Electronic Supplementary Material (ESI) for CrystEngComm

Electronic supplemental information for

Stepwise tuning the substituent groups from mother BTB ligands to two hexaphenylbenzene based ligands for construction of diverse coordination polymers

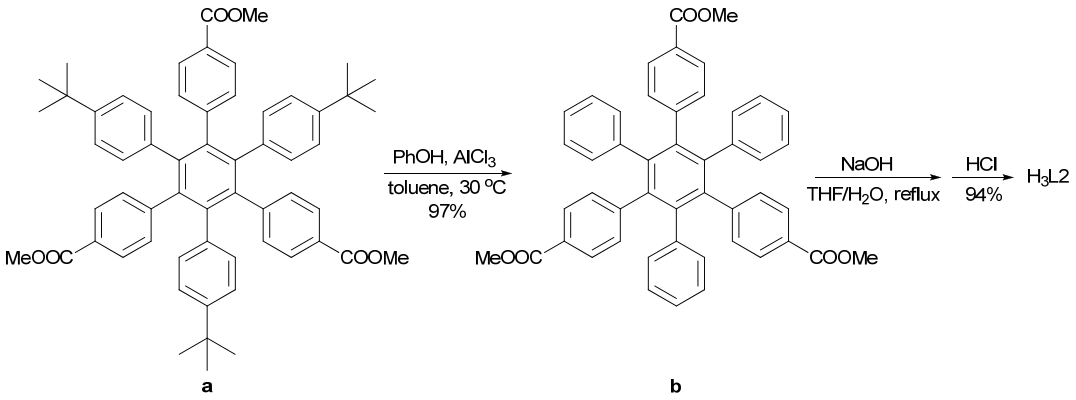
Lian-Cheng Wang,[a] Junliang Sun,*[b] Zhi-Tang Huang,[a] and Qi-Yu Zheng*[a]

[a]*Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.*
[b]*Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China.*

*Email: junliang.sun@pku.edu.cn (J. S.); zhengqy@iccas.ac.cn (Q.-Y. Z.)

Contents

1. Synthesis of H_3L2.



Scheme S1. Synthesis of ligand H_3L2.

a is prepared according to the literature method.[S1] 1.26 g **a** (1.44 mmol), 487 mg PhOH (3.6 equiv.) and 1.92 g $AlCl_3$ (10 equiv.) were added into a 100 ml two-necked round bottle. The flask was degassed by three evacuation-Ar-backfilled cycles. 60 ml anhydrous toluene was added and the flask was again degassed by three evacuation-Ar-backfilled cycles. The reaction mixture was reacted at 30 °C for 40 hrs, and then poured into dilute hydrochloric acid solution. The aqueous solution was extracted with ethyl acetate (50 ml x 3). The combined organic phase was washed with water and brine, respectively, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, PE (petralether) : ethyl acetate = 5 : 1 then washed with dichloromethane) to give 986 mg white solid **b** in 97% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.547 (d, J = 8.4 Hz, 6H), 6.872 (d, J = 8.0 Hz, 6H), 6.849-6.771 (m, 15H), 3.787 (s, 9H)
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 167.24, 145.60, 140.58, 139.91, 139.68, 131.54, 131.30, 128.29, 127.31, 127.26, 126.17, 52.07
IR (cm^{-1}): 3026.1, 2950.6, 1723.7, 1608.3, 1568.3, 1492.9, 1435.4, 1402.6, 1309.3, 1273.9, 1178.0, 1141.8, 1102.2, 1019.8, 856.6, 822.3, 739.4, 717.2, 700.1
Melting point: > 300 °C
MS: m/z = 731.3 (MALDI-TOF); cald. for [$C_{48}H_{36}O_6$ + Na] m/z = 731.2
Elemental Analysis: calculated for $C_{45}H_{36}O_6 \cdot 0.5H_2O$: C 80.32, H 5.20, O 14.49; found: C 80.56, H 5.28.

822 mg (1.16 mmol) **b** and 1.39 g (30 equiv.) NaOH in a mixture of 20 ml tetrahydrofuran (THF) and 20 ml H_2O were refluxed for 2 days. THF was removed under reduced pressure. The aqueous phase was filtered, and the filtrate was acidified with hydrochloric acid. The white precipitate was filtered and washed with water, dried in vacuum to obtain 728 mg H_3L2 in 94% yield.

^{1}H-NMR (400 MHz, DMSO-D6): δ (ppm) 12.725 (s, 3H), 7.416 (d, *J* = 8.4 Hz, 6H), 7.018 (d, *J* = 8.0 Hz, 6H), 6.914-6.819 (m, 15H)
^{13}C-NMR (100 MHz, DMSO-D6): δ (ppm) 167.90, 145.51, 140.73, 140.25, 140.11, 131.98, 131.67, 128.62, 128.48, 127.68, 126.79
IR (cm^{-1}): 3458.3, 3057.4, 2657.1, 1693.5, 1608.5, 1567.9, 1492.8, 1405.7, 1312.3, 1272.9, 1177.1, 1142.3, 1104.6, 913.9, 858.0, 799.7, 729.3, 700.2
Melting point: > 300 ^{o}C
MS: m/z = 665.3 (ESI-); cald. for $C_{45}H_{30}O_6$ m/z = 666.2
Elemental Analysis: calculated for $C_{45}H_{30}O_6 \cdot 1.5H_2O$: C 77.91, H 4.79, O 17.30; Found: C 77.86, H 4.68.

[S1] W. Xiao, X. Feng, P. Ruffieux, O. Gröning, K. Müllen and R. Fasel, *J. Am. Chem. Soc.*, 2008, **130**, 8910.

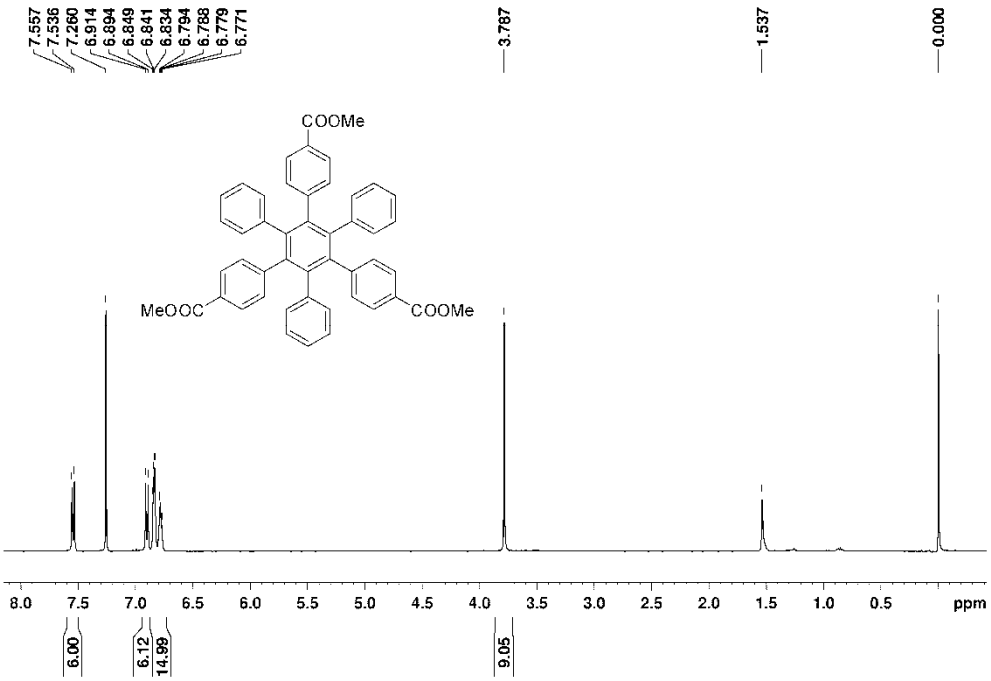


Figure S1. ^{1}H-NMR spectra of **b**.

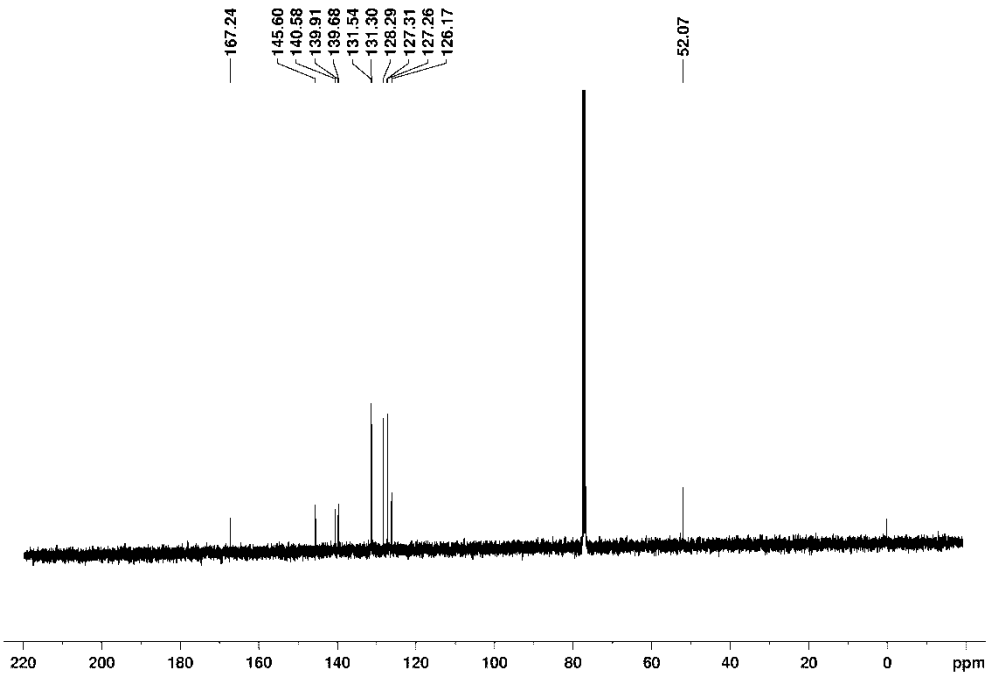


Figure S2. ^{13}C-NMR spectra of **b**.

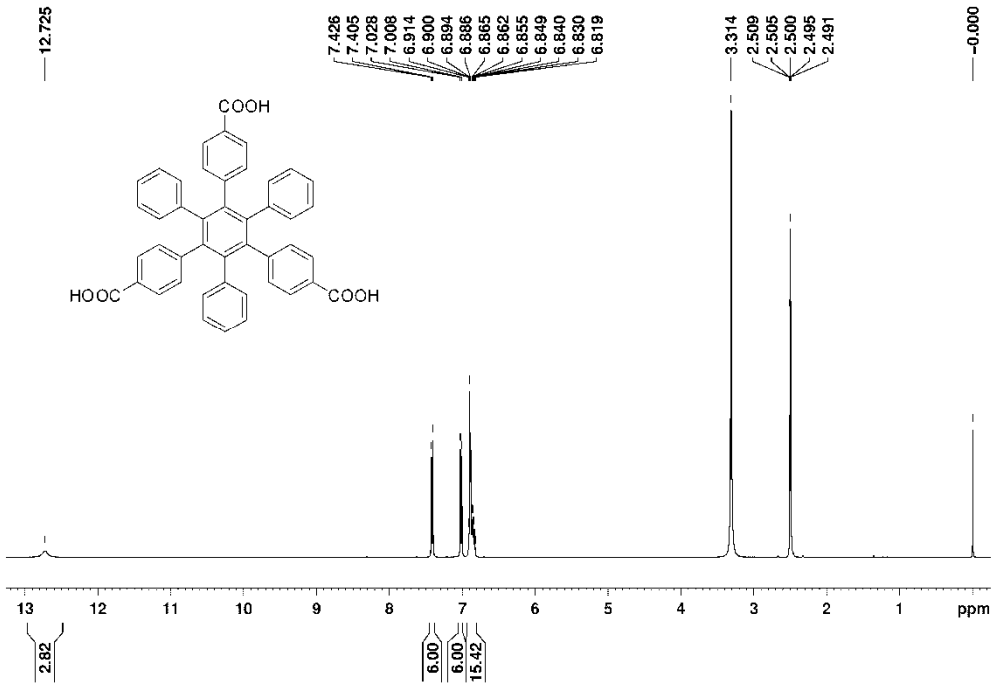


Figure S3. ^{1}H-NMR spectra of H_3L2.

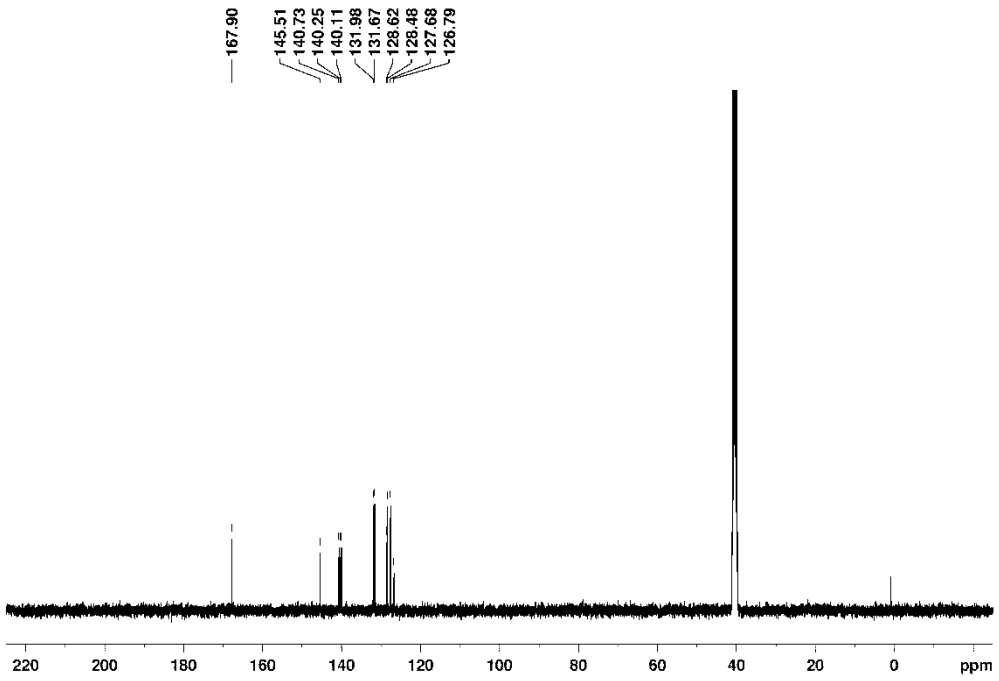


Figure S4. ^{13}C-NMR spectra of H_3L2.

2. Selected bond lengths and angles for 1–6

Table S1. Selected bond lengths (Å) and angles (deg) for complexes **1–6**

compound **1**

Zn1–O1OH	1.896(3)	Zn1–O7	1.915(3)	Zn1–O14	1.906(5)	Zn1–O13	2.004(11)
Zn1–O14A	2.126(7)	Zn2–O9	1.948(3)	Zn2–O1OH	1.946(3)	Zn2–O3	1.976(2)
Zn2–O1w	1.976(3)	Zn3–O2OH	1.924(3)	Zn3–O1	1.939(3)	Zn3–O11	1.962(2)
Zn3–O4	2.032(2)	Zn4–O2OH	1.903(3)	Zn4–O5	1.929(3)	Zn4–O15	1.982(3)
Zn4–O16	1.967(9)	O1OH–Zn1–O7	129.37(13)	O1OH–Zn1–O14	98.7(2)	O7–Zn1–O14	115.0(2)
O1OH–Zn1–O13	112.9(4)	O14–Zn1–O13	101.1(3)	O14–Zn1–O14’	24.4(2)	O9–Zn2–O1OH	104.05(12)
O9–Zn2–O3	123.76(11)	O1OH–Zn2–O3	110.38(11)	O9–Zn2–O1w	116.19(12)	O1OH–Zn2–O1w	99.87(12)
O3–Zn2–O1w	100.24(11)	O2OH–Zn3–O1	109.73(12)	O2OH–Zn3–O11	122.05(12)	O1–Zn3–O11	120.52(11)
O2OH–Zn3–O4	105.80(11)	O1–Zn3–O4	101.05(11)	O11–Zn3–O4	91.68(10)	O2OH–Zn4–O5	129.72(13)
O2OH–Zn4–O15	106.87(12)	O5–Zn4–O15	100.67(12)	O2OH–Zn4–O16	102.1(3)	O5–Zn4–O16	105.6(3)
O15–Zn4–O16	111.6(3)						

compound **2**							
Cd1–O3	2.208(2)	Cd1–O6	2.302(2)	Cd1–O2	2.333(2)	Cd1–O4	2.349(3)
Cd1–O5	2.380(2)	Cd1–O1	2.421(2)	Cd1–O7	2.572(2)	Cd2–O9	2.221(2)
Cd2–O7	2.278(2)	Cd2–O10	2.276(2)	Cd2–O8	2.269(3)	Cd2–O11	2.271(2)
Cd2–O5	2.381(2)	Cd3–O15	2.202(2)	Cd3–O12	2.210(2)	Cd3–O13	2.238(2)
Cd3–O17	2.247(3)	Cd3–O14	2.404(3)	Cd3–O11	2.428(2)	O3–Cd1–O6	95.10(9)
O6–Cd1–O2	91.68(8)	O6–Cd1–O4	87.30(9)	O3–Cd1–O5	91.63(8)	O2–Cd1–O5	142.13(7)
O3–Cd1–O1	102.65(8)	O2–Cd1–O1	55.04(8)	O5–Cd1–O1	87.42(8)	O6–Cd1–O7	52.87(7)
O4–Cd1–O7	83.60(8)	O1–Cd1–O7	154.26(8)	O9–Cd2–O7	81.87(9)	O7–Cd2–O10	98.32(8)
O7–Cd2–O8	88.22(13)	O9–Cd2–O11	105.34(9)	O10–Cd2–O11	91.73(8)	O9–Cd2–O5	92.56(8)
O10–Cd2–O5	174.80(9)	O11–Cd2–O5	91.30(7)	O15–Cd3–O13	101.78(9)	O15–Cd3–O17	89.99(8)
O13–Cd3–O17	82.44(9)	O12–Cd3–O14	77.35(9)	O17–Cd3–O14	83.96(10)	O12–Cd3–O11	85.22(8)
O17–Cd3–O11	165.13(8)						

compound **3**							
Cd1–O2	2.263(2)	Cd1–O1	2.288(2)	Cd1–O6	2.314(2)	Cd1–O4	2.322(2)
Cd1–O5	2.346(2)	Cd1–O7	2.379(2)	O5–O9	2.725	O2–Cd1–O1	92.11(9)
O1–Cd1–O6	109.35(10)	O1–Cd1–O4	93.07(9)	O2–Cd1–O5	94.32(9)	O6–Cd1–O5	99.88(9)
O2–Cd1–O7	149.34(8)	O6–Cd1–O7	56.13(8)	O5–Cd1–O7	102.27(9)		

compound **4**							
Co1–O19	2.037(3)	Co1–O16	2.036(4)	Co1–O20	2.116(4)	Co1–O8	2.157(4)
Co1–O17	2.150(3)	Co1–O7	2.225(4)	Co2–O4	2.051(3)	Co2–O10	2.014(4)
Co2–O1	2.057(4)	Co2–O9	2.114(3)	Co2–O14	2.204(3)	Co2–O13	2.196(4)
Co3–O3	2.031(4)	Co3–O23	2.032(4)	Co3–O15	2.070(3)	Co3–O18	2.093(3)
Co3–O25	2.087(5)	Co3–O14	2.133(3)	O19–Co1–O16	99.15(15)	O16–Co1–O20	93.55(19)
O16–Co1–O8	152.21(15)	O19–Co1–O17	92.68(13)	O20–Co1–O17	178.34(15)	O19–Co1–O7	164.23(14)
O20–Co1–O7	81.99(15)	O17–Co1–O7	96.35(12)	O4–Co2–O1	169.08(15)	O4–Co2–O9	88.06(14)
O1–Co2–O9	89.52(14)	O10–Co2–O14	86.09(14)	O9–Co2–O14	173.44(13)	O4–Co2–O13	84.41(14)

O9–Co2–O13	88.46(14)	O3–Co3–O23	89.71(15)	O23–Co3–O15	82.88(14)	O23–Co3–O18	100.47(13)
O3–Co3–O25	178.91(18)	O15–Co3–O25	89.74(19)	O3–Co3–O14	94.07(13)	O15–Co3–O14	85.22(13)
O25–Co3–O14	85.36(17)						
compound **5**							
Mn1–O19	2.098(4)	Mn1–O11	2.118(4)	Mn1–O13	2.188(5)	Mn1–O20	2.181(4)
Mn1–O8	2.259(4)	Mn1–O7	2.299(4)	Mn2–O21	2.093(4)	Mn2–O5	2.138(4)
Mn2–O16	2.044(6)	Mn2–O15	2.181(5)	Mn2–O3	2.200(4)	Mn3–O6	2.117(4)
Mn3–O14	2.134(5)	Mn3–O1	2.158(4)	Mn3–O12	2.152(4)	Mn3–O17	2.204(4)
Mn3–O18	2.264(4)	O19–Mn1–O11	103.34(17)	O11–Mn1–O13	87.71(18)	O11–Mn1–O20	91.25(16)
O19–Mn1–O8	157.45(16)	O13–Mn1–O8	92.37(17)	O19–Mn1–O7	100.96(16)	O13–Mn1–O7	85.74(17)
O8–Mn1–O7	57.16(14)	O21–Mn2–O5	92.02(18)	O5–Mn2–O16	96.6(3)	O5–Mn2–O15	89.9(2)
O21–Mn2–O3	97.19(17)	O16–Mn2–O3	87.2(2)	O6–Mn3–O14	179.8(2)	O14–Mn3–O1	92.5(2)
O14–Mn3–O12	89.4(2)	O6–Mn3–O17	88.31(16)	O1–Mn3–O17	169.55(16)	O6–Mn3–O18	87.74(18)
O1–Mn3–O18	89.02(16)	O17–Mn3–O18	81.30(15)				
compound **6**							
Zn1–O2	1.962(4)	Zn1–O1	1.992(4)	Zn1–O4	1.984(7)		
Zn1–O5	2.170(13)	Zn1–Cl1	2.222(4)	O3–Zn1–O2	118.82(18)	O3–Zn1–O1	104.06(19)
O2–Zn1–O1	104.25(18)	O3–Zn1–O4	128.9(3)	O2–Zn1–O4	107.3(3)	O1–Zn1–O4	83.5(3)
O3–Zn1–O5	78.1(4)	O2–Zn1–O5	78.6(4)	O1–Zn1–O5	174.7(4)	O4–Zn1–O5	91.4(5)
O3–Zn1–Cl1	104.38(17)	O2–Zn1–Cl1	112.49(16)	O1–Zn1–Cl1	112.74(17)		

3. Bond-valence Calculations of 1 and 2

Table S2. Bond-valence calculations between metal and oxygen atoms of **1** and **2**.

M-O bond	Bond length (Å)	Bond valence
Zn1-O1OH	1.896(3)	0.595
Zn2-O1OH	1.946(3)	0.520
Zn3-O2OH	1.924(3)	0.552
Zn4-O2OH	1.903(3)	0.584
Cd1-O5	2.380(2)	0.276

Cd2-O5	2.381(2)	0.275
Cd2-O11	2.271(2)	0.371
Cd3-O11	2.428(2)	0.243

4. Additional Figures

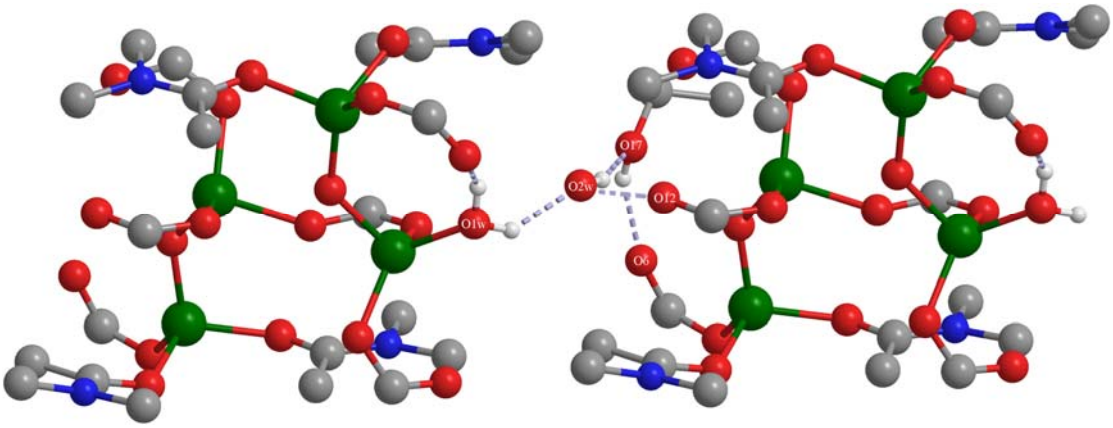


Fig. S5 The adjacent bilayers are connected by hydrogen bonds between {Zn_4} clusters by one water and one ethanol molecules in **1**.

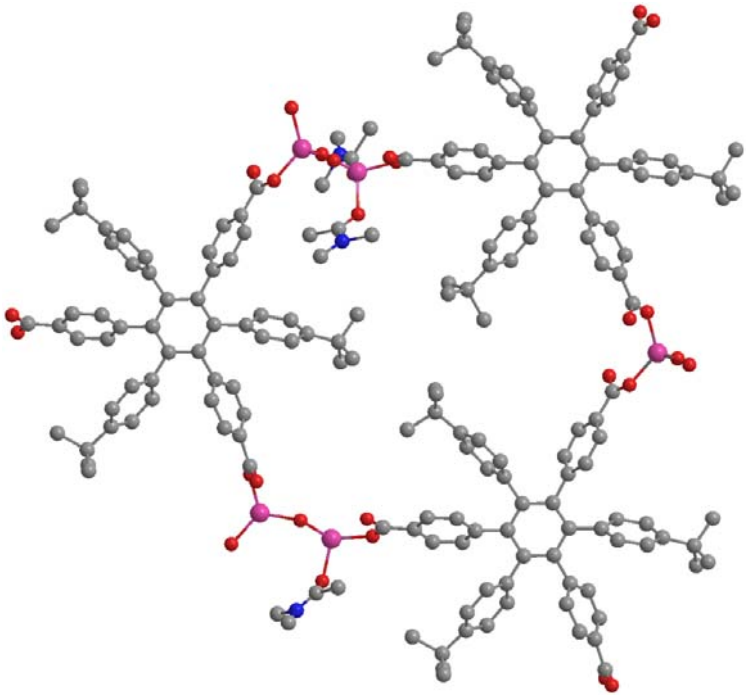


Fig. S6 The honeycomb in **1**.

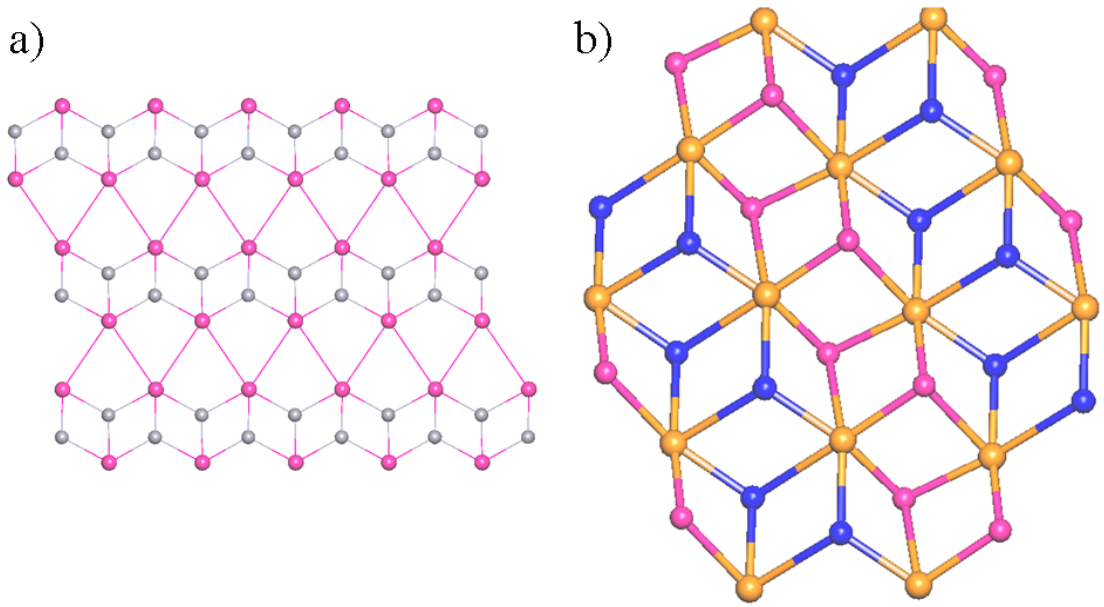


Fig. S7 (a) The (3, 5)-connected **3,5L24** topological structure only considering coordination interactions. (b) The (3, 6)-connected **kgd** topological structure taking both coordination bonds and hydrogen bonds into consideration.

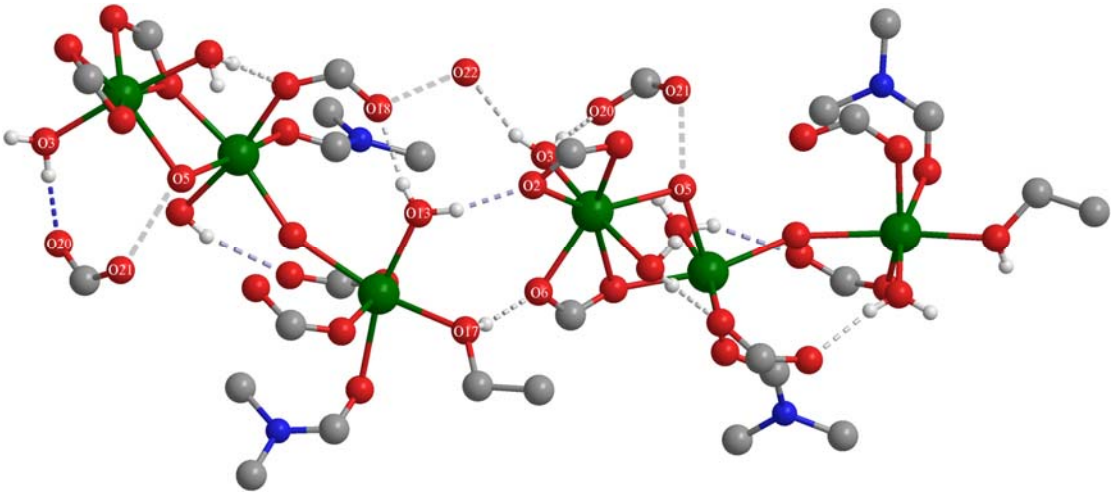


Fig. S8 The adjacent bilayers are connected by hydrogen bonds between $\{Cd_3\}$ clusters in **2**.

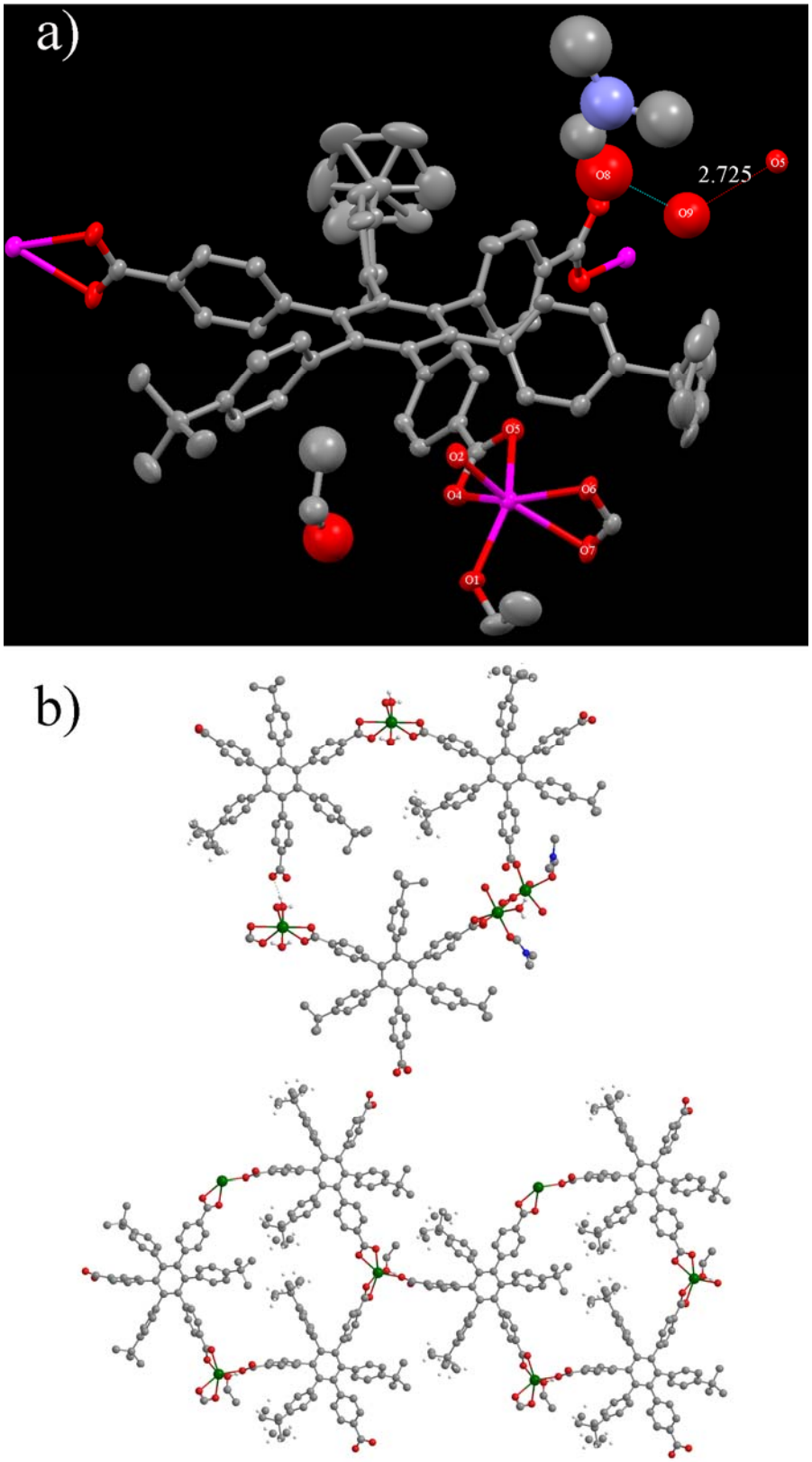


Fig. S9 (a) The asymmetric unit in **3**, including the disordered solvents; the hydrogen bonded oxygen O9 was recognized as H_3O^+. (b) The honeycomb in **2** (top), and the corrugated honeycomb in **3** (down).

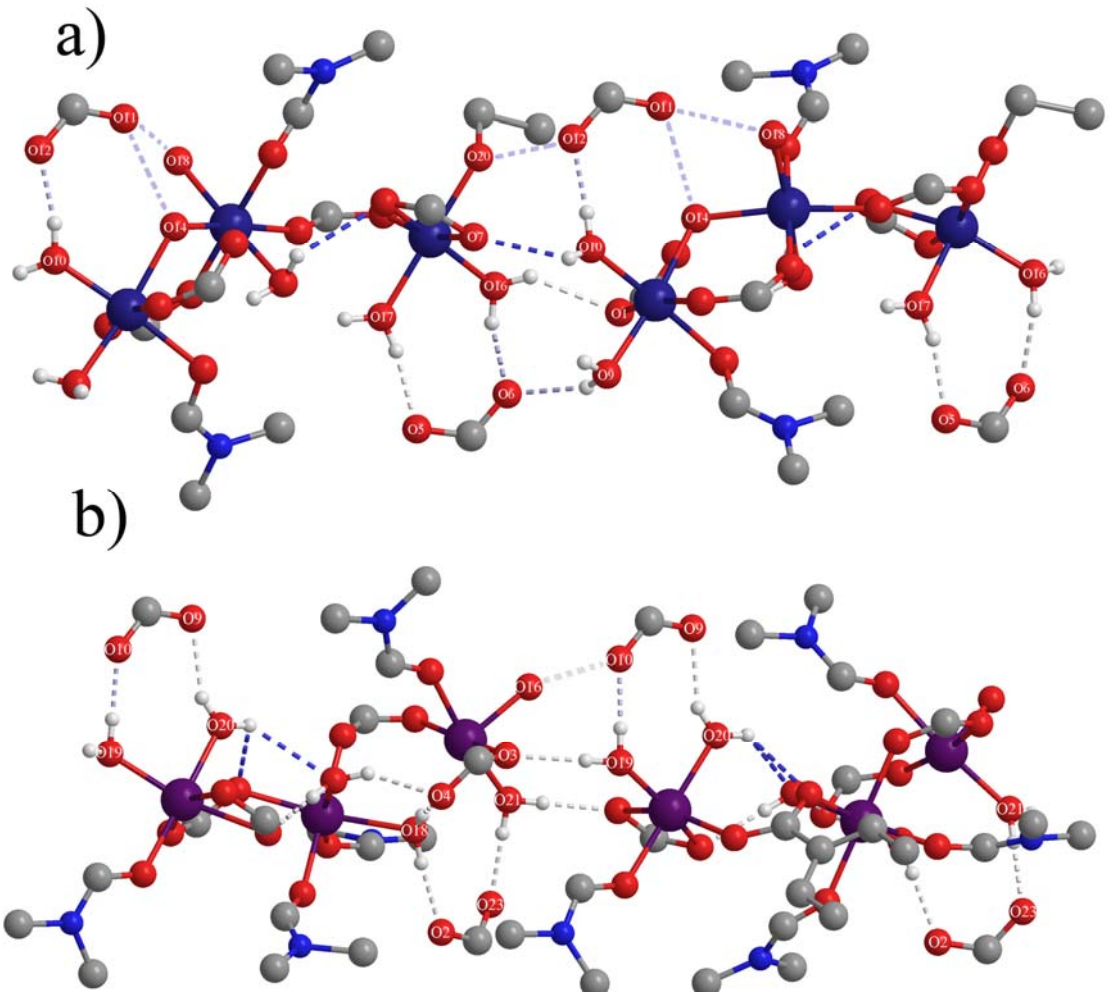


Figure S10. Hydrogen bonding interactions between coordination chains. (a) $\{Co_3\}$ clusters in **4** and (b) $\{Mn_3\}$ clusters in **5**.

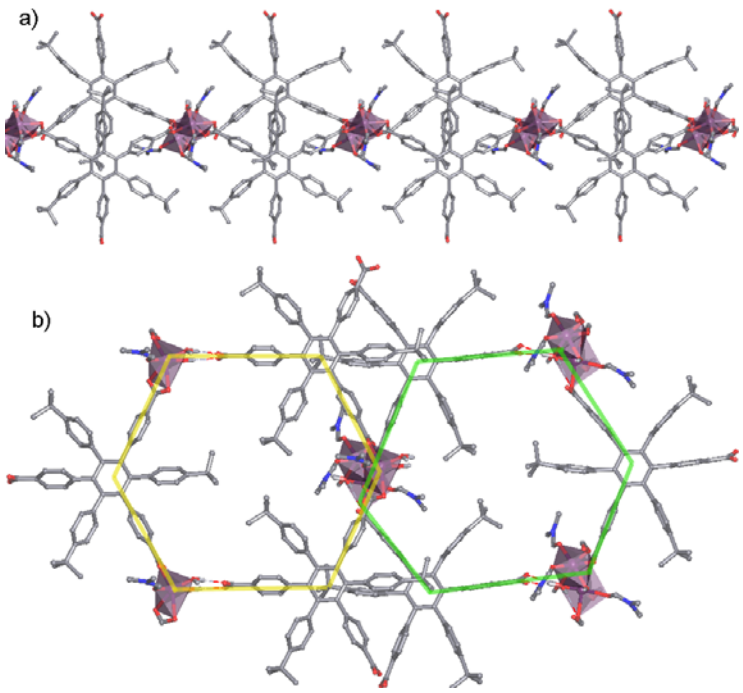


Fig. S11 (a) The 1D nonplanar coordination chain in **5**. (b) The 2D hydrogen-bonded honeycomb bilayer sheet in **5**.

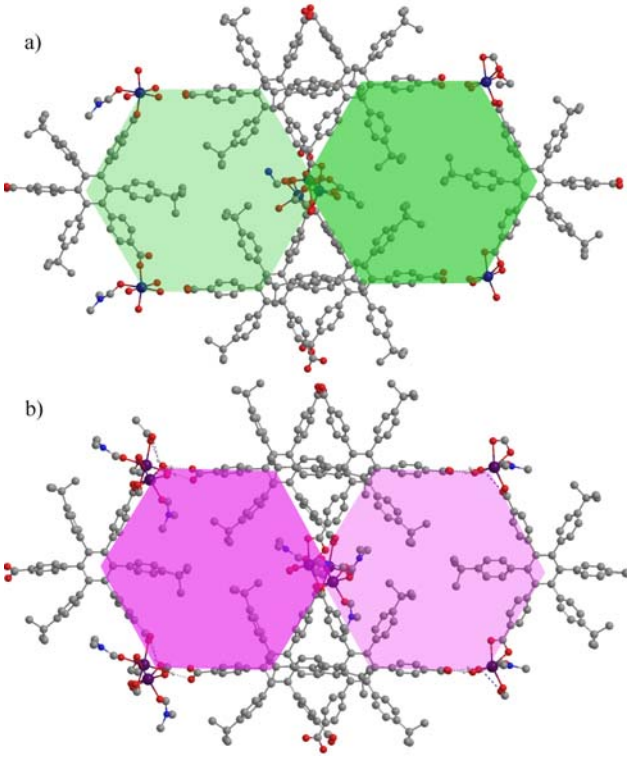


Fig. S12 Hydrogen bonding interactions between carboxylate groups and coordination water molecules formed honeycombs in (a) **4** and (b) **5**.

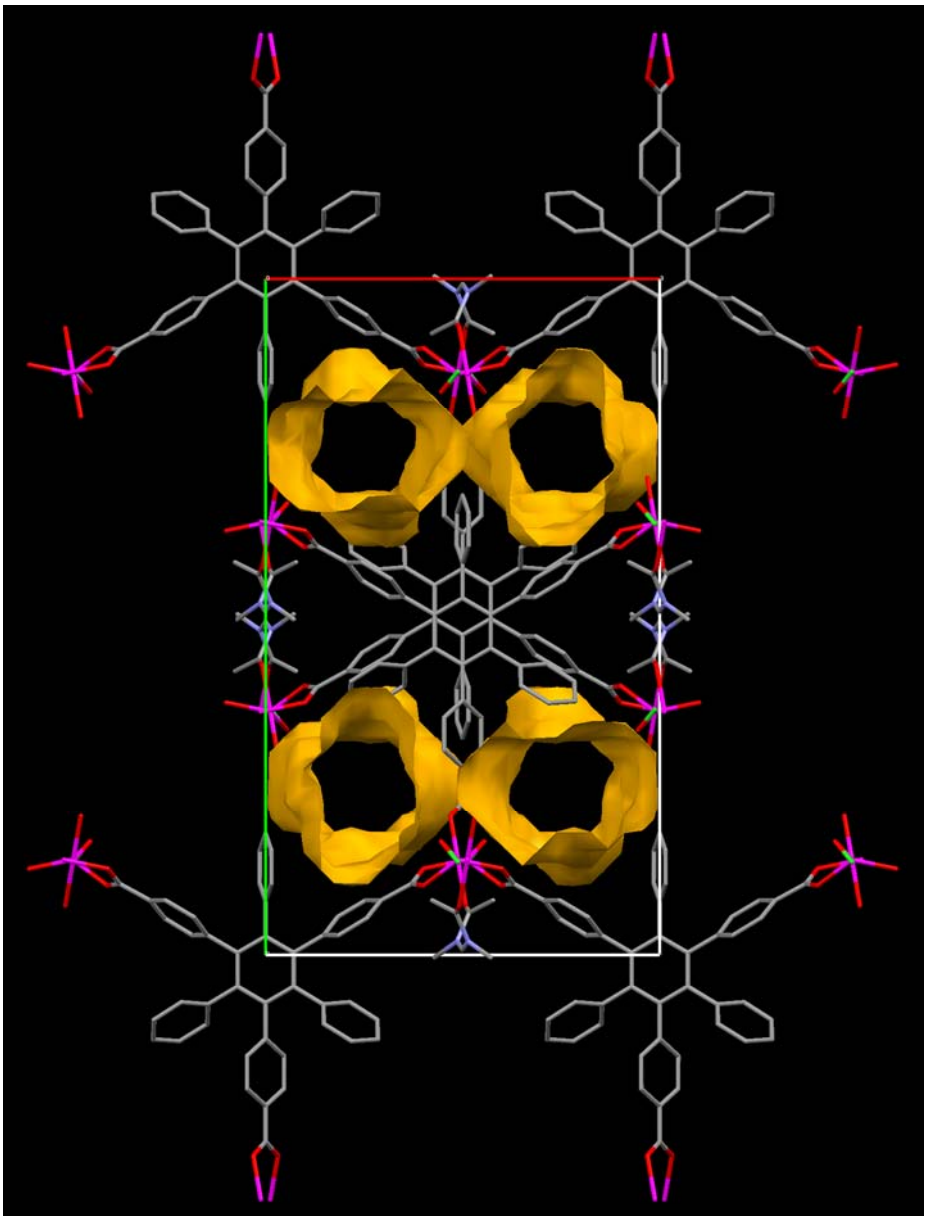


Fig. S13 The 1D channels in **6** viewed along *c* axis.

5. Powder X-ray diffraction

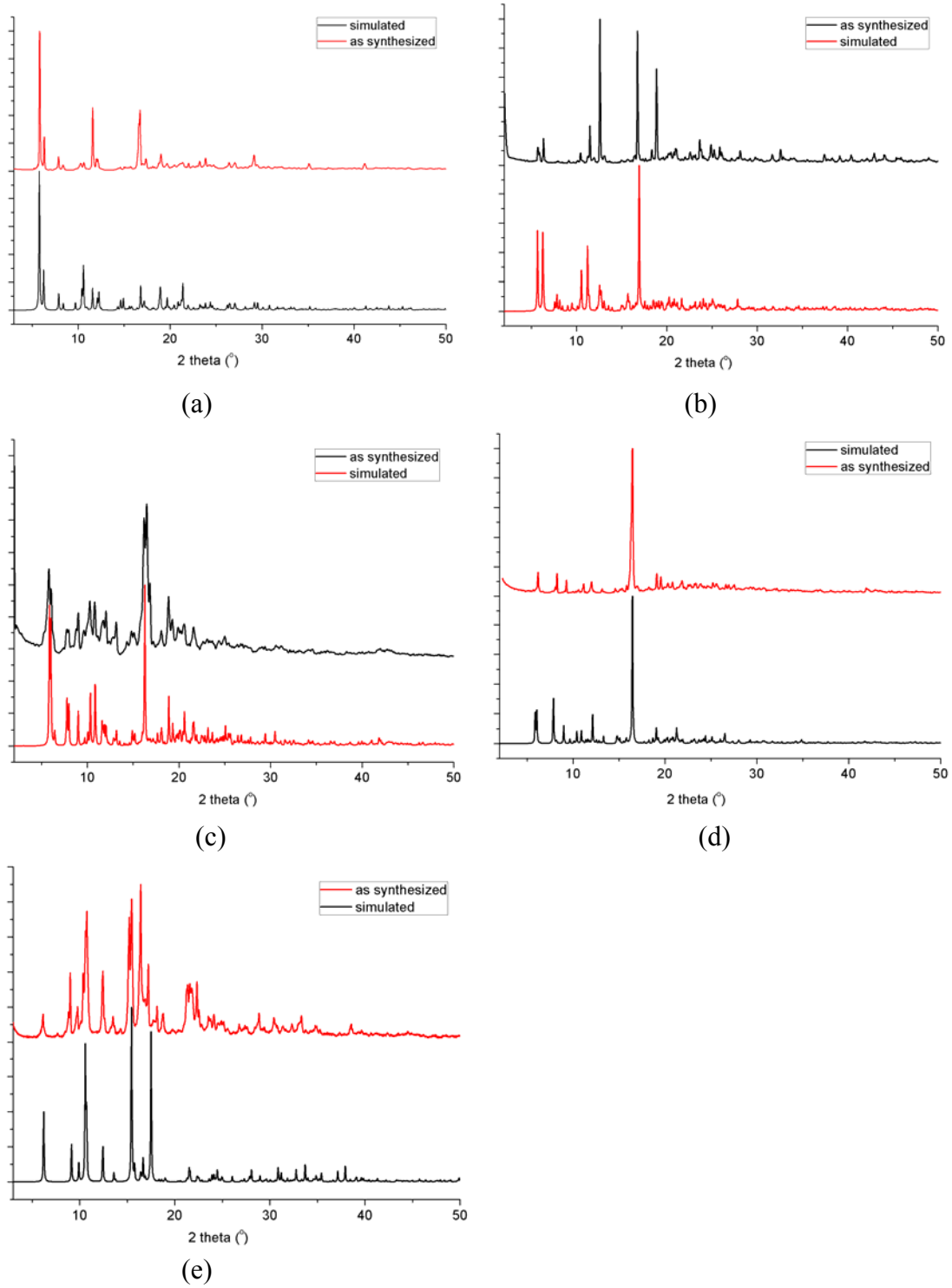


Fig. S14 Powder X-ray diffraction of (a) compound **1**; (b) compound **2**; (c) compound **4**; (d) compound **5**; (e) compound **6**.

6. Thermogravimetric analysis

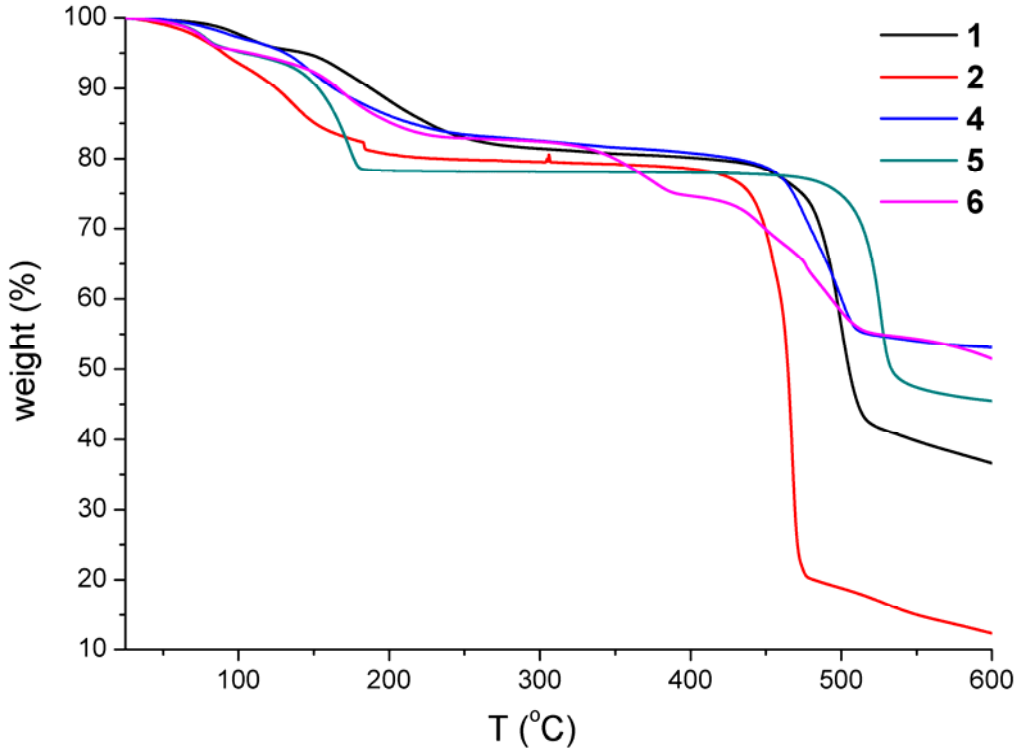


Fig. S15 TGA curves for complex **1**, **2**, and **4–6**

7. Fitting of $\chi_M T$ vs. T plots

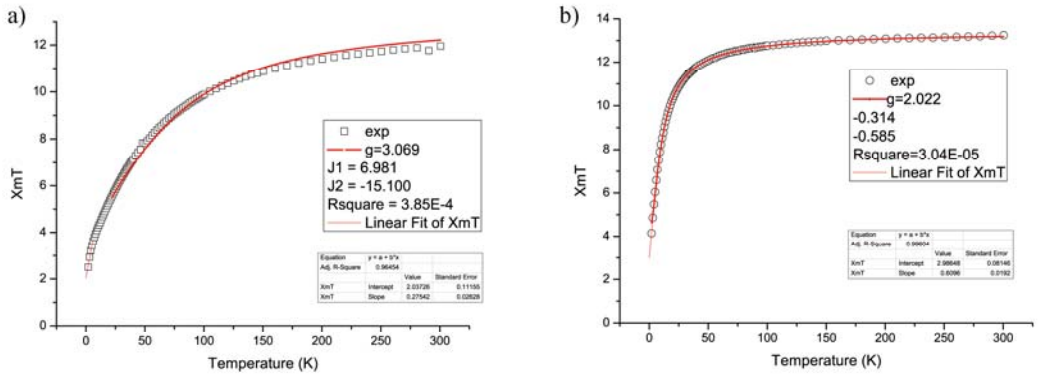


Fig. S16 Fitting of $\chi_M T$ vs. T for a) complex **4** b) complex **5**.