Electronic Supplementary Information

Three Novel 3D (3,8)-connected Metal-Organic Frameworks Constructed from Flexible-Rigid Mixed Ligands

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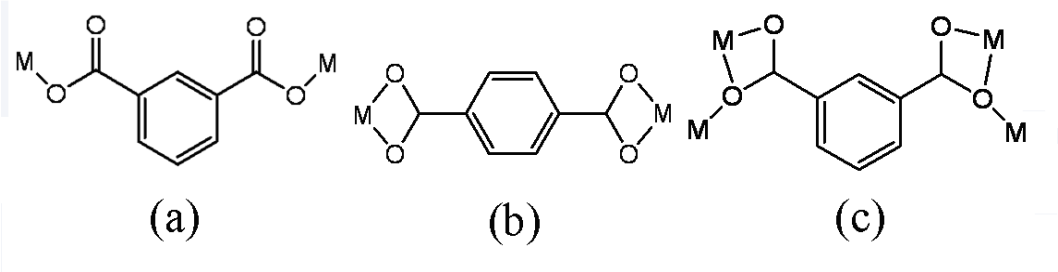
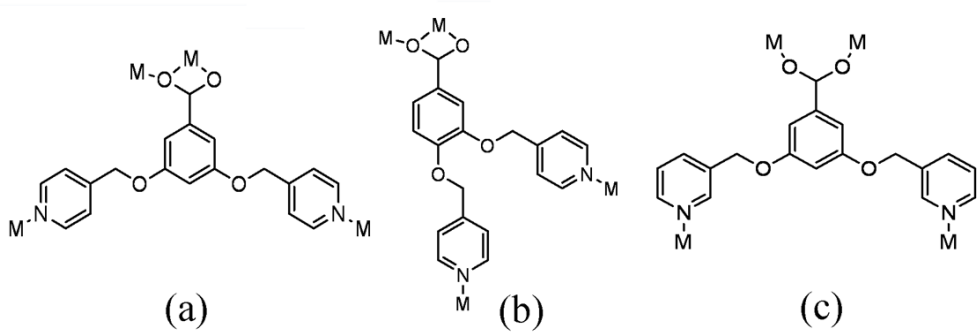


Scheme S1. Coordination modes of the organic ligands: (a) 1,3-bdc for complex **1**, (b) 1,4-bdc for complex **2**, (c) 1,3-bdc for complex **3**.



Scheme S2. Coordination modes of the organic ligands: (a) L1 for complex **1**, (b) L2 for complex **2**, (c) L3 for complex **3**.

Table S1 Selected bond lengths (Å) and angles (°) for complexes **1**, **2** and **3**[a]

Complex **1**

Cd(1)-O(5)	2.193(4)	Cd(1)-O(2)#2	2.359(3)
Cd(1)-N(1)#1	2.303(3)	Cd(1)-O(1)#2	2.450(3)
Cd(1)-N(2)	2.366(4)	Cd(1)-O(1)#3	2.463(3)
O(5)-Cd(1)-N(1)#1	114.7(2)	O(5)-Cd(1)-O(1)#3	148.2(1)
O(5)-Cd(1)-O(2)#2	113.1(1)	O(2)#2-Cd(1)-O(1)#2	54.67(8)
N(1)#1-Cd(1)-O(2)#2	87.2(1)	N(2)-Cd(1)-O(1)#2	114.87(9)
O(5)-Cd(1)-N(2)	83.3(1)	N(1)#1-Cd(1)-O(1)#3	92.9(1)
N(1)#1-Cd(1)-N(2)	97.7(1)	O(2)#2-Cd(1)-O(1)#3	82.4(1)
O(2)#2-Cd(1)-N(2)	159.3(1)	N(2)-Cd(1)-O(1)#3	77.3(1)
O(5)-Cd(1)-O(1)#2	91.6(1)	O(1)#2-Cd(1)-O(1)#3	74.5(1)
N(1)#1-Cd(1)-O(1)#2	140.6(1)		

Complex **2**

Cd(1)-N(1)	2.328(7)	Cd(1)-O(2)#1	2.464(6)
Cd(1)-O(5)	2.341(7)	Cd(1)-O(6)	2.456(7)
Cd(1)-O(1)#1	2.359(6)	Cd(1)-O(2)#3	2.486(6)
Cd(1)-N(2)#2	2.390(7)		
N(1)-Cd(1)-O(5)	87.7(3)	O(5)-Cd(1)-O(6)	52.6(3)
N(1)-Cd(1)-O(1)#1	143.5(2)	O(1)#1-Cd(1)-O(6)	84.6(3)
O(5)-Cd(1)-O(1)#1	123.1(3)	N(2)#2-Cd(1)-O(6)	113.0(3)
N(1)-Cd(1)-N(2)#2	85.7(2)	O(2)#1-Cd(1)-O(6)	122.6(3)
O(5)-Cd(1)-N(2)#2	84.0(3)	N(1)-Cd(1)-O(2)#3	85.2(2)
O(1)#1-Cd(1)-N(2)#2	79.4(2)	O(5)-Cd(1)-O(2)#3	104.2(2)
N(1)-Cd(1)-O(2)#1	95.9(2)	O(1)#1-Cd(1)-O(2)#3	103.2(2)
O(5)-Cd(1)-O(2)#1	176.0(3)	N(2)#2-Cd(1)-O(2)#3	167.4(2)
O(1)#1-Cd(1)-O(2)#1	54.3(2)	O(2)#1-Cd(1)-O(2)#3	74.2(2)
N(2)#2-Cd(1)-O(2)#1	98.2(2)	O(6)-Cd(1)-O(2)#3	79.6(3)
N(1)-Cd(1)-O(6)	131.9(3)		

Complex **3**

Cd(1)-O(1)	2.210(5)	Cd(1)-O(8)#2	2.297(5)
Cd(1)-O(6)	2.286(4)	Cd(2)-O(2)	2.239(5)
Cd(2)-O(6)	2.341(5)	Cd(2)-O(8)#2	2.485(6)
Cd(2)-O(7)#2	2.372(5)	Cd(2)-O(5)	2.557(5)
Cd(2)-N(1)#4	2.313(6)	Cd(2)-N(2)	2.358(5)
O(1)#1-Cd(1)-O(1)	166.0(3)	O(6)-Cd(1)-O(8)#2	78.4(2)
O(1)#1-Cd(1)-O(6)	85.3(2)	O(1)#1-Cd(1)-O(8)#2	90.5(2)
O(1)-Cd(1)-O(6)	86.7(2)	O(1)-Cd(1)-O(8)#2	99.0(2)
O(6)-Cd(1)-O(6)#1	109.4(2)	O(6)#1-Cd(1)-O(8)#2	171.4(2)
O(8)#2-Cd(1)-O(8)#3	94.1(3)	O(2)-Cd(2)-O(6)	92.7(2)
N(1)#4-Cd(2)-O(6)	147.7(2)	N(1)#4-Cd(2)-O(8)#2	137.6(2)
O(2)-Cd(2)-N(2)	172.3(2)	O(6)-Cd(2)-O(8)#2	73.7(2)
N(1)#4-Cd(2)-N(2)	90.8(2)	N(2)-Cd(2)-O(8)#2	88.4(2)
O(6)-Cd(2)-N(2)	80.7(2)	O(7)#2-Cd(2)-O(8)#2	53.5(2)
O(2)-Cd(2)-O(7)#2	92.2(2)	O(2)-Cd(2)-O(5)	90.0(2)
N(1)#4-Cd(2)-O(7)#2	84.4(2)	N(1)#4-Cd(2)-O(5)	95.1(2)
O(6)-Cd(2)-O(7)#2	127.1(2)	O(6)-Cd(2)-O(5)	53.1(2)
N(2)-Cd(2)-O(7)#2	95.1(2)	N(2)-Cd(2)-O(5)	82.8(2)
O(2)-Cd(2)-O(8)#2	93.7(2)	O(7)#2-Cd(2)-O(5)	177.8(2)
O(2)-Cd(2)-N(1)#4	92.6(2)	O(8)#2-Cd(2)-O(5)	126.7(2)

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

Synthesis of 3,5-bis(pyridin-4-ylmethoxy)benzoic acid (L1)

A mixture of methyl 3,5-dihydroxybenzoate (20 mmol, 3.64 g) and NaOH (40 mmol, 1.60 g) in DMF (50 ml) was stirred at 5 ºC for 2 h, then 4-(chloromethyl)pyridine (40 mmol, 6.50 g) was added. The mixture was cooled to room temperature after stirring

at 70 ºC for 10 h, and then poured into 200 ml of water. A light yellow solid of methyl 3,5-bis(pyridin-4-ylmethoxy)benzoate was deposited, which was isolated by filtration in 78 % yield after drying in air.

Then a mixture of methyl 3,5-bis(pyridin-4-ylmethoxy)benzoate (18 mmol, 6.55 g) and sodium hydroxide (100 mmol, 4.00 g) in water (80 ml) was stirred at 100 ºC for 6 h, and was cooled to room temperature. The mixture was adjusted to approximately pH 4.5 with dilute hydrochloric acid. A light yellow solid of L1 formed immediately, which was isolated by filtration in 65 % yield after drying in air.

^{1}H NMR (DMSO, 500 MHz) δ: 5.23 (s, 4H), 6.92 (s, 1H), 7.17 (d, J = 2 Hz, 2H), 7.44 (d, J = 5 Hz, 4H), 8.57 (m, 4H). Elemental analyses calcd (%) for $C_{19}H_{16}N_2O_4$ (336.35): C, 67.84; H, 4.81; N, 8.33. Found C, 67.87; H, 4.79; N, 8.31. IR (KBr pellet, cm^{-1}): 3422 (m), 3083 (w), 1714 (m), 1597 (s), 1444 (m), 1381 (m), 1330 (m), 1301 (s), 1243 (m), 1166 (s), 1059 (s), 801 (w), 769 (w).

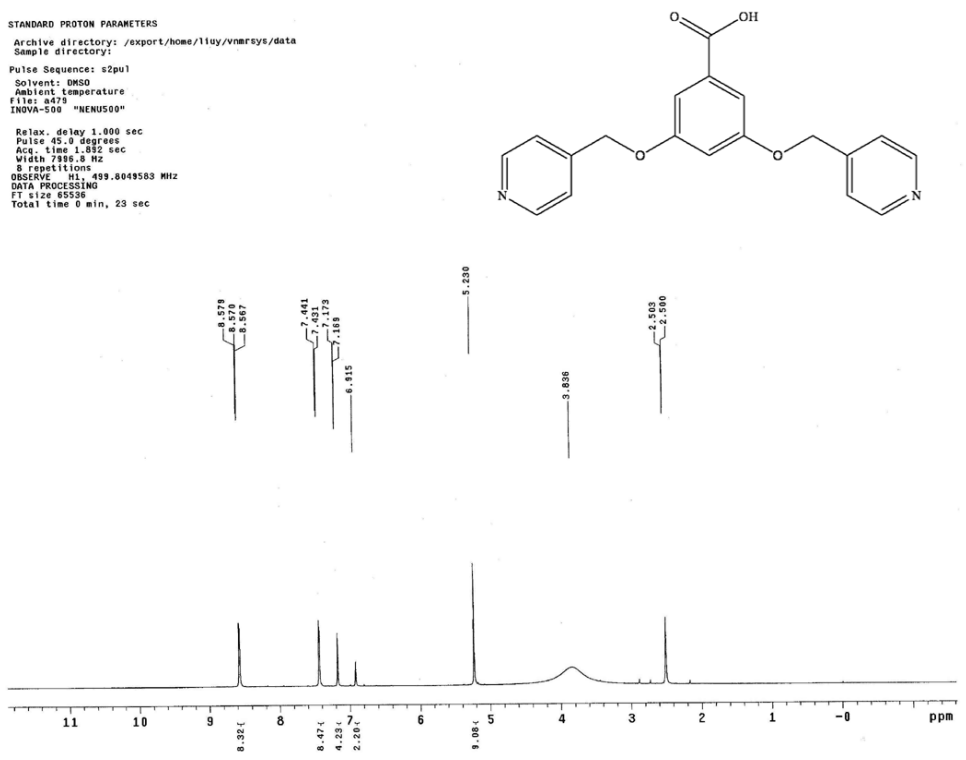


Fig. S1 ^{1}H NMR spectrum for L1 in DMSO.

Synthesis of 3,4-bis(pyridin-4-ylmethoxy)benzoic acid (L2)

L2 was prepared in the same way as L1, by using methyl 3,4-dihydroxybenzoate instead of methyl 3,5-dihydroxybenzoate (62 % yield).

^{1}H NMR (DMSO, 500 MHz) δ: 5.22 (s, 1H), 5.30 (m, 3H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.46 (q, *J* = 5.5 Hz, 5H), 7.55 (t, *J* = 6 Hz, 1H), 8.58 (m, 4H). Elemental analyses calcd (%) for $C_{19}H_{16}N_2O_4$ (336.35): C, 67.84; H, 4.81; N, 8.33. Found C, 67.86; H, 4.78; N, 8.34. IR (KBr pellet, cm^{-1}): 3428 (m), 2928 (w), 1698 (s), 1601 (s), 1517 (m), 1381 (s), 1350 (s), 1274 (s), 1211 (s), 1124 (m), 1024 (m), 811 (w), 759 (w).

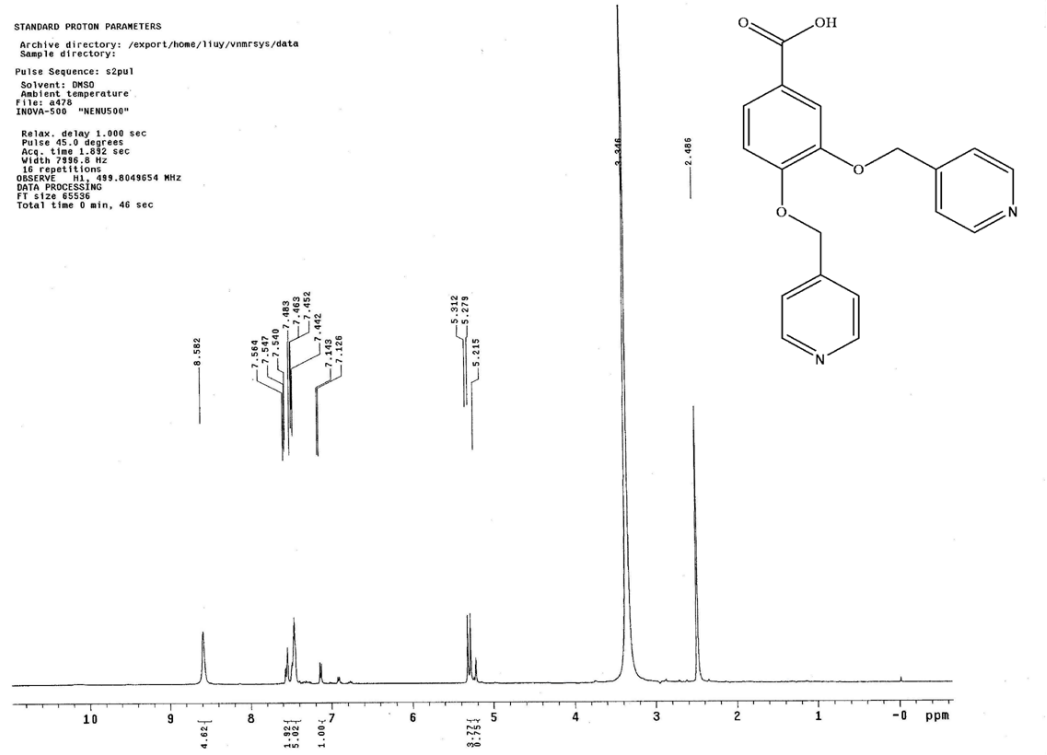


Fig. S2 ^{1}H NMR spectrum for L2 in DMSO.

Synthesis of 3,5-bis(pyridin-3-ylmethoxy)benzoic acid (L3)

L3 was prepared in the same way as L1, by using 3-(chloromethyl)pyridine instead of 4-(chloromethyl)pyridine (60 % yield).

^{1}H NMR (DMSO, 500 MHz) δ: 5.19 (s, 4H), 6.94 (s, 1H), 7.19 (s, 2H), 7.43 (q, *J* = 2.5 Hz, 2H), 7.87 (d, *J* = 7.5 Hz, 2H), 8.55 (d, *J* = 2.5 Hz, 2H), 8.67 (s, 2H). Elemental analyses calcd (%) for $C_{19}H_{16}N_2O_4$ (336.35): C, 67.84; H, 4.81; N, 8.33. Found C, 67.86; H, 4.80; N, 8.35. IR (KBr pellet, cm^{-1}): 3404 (m), 3094 (m), 1699 (m), 1599 (s), 1452 (m), 1352 (s), 1299 (s), 1258 (m), 1166 (s), 1046 (s), 791 (m), 704 (m).

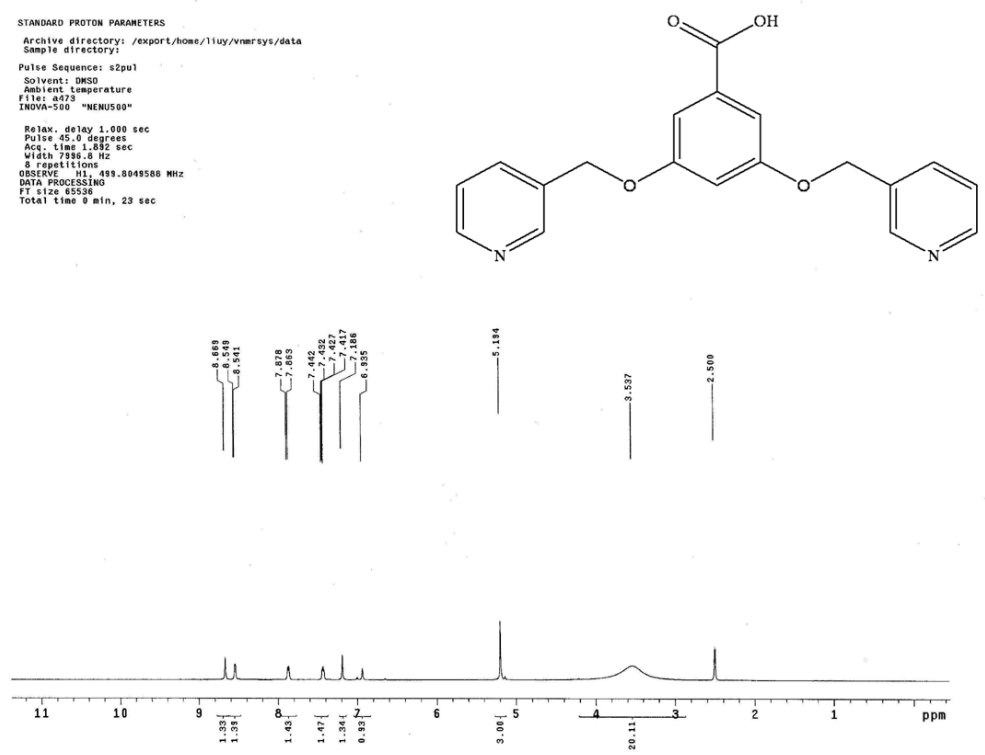


Fig. S3 ^{1}H NMR spectrum for L3 in DMSO.

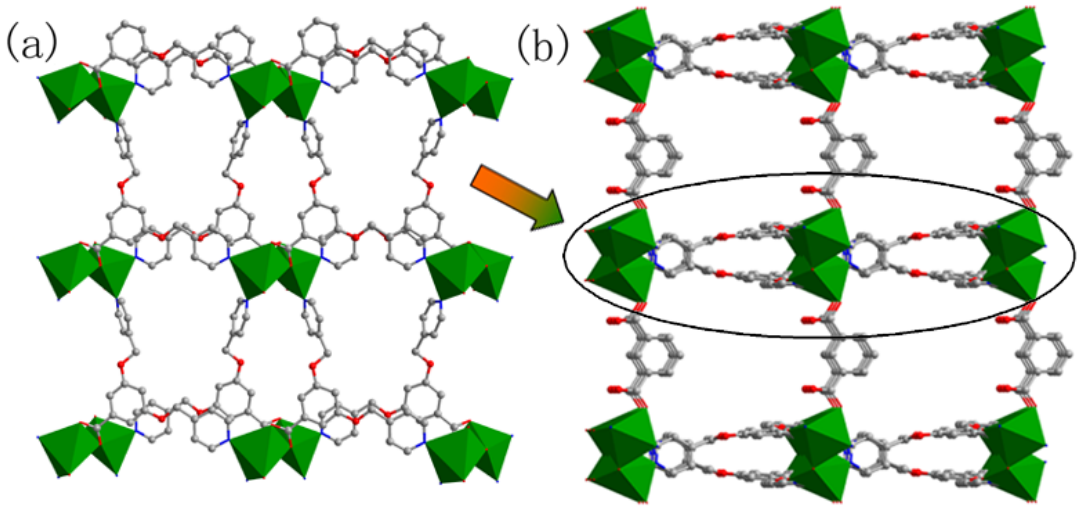


Fig. S4 Polyhedral representations of **1** (a) 2D bilayer structure; (b) 3D framework structure.

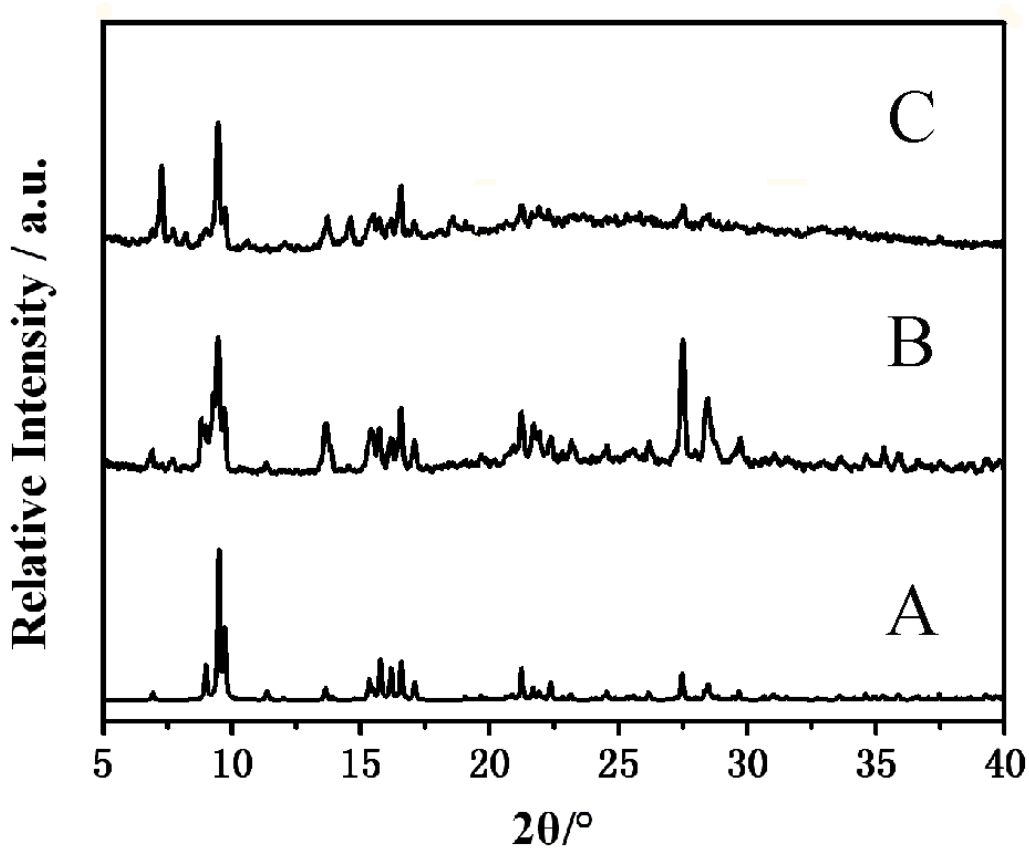


Fig. S5 The XRPD patterns of **1** at different temperatures: (a) simulated; (b) as-synthesized at 25 °C; (c) after heating at 240 °C (the simulated patterns are generated from single crystal diffraction data).

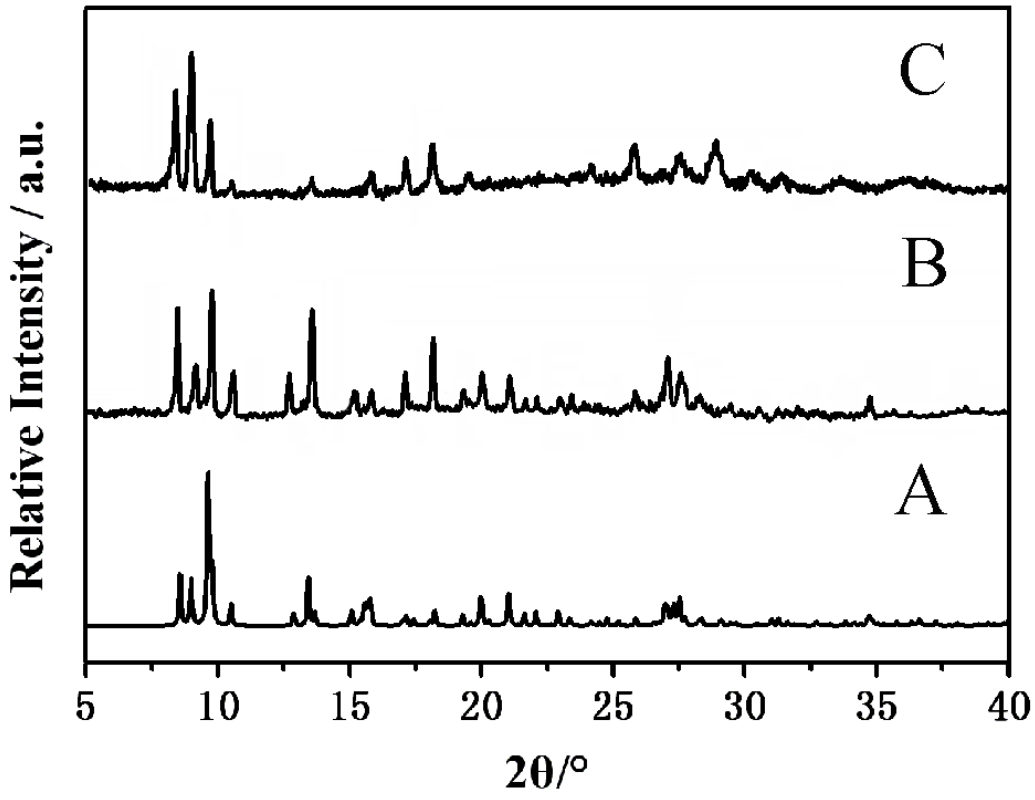


Fig. S6 The XRPD patterns of **2** at different temperatures: (a) simulated; (b) as-synthesized at 25 °C; (c) after heating at 300 °C (the simulated patterns are generated from single crystal diffraction data).

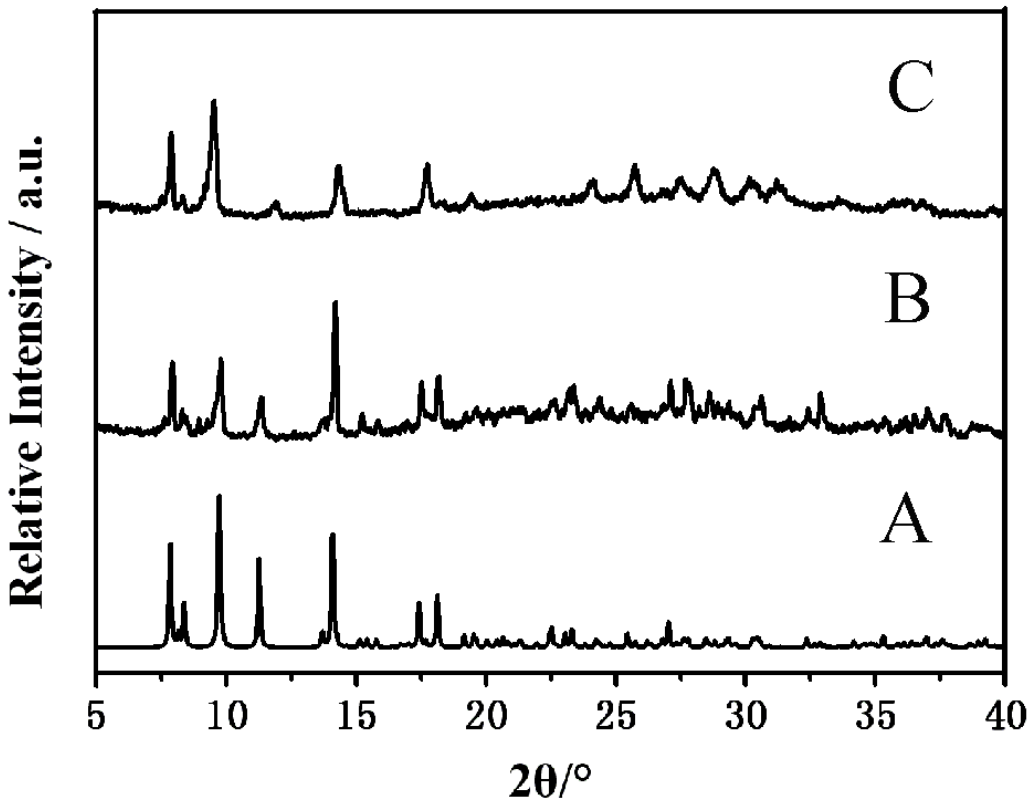


Fig. S7 The XRPD patterns of **3** at different temperatures: (a) simulated; (b) as-synthesized at 25 °C; (c) after heating at 240 °C (the simulated patterns are generated from single crystal diffraction data).

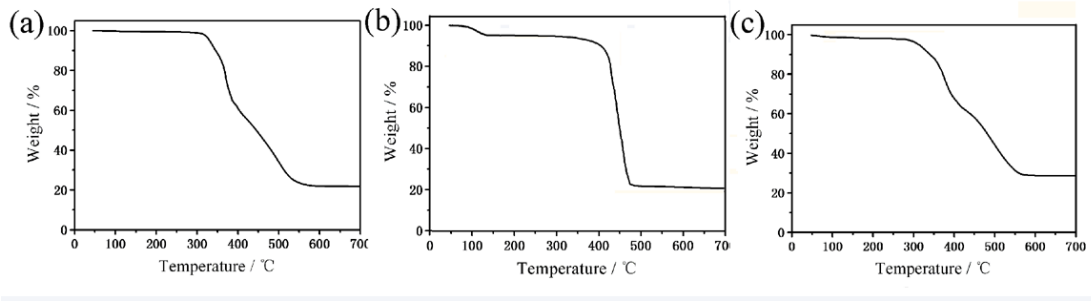


Fig. S8 TG curves of (a) **1**, (b) **2** and (c) **3**.