.167(17)				
Bond Angles (°)					
O1-Cd1-N1	128.8(2)	N1-Cd1-$O2^{i}$	89.7(2)	N1-Cd1-$O3^{ii}$	89.8(2)
N1-Cd1-$O4^{ii}$	143.6(2)	N1-Cd1-O8	85.3(2)	O1-Cd1-$O2^{i}$	100.3(2)
O1-Cd1-$O3^{ii}$	135.2(2)	O1-Cd1-$O4^{ii}$	86.5(2)	O1-Cd1-O8	82.6(2)
$O2^{i}$-Cd1-$O3^{ii}$	101.8(2)	$O2^{i}$-Cd1-$O4^{ii}$	92.2(2)	$O2^{i}$-Cd1-O8	174.91(19)
$O3^{ii}$-Cd1-$O4^{ii}$	54.3(2)	$O3^{ii}$-Cd1-O8	78.7(2)	O8-Cd1-$O4^{ii}$	92.1(2)

Symmetry Code :
(i) 1-x, 2-y, 1-z; (ii) x, 1+y, z; (iii) x, -1+y, z; (iv) 2-x, 3-y, 2-z.

$\{[Cd(HL)(1,2\text{-dpe})_{0.5}]\}_n$ **(5)**					
Bond Distances (Å)					
Cd1—N1	2.282(3)	Cd1—O1	2.283(3)	Cd1—$O2^{i}$	2.258(3)
Cd1—$O3^{ii}$	2.359(3)	Cd1—$O4^{ii}$	2.308(3)	Cd1—$O6^{iii}$	2.362(3)
Bond Angles (°)					
$O2^{i}$-Cd1-N1	96.56(11)	N1-Cd1-O1	108.96(11)	N1-Cd1-$O3^{ii}$	89.76(10)
N1-Cd1-$O4^{ii}$	100.02(11)	N1-Cd1-$O6^{iii}$	167.82(11)	$O2^{i}$-Cd1-O1	113.57(10)
O1-Cd1-$O3^{ii}$	145.83(10)	O1-Cd1-$O4^{ii}$	91.75(10)	O1-Cd1-$O6^{iii}$	82.95(11)

$O2^{i}$-Cd1-$O3^{ii}$	91.45(10)	$O2^{i}$-Cd1-$O4^{ii}$	143.12(10)	$O2^{i}$-Cd1-$O6^{iii}$	75.66(12)
$O4^{ii}$-Cd1-$O3^{ii}$	56.14(9)	$O3^{ii}$-Cd1-$O6^{iii}$	81.19(10)	$O4^{ii}$-Cd1-$O6^{iii}$	81.75(11)

Symmetry Code :

(i) 2-x, 1-y, 1-z; (ii) x, -1+y, z; (iii) 1+x, -1+y, z; (iv) x, 1+y, z; (v) -1+x, 1+y, z; (vi) 1-x, 1-y, -z.

$\{[Cd_3(L)_2(1,3\text{-dpp})_2]\cdot 3H_2O\}_n$ **(6)**					
Bond Distances (Å)					
N1—Cd1	2.261(5)	Cd1—$N2^{v}$	2.344(5)	Cd1—$O7^{iv}$	2.333(4)
Cd1—$O3^{ii}$	2.335(4)	Cd1—$O4^{ii}$	2.542(4)	O1—Cd1	2.301(4)
O2—Cd1	2.604(4)	Cd2—$O1^{vi}$	2.302(4)	Cd2—$O4^{vii}$	2.276(4)
Cd2—$O6^{iii}$	2.182(4)	Cd1—$Cd2^{ii}$	3.4543(13)		
Bond Angles (°)					
Cd1-O1-$Cd2^{ii}$	97.26(14)	Cd2-O4-$Cd1^{iii}$	91.43(13)	N1-Cd1-O1	141.83(15)
N1-Cd1-$O7^{iv}$	90.10(16)	O1-Cd1-$O7^{iv}$	89.96(15)	N1-Cd1-$O3^{ii}$	90.35(16)
O1-Cd1-$O3^{ii}$	127.63(14)	$O7^{iv}$-Cd1-$O3^{ii}$	84.71(15)	N1-Cd1-$N2^{v}$	98.54(17)
O1-Cd1-$N2^{v}$	81.70(15)	$O7^{iv}$-Cd1-$N2^{v}$	171.00(16)	$O3^{ii}$-Cd1-$N2^{v}$	97.68(15)
N1-Cd1-$O4^{ii}$	142.66(15)	O1-Cd1-$O4^{ii}$	75.27(13)	$O7^{iv}$-Cd1-$O4^{ii}$	95.02(14)
$O3^{ii}$-Cd1-$O4^{ii}$	53.55(13)	$N2^{v}$-Cd1-$O4^{ii}$	79.65(15)	N1-Cd1-O2	89.34(15)
O1-Cd1-O2	52.77(13)	$O7^{iv}$-Cd1-O2	96.37(15)	$O3^{ii}$-Cd1-O2	178.88(14)
$N2^{v}$-Cd1-O2	81.30(15)	$O4^{ii}$-Cd1-O2	126.56(13)	N1-Cd1-$Cd2^{ii}$	164.85(12)
O1-Cd1-$Cd2^{ii}$	41.39(9)	$O7^{iv}$-Cd1-$Cd2^{ii}$	74.77(11)	$O3^{ii}$-Cd1-$Cd2^{ii}$	87.49(10)
$N2^{v}$-Cd1-$Cd2^{ii}$	96.61(12)	$O4^{ii}$-Cd1-$Cd2^{ii}$	41.19(9)	O2-Cd1-$Cd2^{ii}$	93.09(9)
$O6^{vi}$-Cd2-$O6^{iii}$	180.000(2)	$O6^{vi}$-Cd2-O4	90.93(16)	$O6^{iii}$-Cd2-O4	89.07(16)
$O4^{vii}$-Cd2-O4	179.999(1)	$O6^{vi}$-Cd2-$O1^{vi}$	86.70(15)	$O6^{iii}$-Cd2-$O1^{vi}$	93.30(15)

$O4^{vii}$-Cd2-$O1^{vi}$	80.67(14)	O4-Cd2-$O1^{vi}$	99.33(14)	$O1^{vi}$-Cd2-$O1^{iii}$	180.000(1)
$O6^{vi}$-Cd2-$Cd1^{vi}$	107.33(12)	$O6^{iii}$-Cd2-$Cd1^{vi}$	72.67(12)	$O4^{vii}$-Cd2-$Cd1^{vi}$	47.37(10)
O4-Cd2-$Cd1^{vi}$	132.63(10)	$O1^{vi}$-Cd2-$Cd1^{vi}$	41.35(10)	$O1^{iii}$-Cd2-$Cd1^{vi}$	138.65(10)

Symmetry Code :

(i) x, y, -1+z; (ii) -1+x, y, z; (iii) 1+x, y, z; (iv) -x, 2-y, 2-z; (v) x, y, 1+z; (vi) 1-x, 2-y, 2-z;

(vii) 2-x, 2-y, 2-z.

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