Electronic Supplementary Information

From two-dimensional networks to three-dimensional metal-organic frameworks mediated by solvent ratio: Luminescence and gas adsorption properties

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1		2		3	
Co(1)-O(1)	2.004(7)	Co(1)-O(1)	2.049(3)	Co(1)-O(1)	2.0458(18)
Co(1)-O(1)#2	2.004(7)	Co(1)-O(3)	2.050(3)	Co(1)-O(2)#15	2.1240(18)
Co(1)-N(3)	2.229(8)	Co(1)-O(6)	2.071(3)	Co(1)-O(3)	2.170(2)
Co(1)-N(3)#2	2.229(8)	Co(1)-N(3)	2.213(3)	Co(1)-O(6)	2.1072(19)
Co(1)-N(8)	2.218(7)	Co(1)-N(4)#2	2.154(3)	Co(1)-N(3)	2.192(2)
Co(1)-N(8)#2	2.218(7)	Co(1)-N(7)	2.223(3)	Co(1)-N(4)#10	2.121(2)
Co(2)-O(3)	1.998(7)	Co(2)-O(2)	2.139(2)	O(1)-Co(1)-O(2)#15	91.97(7)
Co(2)-O(3)#2	1.998(7)	Co(2)-O(2)#2	2.139(2)	O(1)-Co(1)-O(3)	93.48(9)
Co(2)-N(4)	2.234(8)	Co(2)-O(5)	2.056(3)	O(1)-Co(1)-O(6)	86.51(8)
Co(2)-N(4)#2	2.234(8)	Co(2)-O(5)#2	2.056(3)	O(1)-Co(1)-N(3)	77.92(7)
Co(2)-N(7)	2.258(8)	Co(2)-N(8)	2.193(3)	O(1)-Co(1)-N(4)#10	173.39(8)
Co(2)-N(7)#2	2.258(8)	Co(2)-N(8)#2	2.193(3)	O(2)#15-Co(1)-O(3)	173.30(9)
O(1)-Co(1)-O(1)#2	180.0	O(1)-Co(1)-O(3)	87.34(13)	O(2)#15-Co(1)-O(6)	94.17(8)
O(1)-Co(1)-N(3)	79.8(3)	O(1)-Co(1)-O(6)	97.36(13)	O(2)#15-Co(1)-N(3)	91.17(7)
O(1)-Co(1)-N(3)#2	100.2(3)	O(1)-Co(1)-N(3)	76.92(11)	O(2)#15-Co(1)-N(4)#10	88.21(8)
O(1)-Co(1)-N(8)	90.5(3)	O(1)-Co(1)-N(4)#2	171.15(12)	O(3)-Co(1)-O(6)	90.06(9)
O(1)-Co(1)-N(8)#2	89.5(3)	O(1)-Co(1)-N(7)	84.21(11)	O(3)-Co(1)-N(3)	86.16(8)
O(1)#2-Co(1)-N(3)	100.2(3)	O(3)-Co(1)-O(6)	175.24(12)	O(3)-Co(1)-N(4)#10	86.84(9)
O(1)#2-Co(1)-N(3)#2	79.8(3)	O(3)-Co(1)-N(3)	90.13(11)	O(6)-Co(1)-N(3)	163.70(8)
O(1)#2-Co(1)-N(8)	89.5(3)	O(3)-Co(1)-N(4)#2	88.87(12)	O(6)-Co(1)-N(4)#10	86.89(8)

Table S1 Selected bond distances (Å) and angles (°) for 1–3.^{*a*}

90.5(3)	O(3)-Co(1)-N(7)	78.75(11)	N(3)-Co(1)-N(4)#10	108.68(8)
180.0	O(6)-Co(1)-N(3)	91.68(12)		
98.5(3)	O(6)-Co(1)-N(4)#2	86.37(12)		
81.5(3)	O(6)-Co(1)-N(7)	100.88(11)		
81.5(3)	N(3)-Co(1)-N(4)#2	111.10(11)		
98.5(3)	N(3)-Co(1)-N(7)	158.54(11)		
180.0	N(4)#2-Co(1)-N(7)	87.21(11)		
180.0(4)	O(2)-Co(2)-O(2)#2	180.0		
92.0(3)	O(2)-Co(2)-O(5)	86.65(11)		
88.0(3)	O(2)-Co(2)-O(5)#2	93.35(11)		
78.2(3)	O(2)-Co(2)-N(8)	92.08(11)		
101.9(3)	O(2)-Co(2)-N(8)#2	87.92(11)		
88.0(3)	O(2)#2-Co(2)-O(5)	93.35(11)		
92.0(3)	O(2)#2-Co(2)-O(5)#2	86.65(11)		
101.8(3)	O(2)#2-Co(2)-N(8)	87.92(11)		
78.1(3)	O(2)#2-Co(2)-N(8)#2	92.08(11)		
180.0	O(5)-Co(2)-O(5)#2	180.0		
85.3(3)	O(5)-Co(2)-N(8)	93.19(12)		
94.8(3)	O(5)-Co(2)-N(8)#2	86.81(12)		
94.8(3)	O(5)#2-Co(2)-N(8)	86.81(12)		
85.2(3)	O(5)#2-Co(2)-N(8)#2	93.19(12)		
180.0	N(8)-Co(2)-N(8)#2	180.0		
	90.5(3) 180.0 98.5(3) 81.5(3) 98.5(3) 180.0 180.0(4) 92.0(3) 180.0(4) 92.0(3) 78.2(3) 101.9(3) 78.2(3) 101.8(3) 101.8(3) 180.0 85.3(3) 94.8(3) 94.8(3) 185.2(3) 180.0	90.5(3) Q(3)-Co(1)-N(7) 180.0 Q(6)-Co(1)-N(4)#2 98.5(3) Q(6)-Co(1)-N(4)#2 81.5(3) Q(6)-Co(1)-N(7) 81.5(3) N(3)-Co(1)-N(7) 81.5(3) N(3)-Co(1)-N(7) 98.5(3) Q(2)-Co(2)-N(7) 180.0 Q(2)-Co(2)-Q(2)#2 98.0 Q(2)-Co(2)-Q(2)#2 98.0(3) Q(2)-Co(2)-N(8)#2 101.9 Q(2)-Co(2)-N(8)#2 98.0(3) Q(2)#2-Co(2)-N(8)#2 101.9 Q(2)#2-Co(2)-N(8)#2 92.0(3) Q(2)#2-Co(2)-N(8)#2 101.8 Q(2)#2-Co(2)-N(8)#2 101.8 Q(5)-Co(2)-N(8)#2 18.0 Q(5)-Co(2)-N(8)#2 180.0 Q(5)-Co(2)-N(8)#2 180.0 Q(5)#2-Co(2)-N(8)#2 94.8(3) Q(5)#2-Co(2)-N(8)#2 94.8(3) Q(5)#2-Co(2)-N(8)#2 94.8(3) Q(5)#2-Co(2)-N(8)#2 94.8(3) Q(5)#2-Co(2)-N(8)#2 94.8(3) Q(5)#2-Co(2)-N(8)#2 94.8(3) Q(5)#2-Co(2)-N(8)#2	90.5(3) Q(3)-Ca(1)-N(7) 78.75(11) 180.0 Q(6)-Ca(1)-N(3) 91.68(12) 98.5(3) Q(6)-Ca(1)-N(4)#2 86.37(12) 81.5(3) Q(6)-Ca(1)-N(4)#2 81.03 81.5(3) Q(6)-Ca(1)-N(4)#2 100.88(11) 81.5(3) N(3)-Ca(1)-N(4)#2 111.0(11) 98.5(3) N(3)-Ca(1)-N(7) 87.21(11) 180.0 N(4)#2-Ca(1)-N(7) 87.21(11) 180.0 Q(2)-Ca(2)-Q(2)#2 180.0 92.0(3) Q(2)-Ca(2)-Q(5)#2 86.56(11) 78.2(3) Q(2)-Ca(2)-N(8)#2 93.35(11) 92.0(3) Q(2)#2-Ca(2)-Q(5)#2 93.35(11) 92.0(3) Q(2)#2-Ca(2)-Q(5)#2 86.5(11) 92.0(3) Q(2)#2-Ca(2)-Q(5)#2 86.5(11) 92.0(3) Q(2)#2-Ca(2)-N(8)#2 92.08(11) 91.0(3) Q(2)#2-Ca(2)-N(8)#2 86.3(12) 91.1 Q(2)#2-Ca(2)-N(8)#2 18.0 91.1 Q(3) Q(3)#2-Ca(2)-N(8)#2 86.81(12) 91.80.0 Q(5)#2-Ca(2)-N(8)#2 86.81(12) 91.91(1)	90.5(3) O(3)-Co(1)-N(7) 78.75(11) N(3)-Co(1)-N(4)#10 180.0 O(6)-Co(1)-N(3) 91.68(12) 98.5(3) O(6)-Co(1)-N(4)#2 86.37(12) 81.5(3) O(6)-Co(1)-N(7) 100.88(11) 81.5(3) O(3)-Co(1)-N(4)#2 111.10(11) 98.5(3) N(3)-Co(1)-N(7) 185.54(11) 98.5(3) N(3)-Co(1)-N(7) 87.21(11) 180.00 N(4)#2-Co(1)-N(7) 87.21(11) 180.01 O(2)-Co(2)-O(2)#2 180.01 92.03 O(2)-Co(2)-O(5)#2 86.5(11) 78.203 O(2)-Co(2)-N(8)#2 93.35(11) 78.203 O(2)-Co(2)-N(8)#2 93.35(11) 78.203 O(2)-Co(2)-N(8)#2 93.35(11) 78.203 O(2)-Co(2)-N(8)#2 93.35(11) 78.203 O(2)#2-Co(2)-N(8)#2 93.35(11) 78.103 O(2)#2-Co(2)-N(8)#2 86.5(11) 71.104 O(2)#2-Co(2)-N(8)#2 92.08(11) 71.105 O(2)#2-Co(2)-N(8)#2 92.08(11) 71.104 O(2)#2-Co(2)-N(8)#2 92.08(11)

a Symmetry code for 1 and 2: #2=-x, -y, -z; symmetry code for 3: #10=-x, -y, -z, #15=x-y+2/3, x+1/3, -z+1/3.



Scheme S1 The synthesis procedure for HL ligand.



Fig. S1 ¹H NMR (400 MHz, dmso- d_6) of HL ligand.



Fig. S2 Powder XRD profiles of 3 and 4.



Fig. S3 Powder XRD profiles of 1.



Fig. S4 Powder XRD profiles of 2.



Fig. S5 The 3D supramolecular structure of 1.



Fig. S6 The two- and three-connecting ligands in 2.



Fig. S7 The 3D supramolecular structure of 2.



Fig. S8 The quasi-rectangular SBU in 3.



Fig. S9 Space-filling representation of 3, showing guest-free small hexagonal channels.



Fig. S10 Powder XRD profiles of as-synthesized and activated 3 and 4.



Fig. S11 Solid-state excitation spectra of HL ligand and coordination polymers.