Supporting Information

Solvent-Mediated Preparation of a Heterometallic [2×2] Grid via a 1D Metal–Organic Template with Extraordinary Acid/Base-Resistance

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Table S1. Crystal data and structure refinement details of **1** and **2**.

	1	**2**
Formula	$[Fe^{II}L(H_2O)]\cdot 2H_2O$	$[Fe^{III}_2Na_2L_4(H_2O)_4]\cdot 8H_2O$
	$C_{17}H_{14}FeN_{11}O_3$	$C_{68}H_{60}Fe_2N_{44}Na_2O_{12}$
Fw	476.24	1858.68
temp/K	298 (2)	100(2)
cryst syst	monoclinic	triclinic
space group	*C*2	*P*-1
a (Å)	22.027(4)	12.0542(4)
b (Å)	7.4504(15)	12.5534(4)
c (Å)	11.654(2)	15.4060(4)
α (°)	90	112.178(3)
β (°)	90.19(3)	102.023(3)
γ (°)	90	99.933(3)
V (Å^3)	1912.5(7)	2028.63(11)
Z	4	1
D_c (mg·m^{-3})	1.654	1.521
μ/(mm^{-1})	0.838	3.730
F (000)	972	952
rflns collected	3282	8090
unique rflns	3238	6962
R_{int}	0.0201	0.0436
GOF on F^2	1.052	1.068
R_1[a] (I>2sigmaI)	0.0554	0.0940
wR_2 [a]	0.1595	0.2748

[a] $R_1 = \big|\,|F_o| - |F_c|\,\big| / |F_o|$. $wR_2 = [w(|F_o^2| - |F_c^2|)^2 / w|F_o^2|^2]^{1/2}$.

Table S2. Selected bonds distances (Å) and angles (°) in **1** and **2**.

1			
Fe(1)-N(1)	2.145(4)	Fe(1)-N(2)	2.170(4)
Fe(1)-N(7)	2.240(4)	Fe(2)-O(1)	2.011(6)
Fe(2)-N(9)	2.185(4)	Fe(2)-N(10)	2.274(5)
N(1)-Fe(1)-N(2)	74.72(16)	N(1)#1-Fe(1)-N(2)	104.85(16)
N(1)-Fe(1)-N(7)#1	106.41(16)	N(2)#1-Fe(1)-N(7)#1	148.68(16)
N(2)-Fe(1)-N(7)#1	84.29(17)		
2			
Fe(1)-N(1)	1.926(4)	Fe(1)-N(2)	1.942(4)
Fe(1)-N(7)	1.937(4)	Fe(1)-N(12)	1.924(4)
Fe(1)-N(13)	1.941(4)	Fe(1)-N(18)	1.925(4)
N(12)-Fe(1)-N(18)	80.61(16)	N(12)-Fe(1)-N(1)	177.89(18)
N(18)-Fe(1)-N(1)	98.83(17)	N(12)-Fe(1)-N(7)	101.50(17)
N(18)-Fe(1)-N(7)	91.49(18)	N(1)-Fe(1)-N(7)	80.54(17)
N(12)-Fe(1)-N(13)	80.76(16)	N(18)-Fe(1)-N(13)	161.24(17)
N(1)-Fe(1)-N(13)	99.87(16)	N(7)-Fe(1)-N(13)	90.12(18)
N(12)-Fe(1)-N(2)	97.33(17)	N(18)-Fe(1)-N(2)	91.28(17)
N(1)-Fe(1)-N(2)	80.64(18)	N(7)-Fe(1)-N(2)	161.17(17)
N(13)-Fe(1)-N(2)	93.20(18)		

Symmetry codes #1: -x+1,y,-z #2 -x+1,y,-z+1

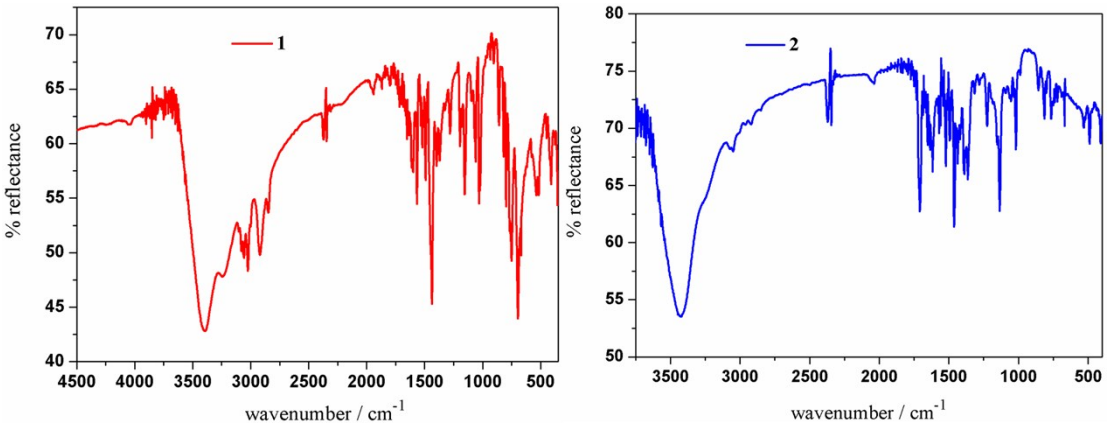


Figure S1. FT-IR of **1** and **2**.

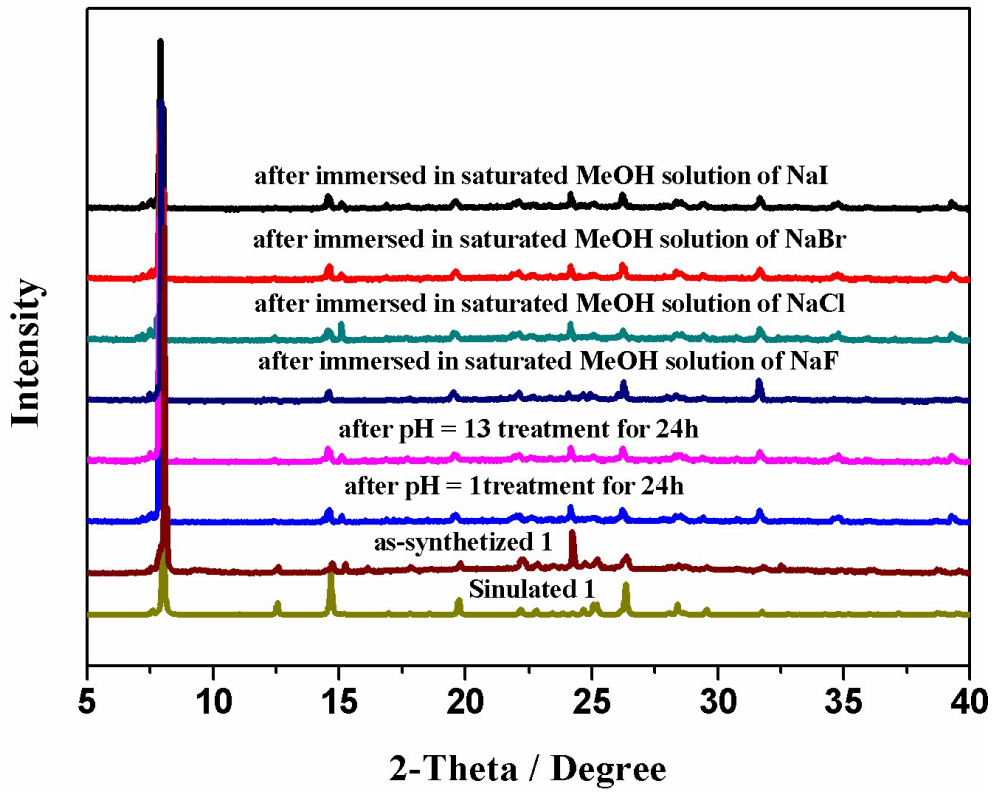


Figure S2. PXRD patterns of **1** after immersion in aqueous solutions with different pH values and NaX (X = F, Cl, Br and I).

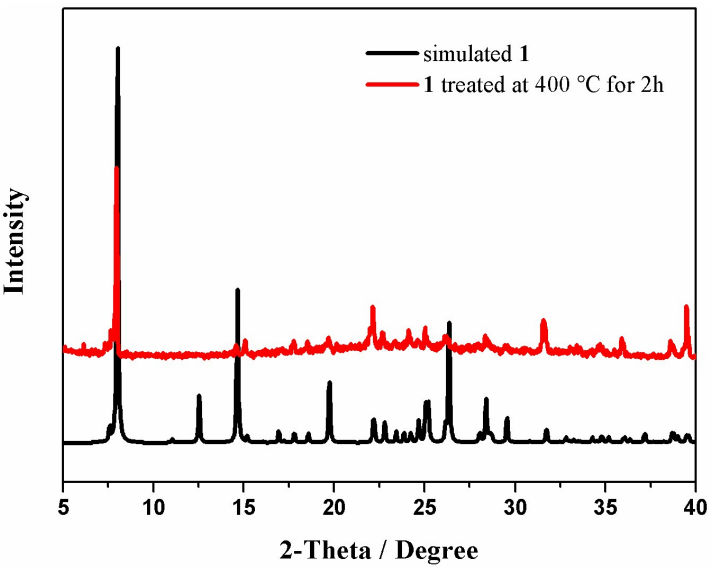
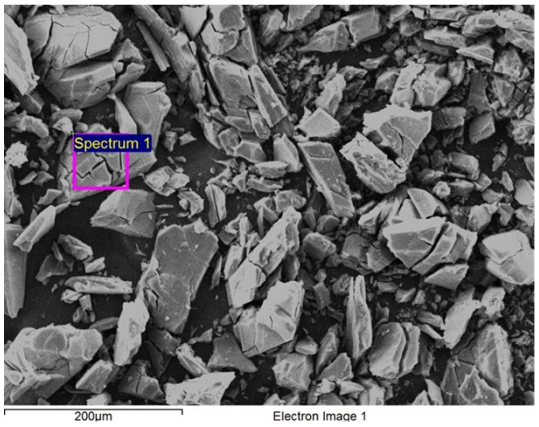


Figure S3. PXRD of **1** treated at 400 °C for 2h.



Element	Weight %	Atomic%
C K	49.71	56.54
N K	40.22	39.22
O K	1.66	1.41
Na K	2.20	1.31
Fe K	6.22	1.52
Totals	100.00	

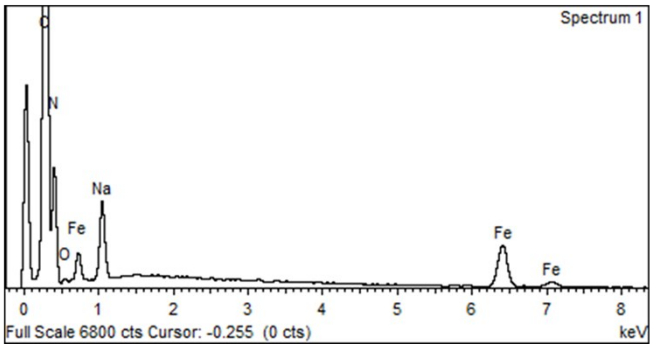


Figure S4. Typical SEM image of products from **2** (EDS was listed on the bottom of SEM images).

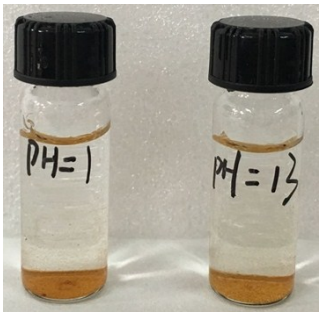


Figure S5. Freshly as-prepared crystals of **1** were respectively soaked in aqueous solutions with pH = 1 and 13 at room temperature.

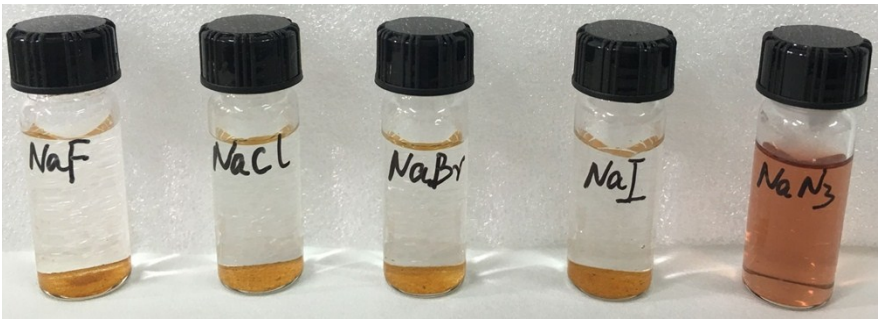


Figure S6. Freshly as-prepared crystals of **1** were respectively immersed in saturated MeOH solutions of NaF, NaCl, NaBr, NaI, and NaN_3 at room temperature.

Figure S7. Freshly as-prepared crystals of **2** can be insoluble in MeOH, EtOH, MeCN, but readily dissolve in DMF, DMA and DMSO.

Figure S8. Freshly as-prepared crystals of **1** were respectively immersed in saturated H_2O, MeOH, EtOH and DMF solutions of NaN_3 at room temperature.

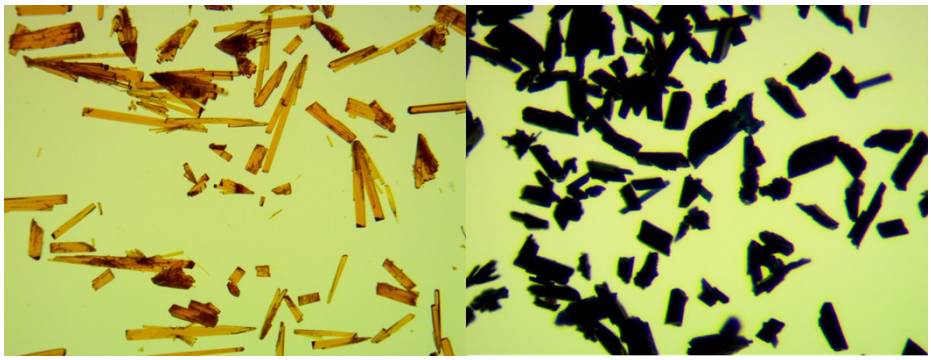


Figure S9. Optical microscopic photographs of 1 (left) and 2 (right).