Electronic Supplementary Information

Self-assembly of metal–organic frameworks based on N-donor ligand and flexible tricarboxylic acids with different angular characters

Lei Chen,[a] Li Zhang,[a] Shun-Li Li,*[b] Yong-Qing Qiu,[a] Kui-Zhan Shao,*[a] Xin-Long Wang[a] and Zhong-Min Su*[a]

[a] Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, P. R. China

[b] Jiangsu Key Laboratory of Biofunctional Materials, College of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, Jiangsu, P. R. China

* Corresponding author.

E-mail: shaokz406@nenu.edu.cn; zmsu@nenu.edu.cn; slli@njnu.edu.cn

Synthesis of 5-(3-carboxybenzyloxy)isophthalic acid (H_3L^1)

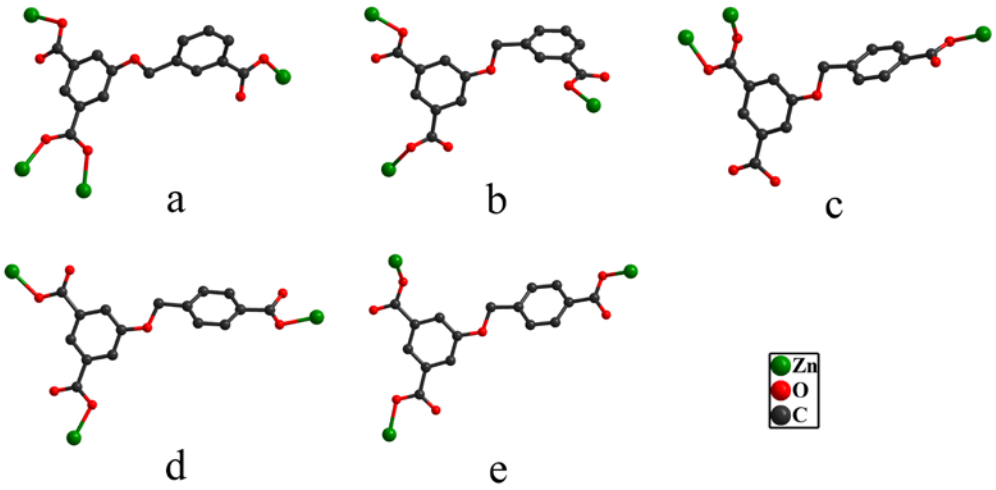
A mixture of diethyl 5-hydroxyisophthalate (20 mmol, 4.76 g) and NaOH (20 mmol, 0.80 g) in DMF (50 mL) was stirred at 5 ºC for 3 h, then 3-(chloromethyl)benzonitrile (20 mmol, 3.02 g) was added. The mixture was cooled to room temperature after stirring at 90 ºC for 12 h, and then poured into 200 mL of water. A white solid of diethyl 5-(3-cyanobenzyloxy)isophthalate was deposited, which was isolated by filtration in 66 % yield after drying in air.

Then a mixture of diethyl 5-(3-cyanobenzyloxy)isophthalate (15.60 mmol, 5.52 g) and sodium hydroxide (100 mmol, 4.00 g) in water (80 mL) was stirred at 100 ºC for 12 h, and was cooled to room temperature. The mixture was adjusted to approximately pH 4.5 with dilute hydrochloric acid. A white solid of H_3L^1 formed immediately, which was isolated by filtration in 60 % yield after drying in air.

Elemental analyses calcd (%) for $C_{16}H_{12}O_7$ (316.26): C, 60.76; H, 3.82. Found C, 60.77; H, 3.81. IR (KBr pellet, cm^{-1}): 2958 (m), 1679 (m), 1628 (s), 1598 (s), 1508 (s), 1423 (m), 1367 (m), 1305 (m), 1240 (s), 1167 (s), 1026 (w), 983 (m), 866 (w), 827 (m), 670 (w), 516 (w).

Synthesis of 5-(4-carboxybenzyloxy)isophthalic acid (H_3L^2)

H_3L^2 was prepared in the same way as H_3L^1 by using the corresponding 4-(chloromethyl)benzonitrile instead of 3-(chloromethyl)benzonitrile. IR (cm^{-1}): 2965 (w), 1734 (s), 1690 (s), 1598 (s), 1460 (m), 1285 (s), 1206 (s), 1121 (m), 1057 (m), 889 (w), 765 (m), 664 (w), 531 (w).



Scheme S1 Coordination modes of the ligand in complexes **1**-**5**.

Table S1 Selected bond lengths (Å) and angles (°) for complexes **1**-**5**.

Complex **1**			
Zn(1)-O(8)#1	1.968(6)	Zn(1)-O(4)#1	2.013(5)
Zn(1)-O(1)	2.012(6)	Zn(1)-N(1)	2.062(6)
Zn(2)-O(8)	1.902(6)	Zn(2)-O(6)#2	1.959(5)
Zn(2)-O(3)	2.013(6)	Zn(2)-N(4)#3	2.016(7)
O(8)#1-Zn(1)-O(4)#1	103.5(2)	O(8)#1-Zn(1)-O(1)	119.0(2)
O(4)#1-Zn(1)-O(1)	96.6(2)	O(8)#1-Zn(1)-N(1)	103.1(2)
O(4)#1-Zn(1)-N(1)	97.3(2)	O(1)-Zn(1)-N(1)	130.7(2)

O(8)-Zn(2)-O(6)#2	116.9(2)	O(8)-Zn(2)-O(3)	103.9(2)
O(6)#2-Zn(2)-O(3)	101.6(2)	O(8)-Zn(2)-N(4)#3	123.7(3)
O(6)#2-Zn(2)-N(4)#3	109.9(3)	O(3)-Zn(2)-N(4)#3	95.3(3)
		Complex **2**	
Zn(1)-O(8)	1.933(3)	Zn(1)-O(2)	1.950(3)
Zn(1)-N(1)	2.000(4)	Zn(1)-N(9)	2.057(4)
Zn(2)-O(10)	1.926(3)	Zn(2)-O(14)#1	1.964(3)
Zn(2)-N(4)#2	2.009(4)	Zn(2)-N(5)	2.011(4)
Zn(3)-O(4)#3	1.965(4)	Zn(3)-O(6)	1.967(3)
Zn(3)-N(11)	2.010(4)	Zn(3)-N(8)#4	2.032(4)
O(8)-Zn(1)-O(2)	119.23(16)	O(8)-Zn(1)-N(1)	112.40(15)
O(2)-Zn(1)-N(1)	108.09(15)	O(8)-Zn(1)-N(9)	94.26(15)
O(2)-Zn(1)-N(9)	104.52(15)	N(1)-Zn(1)-N(9)	118.07(16)
O(10)-Zn(2)-O(14)#1	111.69(16)	O(10)-Zn(2)-N(4)#2	113.89(16)
O(14)#1-Zn(2)-N(4)#2	117.93(18)	O(10)-Zn(2)-N(5)	108.32(15)
O(14)#1-Zn(2)-N(5)	100.13(15)	N(4)#2-Zn(2)-N(5)	103.04(16)
O(4)#3-Zn(3)-O(6)	98.24(16)	O(4)#3-Zn(3)-N(11)	103.62(17)
O(6)-Zn(3)-N(11)	128.73(16)	O(4)#3-Zn(3)-N(8)#4	122.83(16)
O(6)-Zn(3)-N(8)#4	102.01(15)	N(11)-Zn(3)-N(8)#4	103.79(16)
		Complex **3**	
Zn(1)-O(6)	1.935(4)	Zn(1)-O(3)#1	1.967(4)
Zn(1)-O(4)#2	1.996(4)	Zn(1)-N(1)	2.016(5)
O(6)-Zn(1)-O(3)#1	116.45(18)	O(6)-Zn(1)-O(4)#2	112.63(18)
O(3)#1-Zn(1)-O(4)#2	109.84(17)	O(6)-Zn(1)-N(1)	98.38(19)
O(3)#1-Zn(1)-N(1)	114.61(18)	O(4)#2-Zn(1)-N(1)	103.87(19)
		Complex **4**	
Zn(1)-O(3)	1.963(3)	Zn(1)-O(1)#6	1.968(4)
Zn(1)-N(1)	2.005(5)	Zn(1)-N(5)	2.011(4)
Zn(2)-O(9)	1.948(4)	Zn(2)-O(6)	1.984(5)
Zn(2)-N(4)#1	1.994(5)	Zn(2)-N(9)	2.017(5)
Zn(3)-O(11)#5	1.910(4)	Zn(3)-O(14)	1.933(5)
Zn(3)-N(8)#7	2.000(4)	Zn(3)-N(12)#3	1.995(4)
O(3)-Zn(1)-O(1)#6	112.01(16)	O(3)-Zn(1)-N(1)	111.70(17)
O(1)#6-Zn(1)-N(1)	111.27(17)	O(3)-Zn(1)-N(5)	95.35(16)
O(1)#6-Zn(1)-N(5)	109.24(17)	N(1)-Zn(1)-N(5)	116.36(18)

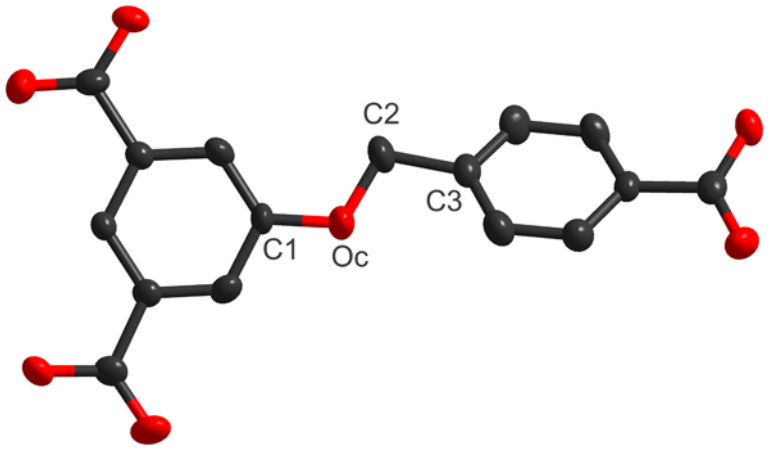
O(9)-Zn(2)-O(6)	108.4(2)	O(9)-Zn(2)-N(4)#1	114.8(2)
O(6)-Zn(2)-N(4)#1	118.7(2)	O(9)-Zn(2)-N(9)	107.43(19)
O(6)-Zn(2)-N(9)	97.2(2)	N(4)#1-Zn(2)-N(9)	108.4(2)
O(11)#5-Zn(3)-O(14)	113.0(2)	O(11)#5-Zn(3)-N(8)#7	107.8(2)
O(14)-Zn(3)-N(8)#7	100.9(2)	O(11)#5-Zn(3)-N(12)#3	104.5(2)
O(14)-Zn(3)-N(12)#3	121.8(2)	N(8)#7-Zn(3)-N(12)#3	108.1(2)
		Complex **5**	
Zn(1)-O(6)#4	1.950(3)	Zn(1)-O(6)#5	1.950(3)
Zn(1)-N(1)	2.020(4)	Zn(1)-N(1)#6	2.020(4)
Zn(2)-O(2)	1.938(3)	Zn(2)-O(4)#7	1.958(3)
Zn(2)-N(4)	2.012(4)	Zn(2)-N(5)	2.008(4)
O(6)#4-Zn(1)-O(6)#5	127.78(19)	O(6)#4-Zn(1)-N(1)	113.42(15)
O(6)#5-Zn(1)-N(1)	99.12(15)	O(6)#4-Zn(1)-N(1)#6	99.12(15)
O(6)#5-Zn(1)-N(1)#6	113.42(15)	N(1)-Zn(1)-N(1)#6	101.6(2)
O(2)-Zn(2)-O(4)#7	120.97(14)	O(2)-Zn(2)-N(4)	117.74(15)
O(4)#7-Zn(2)-N(4)	102.50(15)	O(2)-Zn(2)-N(5)	95.44(15)
O(4)#7-Zn(2)-N(5)	109.26(15)	N(4)-Zn(2)-N(5)	110.63(15)

[a]Symmetry transformations used to generate equivalent atoms: for **1**: #1 x+1, y, z; #2 x, y, z-1; #3 -x+2, -y+1, -z+1; for **2**: #1 x+1, y, z; #2 x, y, z-1; #3 -x+2, -y+1, -z+2; #4 -x+2, -y+2, -z+2; for **3**: #1 x+1, y+1, z-1; #2 -x+2, -y, -z+2; for **4**: #1 -x, -y, -z+2; #3 -x+3, -y, -z+2; #5 -x+2, -y, -z+1; #6 x-1/2, -y+1/2, z-1/2; #7 -x-1/2, y-1/2, -z+3/2; for **5**: #4 -x+1/2, y-5/2, -z+3/2; #5 x-1/2, y-5/2, z; #6 -x, y, -z+3/2; #7 x-1/2, y-1/2, z.

Table S2 Distances (Å) and Angles (°) of Hydrogen bonds for complexes **3**.

D-H···A	*d*(H···A)	*d*(D···A)	∠D-H···A
O(1)-H(1c)···O(1W)	1.680(2)	2.568(5)	165(8)
O(1W)-H(1B)···O(7)#1	1.864(2)	2.700(5)	168(2)
O(1W)-H(1A)···O(2)#2	2.129(2)	2.842(5)	141(2)

Symmetry transformations used to generate equivalent atoms: for **3**: #1 x+1, y+1, z-1; #2 -x+2, -y, -z+2.



Scheme S2 Schematic description of the flexible –O-CH_2- group.

Table S3 The bond distances and angles in the carboxylate ligands.

Compound	Oc-Zn	twisted angle of C1-Oc-C2-C3	dihedral angle of two rings in the same ligand
1	7.79	164.24	81.82
	7.04		
	7.01		
	7.85		
2	7.17	179.27	74.81
	7.02		
	7.66		
	6.92	-175.60	75.55
	7.77		
	8.07		
3	9.08	-176.37	58.60
	5.70		
	7.61		
4	8.93	-170.55	42.39
	7.79		
	8.90		

5	7.51	175.43	33.75
	6.21		
	8.99		

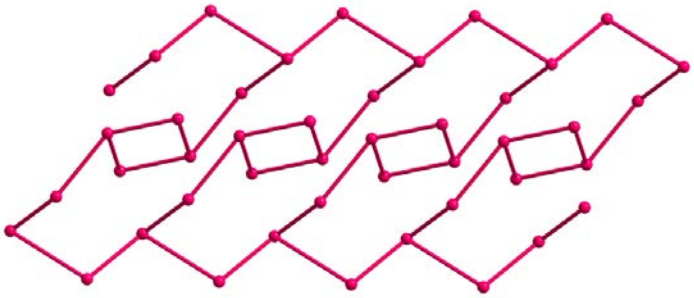


Fig. S1 The 1D infinite chain topology in **2**.

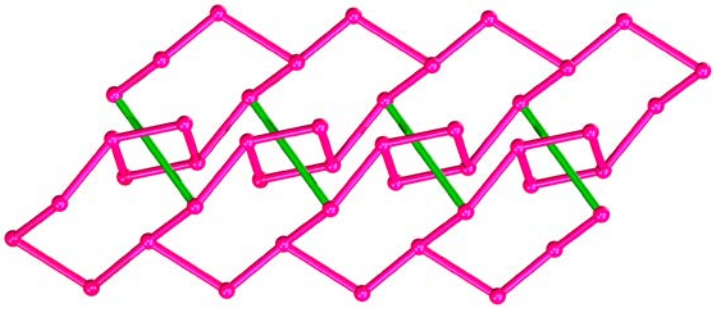


Fig. S2 Schematic representations of the 1D infinite chain self-penetrated by BIMB ligands in **2**

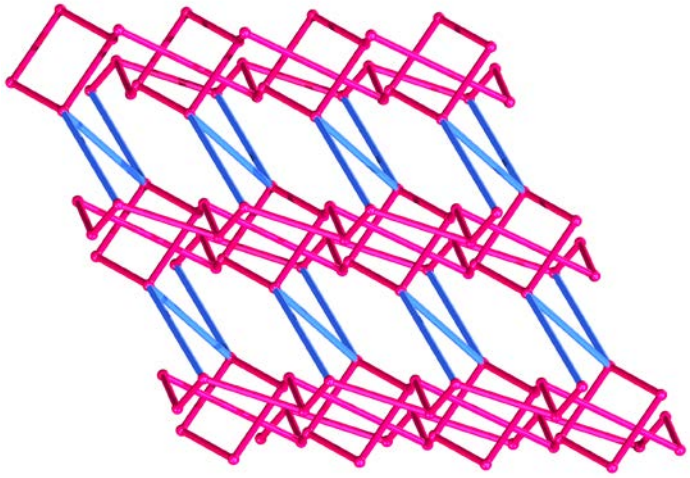


Fig. S3 The 2D layer network of **2**.

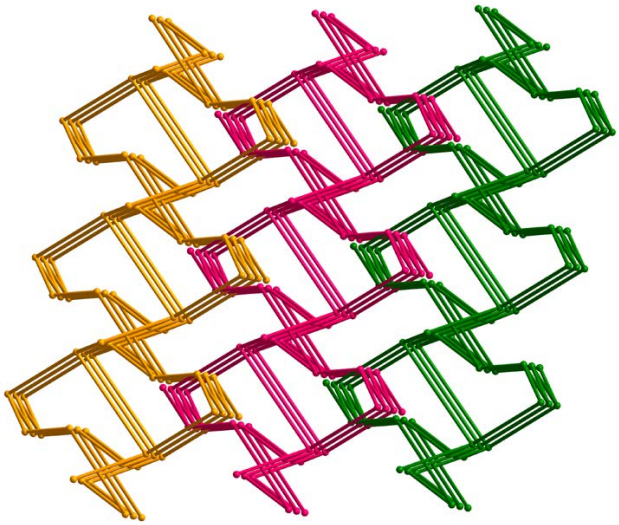


Fig. S4 Each 2D layer is interpenetrated by another two similar layers to form a three-folded framework.

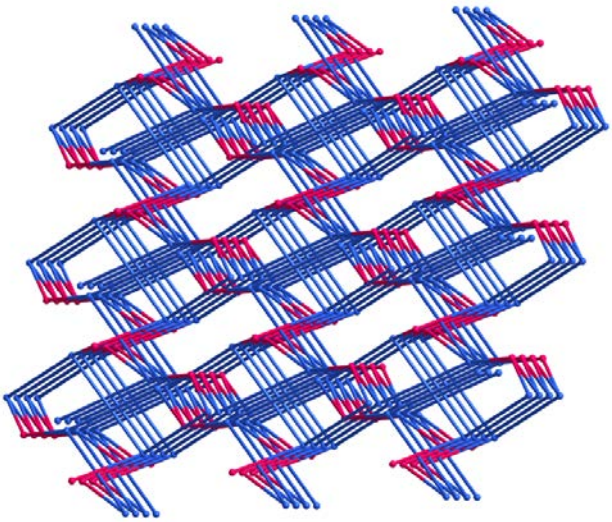


Fig. S5 Schematic illustrating the 3D (3,4)-connected network in **2**.

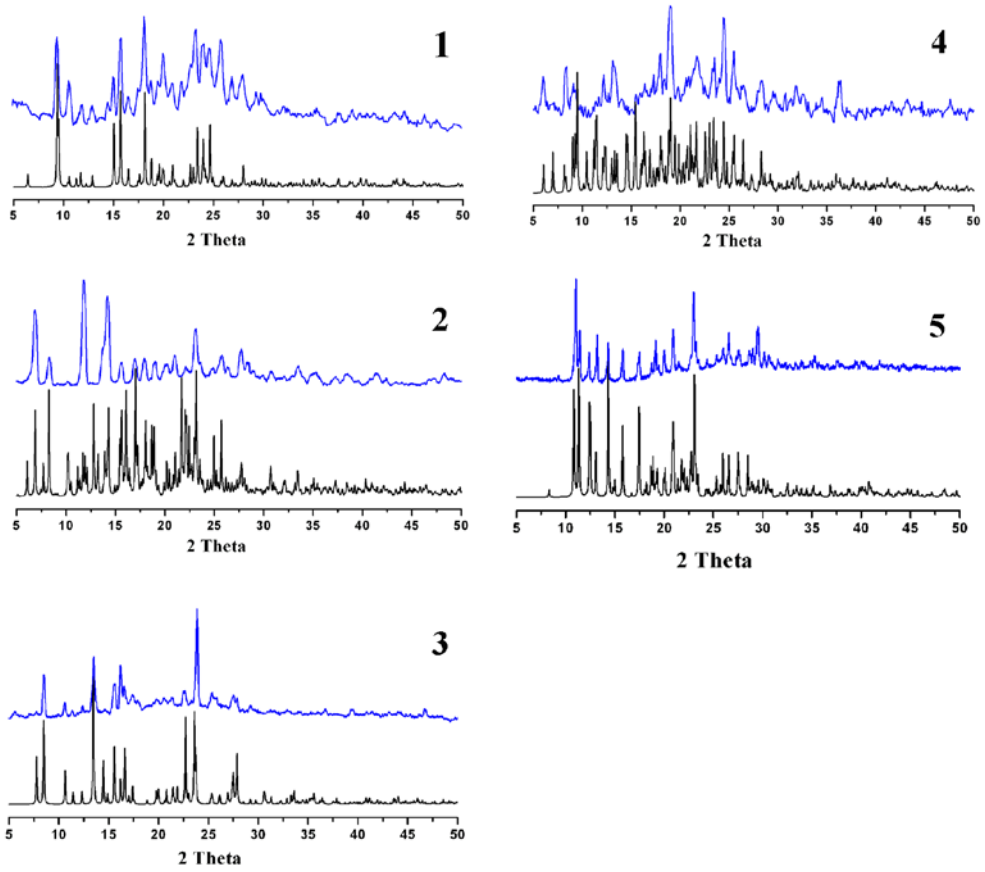


Fig. S6 The simulated (black) and experimental (blue) PXRD patterns for complexs **1-5**

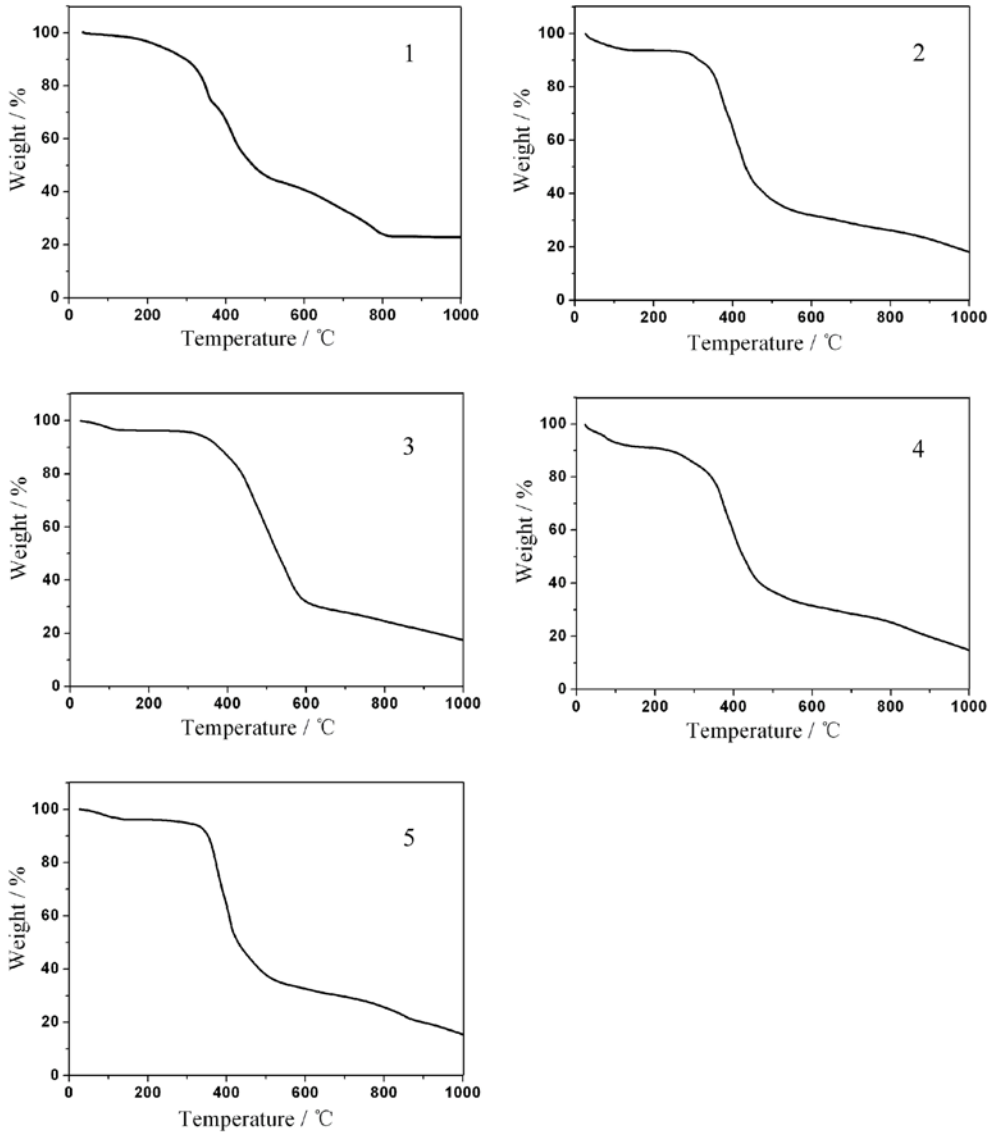


Fig. S7 TG curves of complexes **1**-**5**.