Electronic supporting information (ESI)

Two photoluminescent metal-organic frameworks with highly-connected topological nets

E Yang [a,b*], Qing-Rong Ding [a,b], Yao Kang [b], Fei Wang [b*]

[a] College of Chemistry and Chemistry Engineering, Fujian Normal University, Fuzhou, Fujian 350007, People's Republic of China. E-mail: yangeli66@yahoo.com.cn.

[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China. E-mail: wangfei04@fjirsm.ac.cn.

Table S1 Selected bond lengths [Å] and bond angles [°] for compound **1.**

Cd(1)-O(1)#1	2.290(3)	Cd(2)-N(6)	2.363(4)
Cd(1)-O(1)#2	2.290(3)	Cd(2)-N(2)	2.370(4)
Cd(1)-N(3)	2.308(4)	Cd(2)-O(5)#4	2.456(3)
Cd(1)-N(3)#3	2.308(4)	Cd(2)-O(1)#1	2.625(3)
Cd(1)-N(5)	2.361(4)	Cd(3)-O(4)	2.235(3)
Cd(1)-N(5)#3	2.361(4)	Cd(3)-N(8)#5	2.274(4)
Cd(2)-O(2)#1	2.259(3)	Cd(3)-N(1)	2.303(4)
Cd(2)-O(3)	2.326(3)	Cd(3)-O(7)	2.314(4)
Cd(2)-O(6)#4	2.345(3)	Cd(3)-N(10)#6	2.403(4)
O(1)#1-Cd(1)-O(1)#2	180.00(18)	O(6)#4-Cd(2)-N(2)	100.97(12)
O(1)#1-Cd(1)-N(3)	84.25(12)	N(6)-Cd(2)-N(2)	82.66(14)
O(1)#2-Cd(1)-N(3)	95.75(12)	O(2)#1-Cd(2)-O(5)#4	76.64(12)
O(1)#1-Cd(1)-N(3)#3	95.75(12)	O(3)-Cd(2)-O(5)#4	104.54(12)
O(1)#2-Cd(1)-N(3)#3	84.25(12)	O(6)#4-Cd(2)-O(5)#4	54.70(11)
N(3)-Cd(1)-N(3)#3	180.000(1)	N(6)-Cd(2)-O(5)#4	89.16(13)
O(1)#1-Cd(1)-N(5)	87.71(13)	N(2)-Cd(2)-O(5)#4	154.25(12)
O(1)#2-Cd(1)-N(5)	92.29(13)	O(2)#1-Cd(2)-O(1)#1	53.03(11)
N(3)-Cd(1)-N(5)	84.98(14)	O(3)-Cd(2)-O(1)#1	103.13(11)
N(3)#3-Cd(1)-N(5)	95.02(14)	O(6)#4-Cd(2)-O(1)#1	174.30(11)
O(1)#1-Cd(1)-N(5)#3	92.29(13)	N(6)-Cd(2)-O(1)#1	82.85(12)
O(1)#2-Cd(1)-N(5)#3	87.71(13)	N(2)-Cd(2)-O(1)#1	78.29(12)
N(3)-Cd(1)-N(5)#3	95.02(14)	O(5)#4-Cd(2)-O(1)#1	124.99(11)
N(3)#3-Cd(1)-N(5)#3	84.98(14)	O(4)-Cd(3)-N(8)#5	109.52(13)
N(5)-Cd(1)-N(5)#3	180.000(2)	O(4)-Cd(3)-N(1)	127.94(13)
O(2)#1-Cd(2)-O(3)	97.98(13)	N(8)#5-Cd(3)-N(1)	87.92(14)
O(2)#1-Cd(2)-O(6)#4	129.03(12)	O(4)-Cd(3)-O(7)	94.69(12)
O(3)-Cd(2)-O(6)#4	82.11(12)	N(8)#5-Cd(3)-O(7)	153.17(14)
O(2)#1-Cd(2)-N(6)	103.05(13)	N(1)-Cd(3)-O(7)	86.02(13)
O(3)-Cd(2)-N(6)	157.11(13)	O(4)-Cd(3)-N(10)#6	99.22(13)
O(6)#4-Cd(2)-N(6)	91.46(13)	N(8)#5-Cd(3)-N(10)#6	84.83(14)
O(2)#1-Cd(2)-N(2)	128.98(13)	N(1)-Cd(3)-N(10)#6	131.74(14)
O(3)-Cd(2)-N(2)	77.10(12)	O(7)-Cd(3)-N(10)#6	79.88(13)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+3,-z+2; #2 x,y-1,z; #3 -x,-y+2,-z+2; #4 -x+1,-y+3,-z+2; #5 -x+1,-y+2,-z+2; #6 x+1,y+1,z-1.

Table S2 Selected bond lengths [Å] and bond angles [°] for compound **2**.

Cd(1)-O(1)	2.276(3)	Cd(3)-N(18)#6	2.362(4)
Cd(1)-O(9)#1	2.298(3)	Cd(3)-O(3)#7	2.386(3)
Cd(1)-N(1)	2.300(4)	Cd(3)-O(9)#4	2.481(3)
Cd(1)-N(7)#2	2.318(4)	Cd(4)-O(12)#3	2.248(3)
Cd(1)-N(12)	2.338(4)	Cd(4)-N(11)#1	2.266(4)
Cd(1)-N(17)	2.393(4)	Cd(4)-N(4)	2.289(4)
Cd(2)-O(2)	2.232(3)	Cd(4)-O(2W)	2.323(3)
Cd(2)-O(11)#3	2.346(3)	Cd(4)-N(15)#8	2.433(4)
Cd(2)-O(8)	2.349(3)	Cd(4)-O(11)#3	2.576(3)
Cd(2)-N(9)	2.359(4)	Cd(5)-N(20)#7	2.234(4)
Cd(2)-N(3)	2.374(4)	Cd(5)-O(4)	2.253(3)
Cd(2)-O(7)	2.407(4)	Cd(5)-N(5)#9	2.265(4)
Cd(3)-O(5)	2.221(3)	Cd(5)-O(1W)	2.286(4)
Cd(3)-O(10)#4	2.254(3)	Cd(5)-O(6)#7	2.451(3)
Cd(3)-N(6)#5	2.327(4)	Cd(5)-O(3)	2.602(3)
O(1)-Cd(1)-O(9)#1	172.59(11)	O(10)#4-Cd(3)-O(3)#7	94.20(13)
O(1)-Cd(1)-N(1)	85.50(13)	N(6)#5-Cd(3)-O(3)#7	80.89(12)
O(9)#1-Cd(1)-N(1)	101.15(12)	N(18)#6-Cd(3)-O(3)#7	157.20(12)
O(1)-Cd(1)-N(7)#2	91.12(13)	O(5)-Cd(3)-O(9)#4	145.28(12)
O(9)#1-Cd(1)-N(7)#2	82.35(12)	O(10)#4-Cd(3)-O(9)#4	54.69(11)
N(1)-Cd(1)-N(7)#2	176.01(13)	N(6)#5-Cd(3)-O(9)#4	79.78(12)
O(1)-Cd(1)-N(12)	87.79(13)	N(18)#6-Cd(3)-O(9)#4	82.46(12)
O(9)#1-Cd(1)-N(12)	95.83(12)	O(3)#7-Cd(3)-O(9)#4	108.62(11)
N(1)-Cd(1)-N(12)	86.19(14)	O(12)#3-Cd(4)-N(11)#1	104.49(13)
N(7)#2-Cd(1)-N(12)	91.56(13)	O(12)#3-Cd(4)-N(4)	133.32(12)
O(1)-Cd(1)-N(17)	90.75(13)	N(11)#1-Cd(4)-N(4)	89.93(13)
O(9)#1-Cd(1)-N(17)	85.21(12)	O(12)#3-Cd(4)-O(2W)	90.06(13)
N(1)-Cd(1)-N(17)	97.39(14)	N(11)#1-Cd(4)-O(2W)	160.29(14)
N(7)#2-Cd(1)-N(17)	84.77(14)	N(4)-Cd(4)-O(2W)	89.54(12)
N(12)-Cd(1)-N(17)	176.02(13)	O(12)#3-Cd(4)-N(15)#8	92.92(13)
O(2)-Cd(2)-O(11)#3	97.42(13)	N(11)#1-Cd(4)-N(15)#8	84.77(14)
O(2)-Cd(2)-O(8)	133.39(13)	N(4)-Cd(4)-N(15)#8	132.99(14)
O(11)#3-Cd(2)-O(8)	78.76(12)	O(2W)-Cd(4)-N(15)#8	81.23(13)

O(2)-Cd(2)-N(9)	105.25(14)	O(12)#3-Cd(4)-O(11)#3	53.81(11)
O(11)#3-Cd(2)-N(9)	155.30(13)	N(11)#1-Cd(4)-O(11)#3	112.60(12)
O(8)-Cd(2)-N(9)	92.32(13)	N(4)-Cd(4)-O(11)#3	79.59(11)
O(2)-Cd(2)-N(3)	121.76(13)	O(2W)-Cd(4)-O(11)#3	86.66(11)
O(11)#3-Cd(2)-N(3)	76.45(12)	N(15)#8-Cd(4)-O(11)#3	144.64(12)
O(8)-Cd(2)-N(3)	102.68(13)	N(20)#7-Cd(5)-O(4)	118.74(13)
N(9)-Cd(2)-N(3)	83.26(13)	N(20)#7-Cd(5)-N(5)#9	100.93(14)
O(2)-Cd(2)-O(7)	80.40(13)	O(4)-Cd(5)-N(5)#9	138.17(12)
O(11)#3-Cd(2)-O(7)	98.55(12)	N(20)#7-Cd(5)-O(1W)	112.65(14)
O(8)-Cd(2)-O(7)	54.95(12)	O(4)-Cd(5)-O(1W)	85.95(13)
N(9)-Cd(2)-O(7)	94.83(13)	N(5)#9-Cd(5)-O(1W)	90.92(14)
N(3)-Cd(2)-O(7)	157.55(12)	N(20)#7-Cd(5)-O(6)#7	81.04(13)
O(5)-Cd(3)-O(10)#4	95.08(12)	O(4)-Cd(5)-O(6)#7	82.27(11)
O(5)-Cd(3)-N(6)#5	133.94(13)	N(5)#9-Cd(5)-O(6)#7	91.90(13)
O(10)#4-Cd(3)-N(6)#5	130.10(13)	O(1W)-Cd(5)-O(6)#7	165.20(13)
O(5)-Cd(3)-N(18)#6	93.39(13)	N(20)#7-Cd(5)-O(3)	153.80(13)
O(10)#4-Cd(3)-N(18)#6	108.28(14)	O(4)-Cd(5)-O(3)	53.69(10)
N(6)#5-Cd(3)-N(18)#6	81.66(14)	N(5)#9-Cd(5)-O(3)	84.89(12)
O(5)-Cd(3)-O(3)#7	88.25(12)	O(1W)-Cd(5)-O(3)	92.60(12)
O(6)#7-Cd(5)-O(3)	73.20(11)		

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z; #2 x,y+1,z; #3 -x+1,-y+1,-z; #4 x+1,y+1,z+1; #5 -x+3,-y+1,-z+1; #6 -x+3,-y+2,-z+1; #7 -x+2,-y+2,-z+1; #8 x-1,y-1,z; #9 x-1,y+1,z.

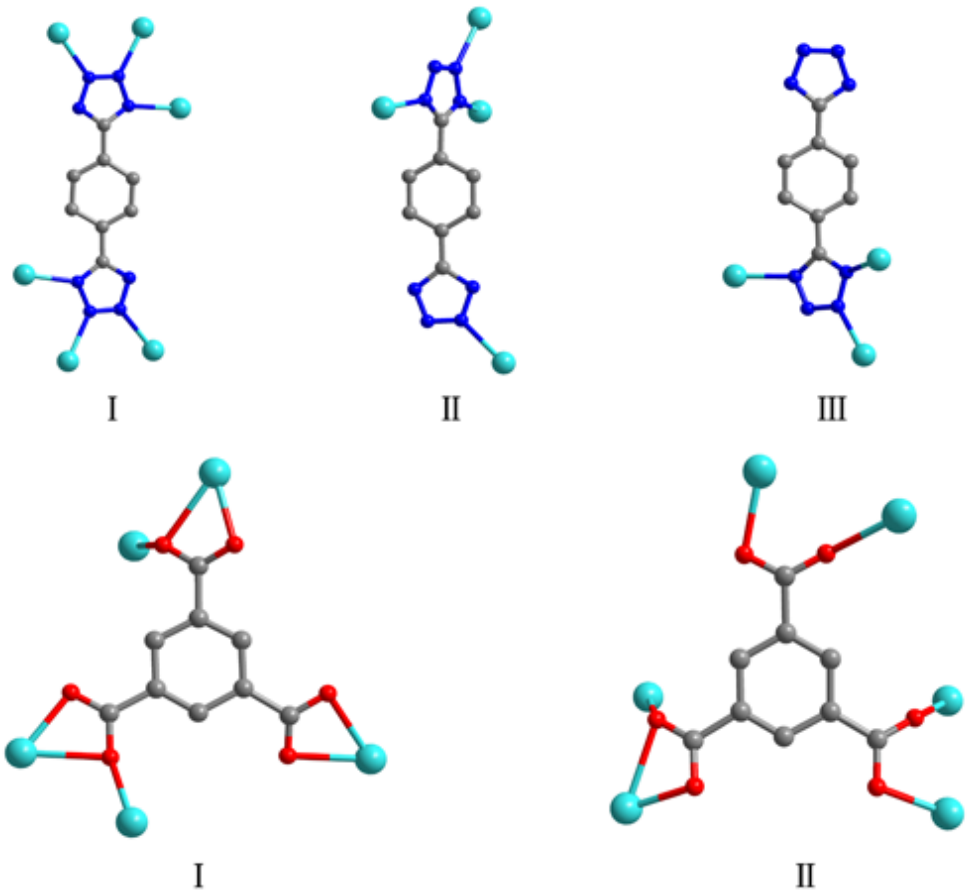

Fig. S1 The coordination modes of the ligands in **2**.

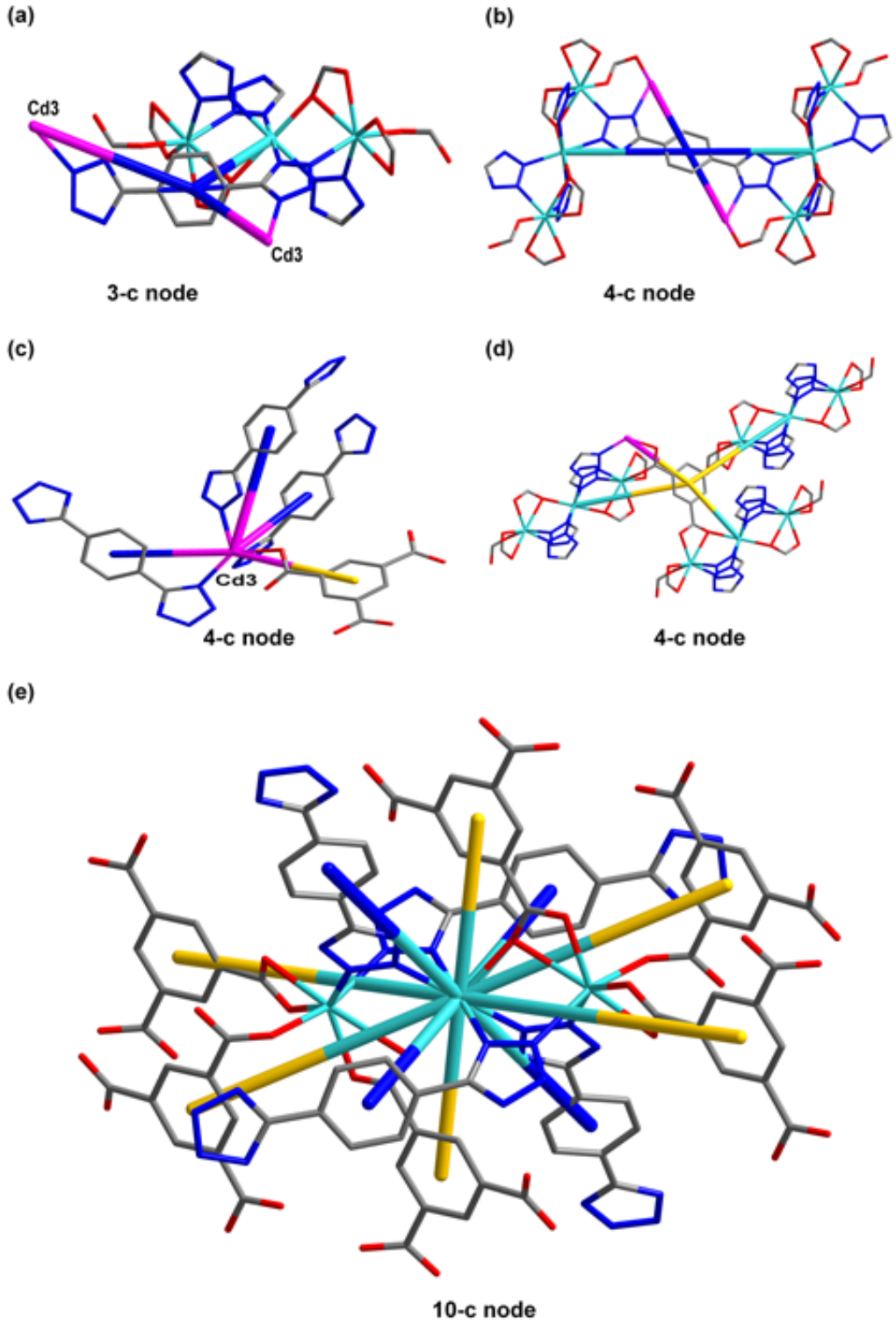

Fig. S2 (a) The defined 3-connected node formed from μ_4-bdt ligand; (b) the defined 4-connected node formed from μ_6-bdt ligand; (c) the defined 4-connected node formed from Cd3 atom; (d) the defined 4-connected node formed from btc ligand; (e) the defined 10-connected node formed from $Cd_3(CO_2)_6(CN_4)_4$ subunit.

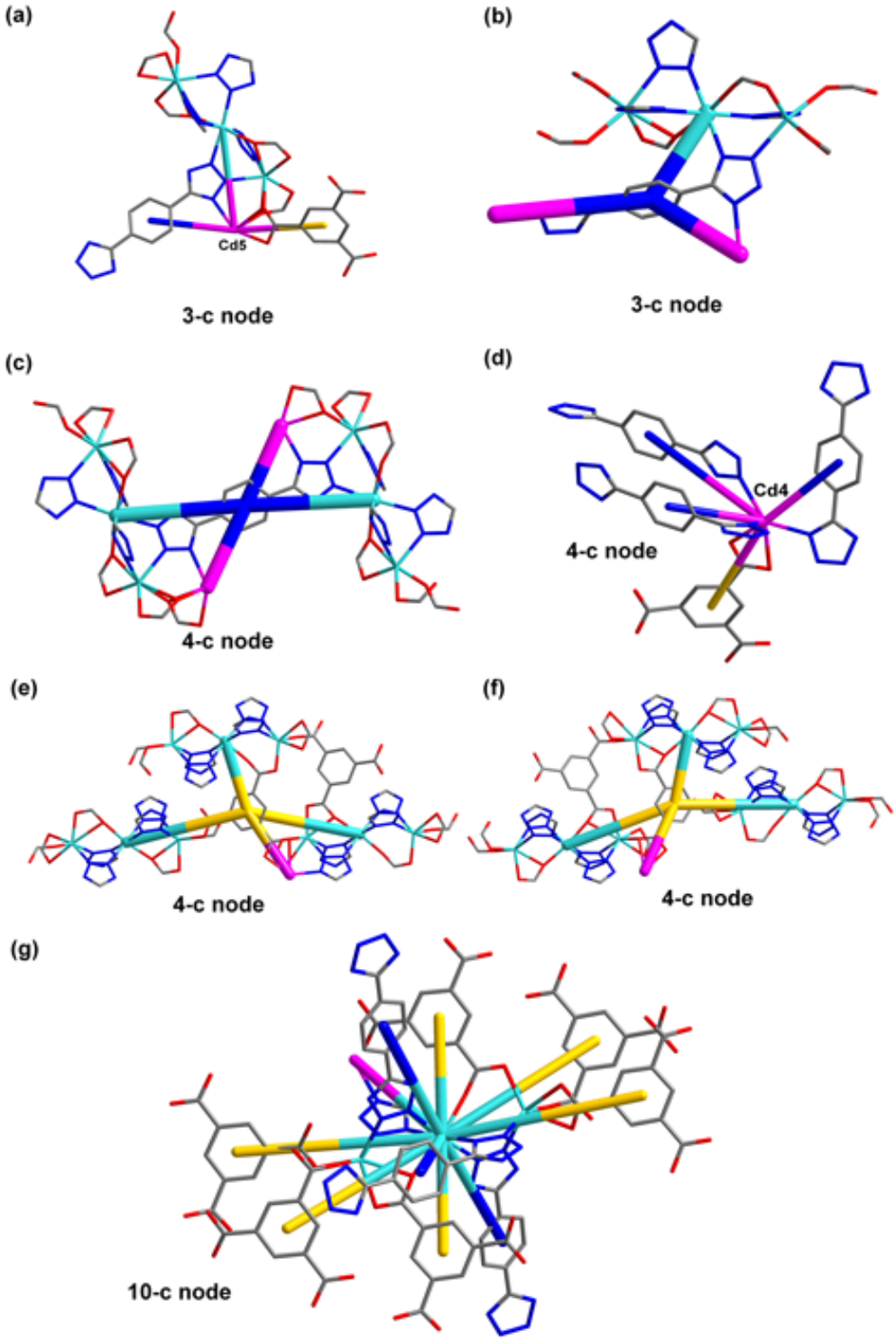

Fig. S3 (a) The defined 3-connected node formed from Cd5 atom; (b) the defined 3-connected node formed from μ_4-Hbdt ligand; (c) the defined 4-connected node formed from μ_6-bdt ligand; (d) the defined 4-connected node formed from Cd4 atom; (e) the defined 4-connected node formed from μ_6-btc ligand; (f) the defined 4-connected node formed from μ_5-btc ligand; (g) the defined 10-connected node formed from $Cd_3(CO_2)_6(CN_4)_4$ subunit.

The powder X-ray diffraction (PXRD) and thermal analysis

The as-synthesized samples of **1** and **2** have been characterized by powder X-ray diffraction (PXRD) (Fig. S4, S5). The experimental PXRD patterns correspond well with the results simulated from the single crystal data, indicating the pure phase of **1** and **2**. The difference in reflection intensities between the simulated and experimental patterns was due to the variation in preferred orientation of the powder samples during the collection of the experimental PXRD data.

Thermogravimetric analyses (TGA) in N_2 atmosphere with a heating rate of 10° C min^{-1} were performed on polycrystalline sample to determine their thermal stabilities from 25 to 600° C. TGA result of **1** indicates that the host framework was stable up to ca. 300° C. And the compound of **2** has thermal stability up to 340° C (Fig. S6). After that temperature, the framework decomposed.

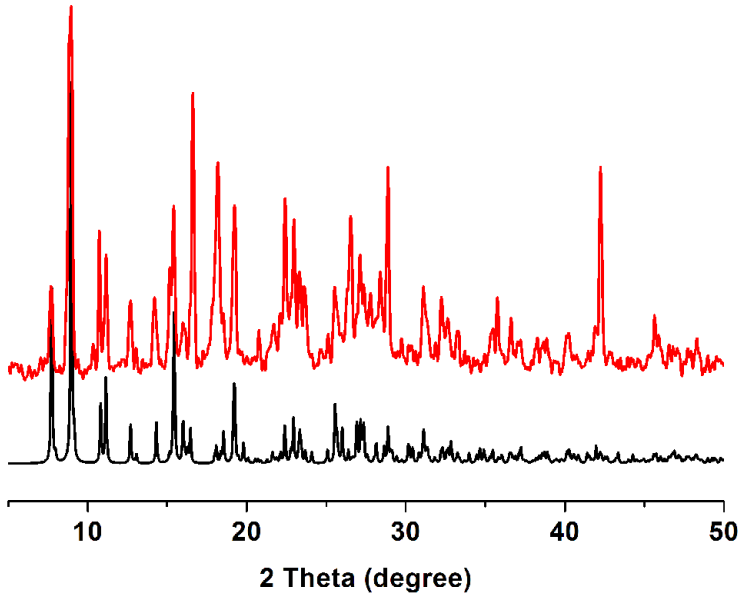

Fig. S4 The Experimental and simulated powder X-Ray diffraction patterns for **1**, black, simulated; red, as-synthesized.

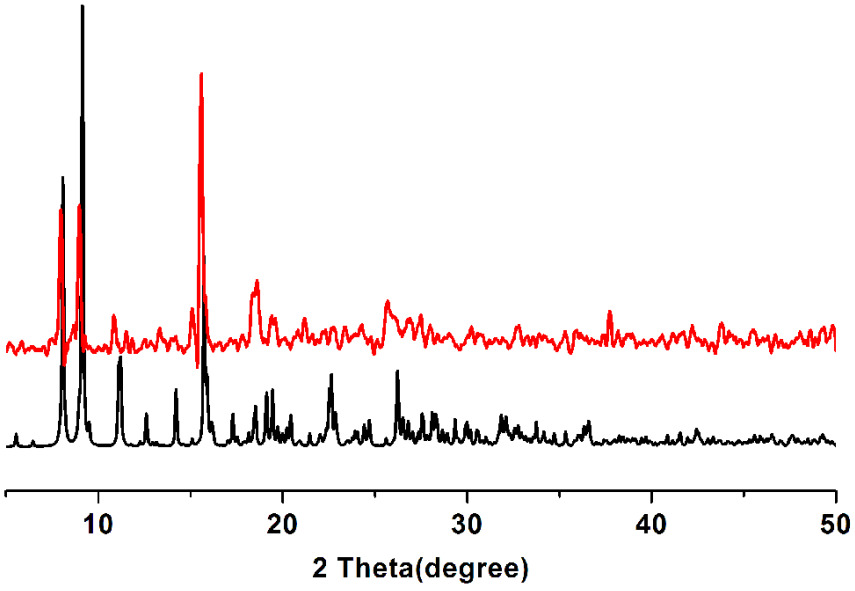

Fig. S5 The Experimental and simulated powder X-Ray diffraction patterns for **2**, black, simulated; red, as-synthesized.

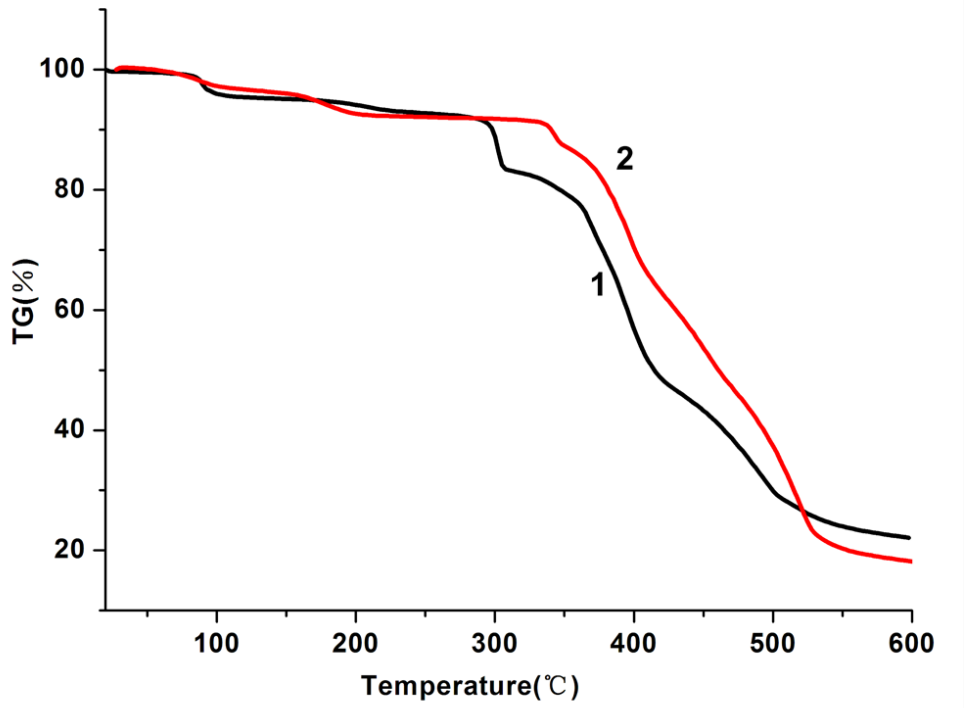

Fig. S6 Thermogravimetric analysis curves of compounds **1** and **2**.