Supplementary Information

Synthesis, structures and magnetic properties of two chiral mixed-valence iron(II, III) coordination networks

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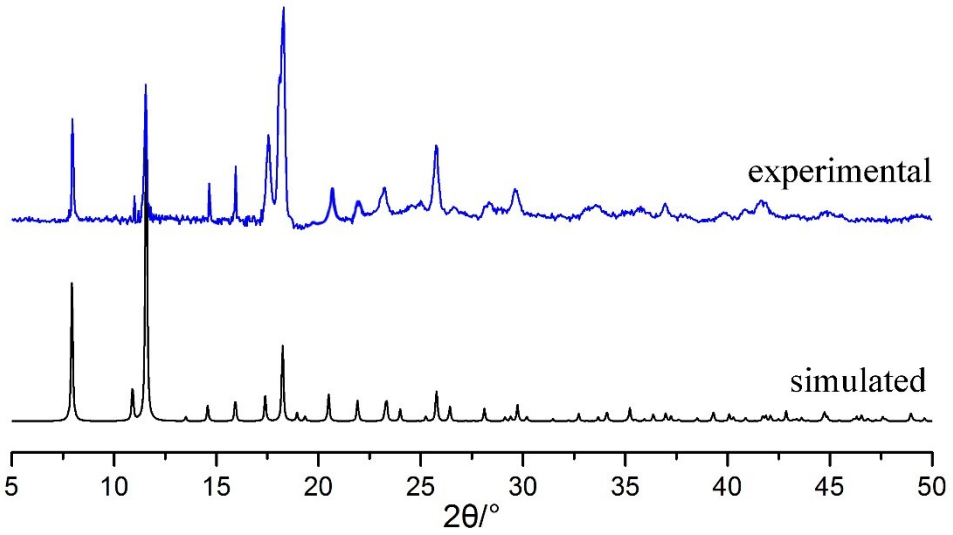

Figure S1. The powder XRD patterns of compound **1**.

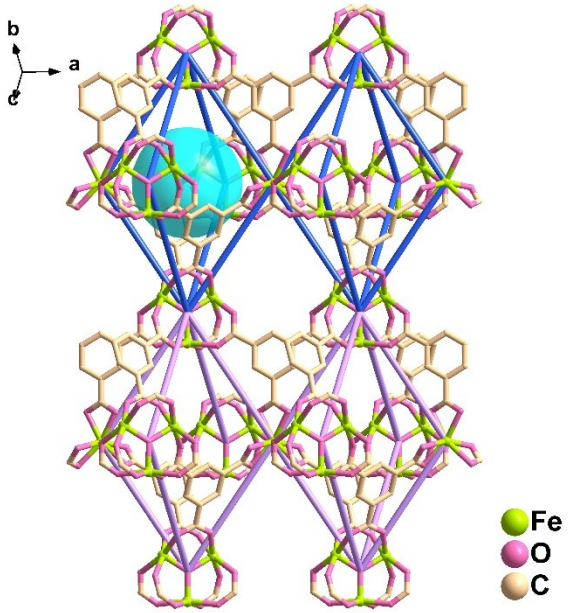

Figure S2 View of 3D coordination framework of D-**1**, showing 1D channels along [111] direction. The coordinated molecules are omitted for clarity.

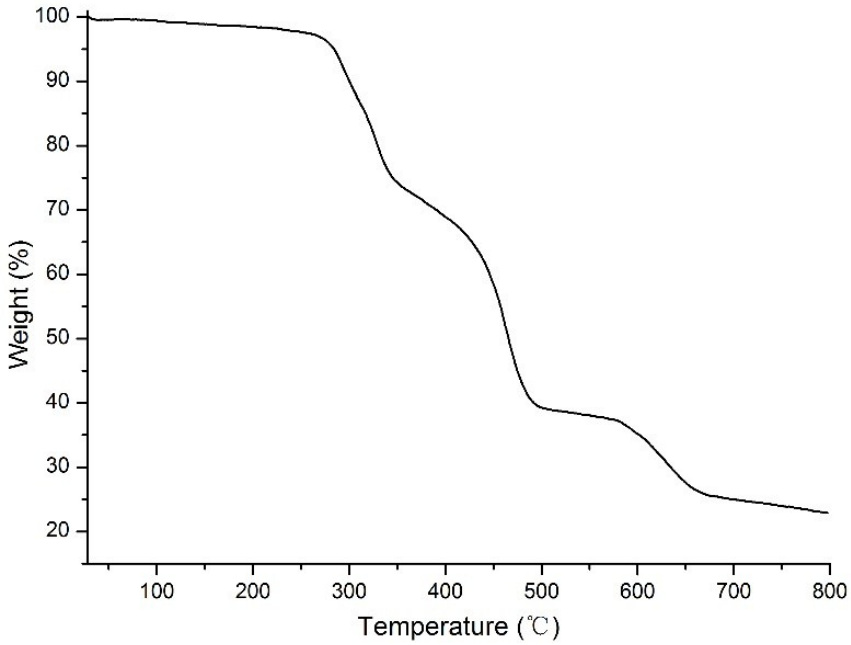

Figure S3. TGA profiles of compound **1**.

X-ray single crystal diffraction analyses reveal that there exists guest water molecule in the framework of **1**. The interaction between the framework and the guest molecules is rather weak. Accordingly, the guest water molecule first escaped from the framework of compound **1** with the heating, which is often observed in MOFs. It is known that the boiling point of water is 100 °C. The guest water molecule should be completely escaped from the framework at more than 120 °C, although weight loss between 40 to 280 °C seems to be continuous decreasing [1].

Above ca. 350 °C, the framework is only comprised of the organic ligand BTC^{3-} and metal clusters because of the departure of the coordinated DEF solvent molecules at 120−350 °C. On further heating, the framework began to decompose. It is possible that the framework firstly lost its organic ligands as a result of thermal decomposition. However, the detailed decomposition form and process of the framework is not clear at present. Therefore, we cannot detailed analyze two step processes of decomposition at the range between 400-480 °C and 580-650 °C. We will further explore the thermal decomposition process of MOFs in the next work."

Reference:

1. J. Zhang, Y.-S. Xue, Y.-Z. Li, H.-B. Du, X-Z. You, *CrystEngComm*, 2012, **14**, 8215-8221.

2. Table

Table S1. Selected bond lengths (Å) and angles (deg) for D-**1**.

Fe1-O1^{ii}	2.092(6)	O4-Fe1^{ix}	1.9126(17)
Fe1-O1^{iii}	2.092(6)	Fe2-O3	2.147(8)
Fe1-O2^{i}	2.048(6)	Fe2-O3^{iv}	2.147(8)
Fe1-O2	2.048(6)	Fe2-O3^{v}	2.147(8)
Fe1-O4	1.9126(17)	Fe2-O3^{vi}	2.147(8)
Fe1-O5	2.100(9)	Fe2-O3^{vii}	2.147(8)
O1-Fe1^{ix}	2.092(6)	Fe2-O3^{viii}	2.147(8)
O4-Fe1^{ii}	1.9126(18)		
O1^{ii}-Fe1-O1^{iii}	164.8(4)	O3-Fe2-O3^{iv}	104.0(3)
O1^{ii}-Fe1-O5	82.40(18)	O3-Fe2-O3^{v}	92.9(5)
O1^{iii}-Fe1-O5	82.40(18)	O3^{iv}-Fe2-O3^{v}	160.3(4)
O2^{i}-Fe1-O1^{ii}	87.5(3)	O3-Fe2-O3^{vi}	160.3(4)
O2-Fe1-O1^{ii}	91.2(3)	O3^{iv}-Fe2-O3^{vi}	61.5(4)
O2^{i}-Fe1-O1^{iii}	91.2(3)	O3^{v}-Fe2-O3^{vi}	104.0(3)
O2-Fe1-O1^{iii}	87.5(3)	O3-Fe2-O3^{vii}	61.5(4)
O2^{i}-Fe1-O2	170.3(4)	O3^{iv}-Fe2-O3^{vii}	92.9(5)
O2-Fe1-O5	85.17(19)	O3^{v}-Fe2-O3^{vii}	104.0(3)
O2^{i}-Fe1-O5	85.18(19)	O3^{vi}-Fe2-O3^{vii}	104.0(3)
O4-Fe1-O1^{ii}	97.60(19)	O3-Fe2-O3^{viii}	104.0(3)
O4-Fe1-O1^{iii}	97.60(19)	O3^{iv}-Fe2-O3^{viii}	104.0(3)
O4-Fe1-O2^{i}	94.82(19)	O3^{v}-Fe2-O3^{viii}	61.5(4)
O4-Fe1-O2	94.83(19)	O3^{vi}-Fe2-O3^{viii}	92.9(5)
O4-Fe1-O5	180.000	O3^{vii}-Fe2-O3^{viii}	160.3(4)

Symmetry transformations used to generate equivalent atoms: (i) -0.66667+x-y, -1.33333-y, 1.66667-z; (ii) 2-x+y, -x, z; (iii) 1.33333+y, -1.33333+x, 1.66667-z; (iv) 1-x+y, -1-x, z; (v) 1+y, -1+x, 2-z; (vi) -x, -x+y, 2-z; (vii) -1+x-y, -2-y, 2-z; (viii) -1-y, -2+x-y, z; (ix) -y, -2+x-y, z.

Table S2. Selected bond lengths (Å) and angles (deg) for L-**1**.

Fe1-O1^{ii}	2.118(5)	O4-Fe1^{ii}	1.928(3)
Fe1-O1^{iii}	2.118(5)	Fe2-O3^{iv}	2.175(6)
Fe1-O2^{i}	2.069(5)	Fe2-O3^{v}	2.175(6)
Fe1-O2	2.069(5)	Fe2-O3^{vi}	2.175(6)
Fe1-O4	1.928(3)	Fe2-O3	2.175(6)
Fe1-O5	2.121(8)	Fe2-O3^{vii}	2.175(6)
O1-Fe1^{ix}	2.118(5)	Fe2-O3^{viii}	2.175(6)
O4-Fe1^{ix}	1.928(3)		
O1^{ii}-Fe1-O1^{iii}	165.0(3)	O3^{iv}-Fe2-O3^{v}	104.01(19)
O1^{ii}-Fe1-O5	82.49(14)	O3^{iv}-Fe2-O3^{vi}	93.1(4)
O1^{iii}-Fe1-O5	82.49(14)	O3^{v}-Fe2-O3^{vi}	160.1(3)

O2^{i}-Fe1-O1^{ii}	87.6(2)	O3^{iv}-Fe2-O3	160.2(3)
O2-Fe1-O1^{ii}	91.2(2)	O3^{v}-Fe2-O3	61.4(3)
O2^{i}-Fe1-O1^{iii}	91.2(2)	O3^{vi}-Fe2-O3	104.01(19)
O2-Fe1-O1^{iii}	87.6(2)	O3^{iv}-Fe2-O3^{vii}	61.4(3)
O2^{i}-Fe1-O2	170.8(3)	O3^{v}-Fe2-O3^{vii}	93.1(4)
O2^{i}-Fe1-O5	85.40(14)	O3^{vi}-Fe2-O3^{vii}	104.01(19)
O2-Fe1-O5	85.40(14)	O3-Fe2-O3^{vii}	104.01(19)
O4-Fe1-O1^{ii}	97.51(14)	O3^{iv}-Fe2-O3^{viii}	104.01(19)
O4-Fe1-O1^{iii}	97.51(14)	O3^{v}-Fe2-O3^{viii}	104.01(19)
O4-Fe1-O2^{i}	94.60(14)	O3^{vi}-Fe2-O3^{viii}	61.4(3)
O4-Fe1-O2	94.60(14)	O3-Fe2-O3^{viii}	93.1(4)
O4-Fe1-O5	180.000	O3^{vii}-Fe2-O3^{viii}	160.1(3)

Symmetry transformations used to generate equivalent atoms: (i) -0.33333+y, 0.33333+x, -1.66667-z; (ii) 1-y, 1+x-y, z; (iii) 0.66667+x-y, 1.33333-y, -1.66667-z; (iv) -0.66667-x, -0.33333-x+y, -1.33333-z; (v) -0.66667+y, 0.66667+x, -1.33333-z; (vi) -1-x+y, -x, z; (vii) -y, 1+x-y, z; (viii) 0.33333+x-y, 0.66667-y, -1.33333-z; (ix) -x+y, 1-x, z; (x) -x, -x+y, -2-z.