Supporting Information

A series of highly stable porphyrinic metal-organic frameworks based on iron-oxo chain cluster: design, synthesis and biomimetic catalysis

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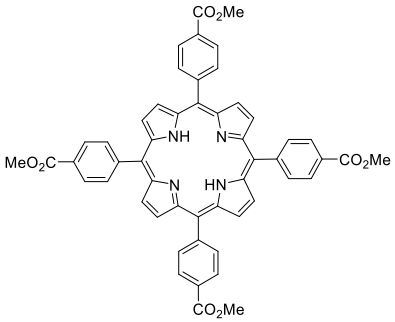
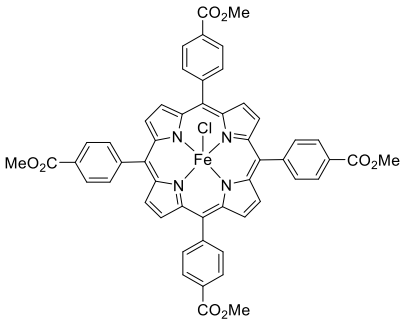
1. Synthesis

Synthesis of (meso-tetrakis[4-(methoxycarbonyl)phenyl]porphyrin) (TMCPP)



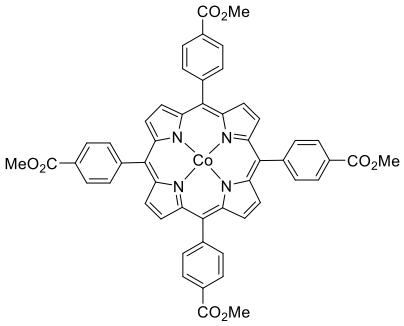
A mixture of pyrrole (4.50 g, 0.067 mol) and 4-formylmethylbenzoate (10 g, 0.0609 mol) in propionic acid (200 mL) is refluxed for 10 h, and then cooled down to room temperature. After being filtered, washed with methanol and a mixed solution of methanol and ethyl acetate (v : v = 4 : 1), and then dried in an oven, TMCPP is obtained as violet solid.

Synthesis of [5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrinato] iron(III) chloride (Fe-TMCPP)



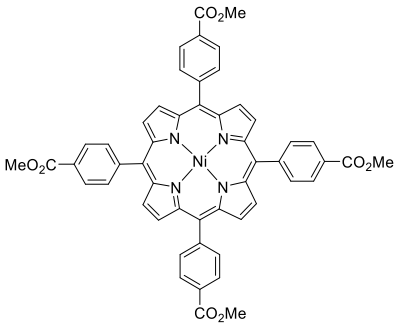
A mixture of TMCPP (0.85 g, 1.0 mmol) and $FeCl_2 \cdot 4H_2O$ (2.5 g, 12.8 mmol) in *N*,*N*-dimethylformamide (30 mL) is refluxed for 6 h, which is then cooled down to room temperature and precipitated with water (150 mL). After being filtered and washed with distilled water (50 mL × 3), the crude product of Fe-TMCPP is obtained, dissolved in chloroform, and then washed with 1 M HCl three times and water twice. The organic layer is dried over anhydrous $MgSO_4$ and then evaporated to afford dark brown solid.

Synthesis of [5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrinato] cobalt (II) (Co-TMCPP)



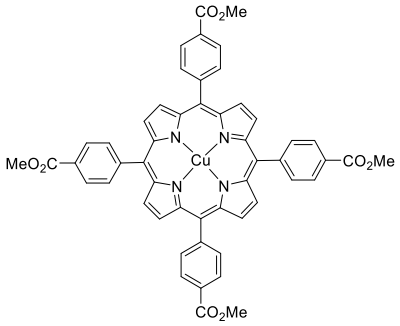
A mixture of TMCPP (1.0 g, 1.18 mmol) and $Co(OAc)_2 \cdot 4H_2O$ (2.35 g, 9.44 mmol) in a mixed solvent of chloroform and methanol (100 mL, *v* : *v* = 8 : 2) is refluxed overnight, and then cooled down to room temperature. Water (100 mL × 3) is used to remove inorganic salts. The organic layer is dried over anhydrous $NaSO_4$ and evaporated by a rotary evaporator, and further purified by silica gel column chromatography using CH_2Cl_2 as eluent. Co-TMCPP is obtained as red solid.

Synthesis of [5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrinato] nickel (II) (Ni-TMCPP)



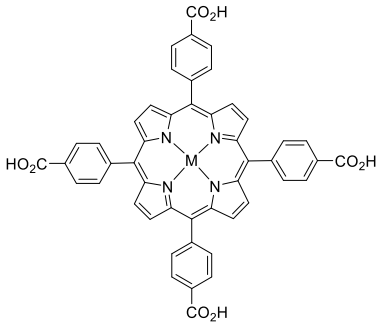
A mixture of TMCPP (1.0 g, 1.18 mmol) and $NiCl_2 \cdot 6H_2O$ (1.12 g, 4.72 mmol) in *N*,*N*-dimethylformamide (60 mL) is refluxed for 10 h, and then cooled down to room temperature and precipitated with water (150 mL). The crude product of Ni-TMCPP is obtained after being filtered and washed with distilled water (50 mL × 2). The organic layer is dried over anhydrous $NaSO_4$ and evaporated by a rotary evaporator, and purified by silica gel column chromatography using CH_2Cl_2 as eluent. Ni-TMCPP is obtained as red solid.

Synthesis of [5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrinato] copper(II) (Cu-TMCPP)



A mixture of TMCPP (1.0 g, 1.18 mmol) and $Cu(OAc)_2 \cdot H_2O$ (1.89 g, 9.44 mmol) in a mixed solvent of chloroform and methanol (100 mL, *v* : *v* = 9 : 1) is refluxed overnight, and then cooled down to room temperature. Water (100 mL × 3) is used to remove inorganic salts. The organic layer is dried over anhydrous $NaSO_4$ and evaporated by a rotary evaporator, and further purified by silica gel column chromatography using CH_2Cl_2 as eluent. Cu-TMCPP is obtained as purple crystal.

General procedure of the synthesis of M-TCPP (M = $Fe^{III}Cl$, Co^{II}, Ni^{II}, Cu^{II}; TCPP = 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin)



A mixture of M-TMCPP (1.5 g) and KOH (2.2 g) in a mixed solvent of tetrahydrofuran, methanol and water (150 mL, *v* : *v* : *v* = 1 : 1 : 1) is refluxed for 24 h, and then cooled down to room temperature. After most of the solvents are removed by evaporation, water is added to the remaining residue until all of them are dissolved. The resultant water solution is acidified with 1M HCl to afford the product, which is then collected by filtration, washed with distilled water and dried in the oven to give the pure M-TCPP.

Synthesis of Fe-PMOF-3(Fe)

A mixture of Fe-TCPP (8 mg, 9.45 μmol), $Fe(NO_3)_3 \cdot 9H_2O$ (9 mg, 22.3 μmol), benzoic acid (400 mg, 3.28 mmol), trifluoroacetic acid (270 μL, 3.64 mmol) and H_2O (20 μL, 1.11 mmol) is ultrasonically dissolved in *N*,*N*-dimethylacetamide (2 mL) in a 15 mL Teflon-lined autoclave. The autoclave is afterwards placed in a programmable oven at 160 ℃ for 12 h with a heating rate of 1.5 ℃/min and a cooling rate of 0.38 ℃/min. After being cooled down to room temperature, the dark red crystals of Fe-PMOF-3(Fe) are obtained by filtration, and washed with DMF for five times with and acetone for three times.

Anal. Calcd. for Fe-PMOF-3(Fe) $\cdot 7(C_6H_5COOH) \cdot 3(CF_3COOH) \cdot DMF \cdot 5H_2O$: C, 53.41; H, 3.61; N, 2.94 Found: C, 53.23; H, 5.32; N, 2.37. FTIR (cm^{-1}, ATR): 3402 (w), 2570 (w), 1607 (w), 1514 (m), 1410 (s), 1180 (m), 995 (m), 773 (m), 711 (m), 543 (m), 509 (m), 439 (m).

Synthesis of Co-PMOF-3(Fe)

A mixture of Co-TCPP (5 mg, 5.88 μmol), $Fe(NO_3)_3 \cdot 9H_2O$ (10 mg, 24.8 μmol), benzoic acid (390 mg, 3.19 mmol), trifluoroacetic acid (240 μL, 3.24 mmol) and H_2O (60 μL, 3.33 mmol) is ultrasonically dissolved in *N*,*N*-dimethylformamide (2 mL) in a 15 mL Teflon-lined autoclave. The autoclave is afterwards placed in a programmable oven at 150 ℃ for 12 h with a heating rate of 1.5 ℃/min and a cooling rate of 0.3 ℃/min. After being cooled down to room temperature, the dark red crystals of Co-PMOF-3(Fe) are obtained by filtration, and washed with DMF for five times with and acetone for three times.

Anal. Calcd. for Co-PMOF-3(Fe) $\cdot 5(C_6H_5COOH) \cdot 2.3(CF_3COOH) \cdot 0.2DMF \cdot 4H_2O$: C, 54.38; H, 3.38; N, 3.02. Found: C, 54.31; H, 6.24; N, 2.66. FTIR (cm^{-1}, ATR): 3390 (w), 1610 (w), 1578 (w), 1508 (m), 1411 (s), 1350 (m), 999 (m), 774 (m), 713 (m), 554 (w), 512 (m), 459 (m).

Synthesis of Ni-PMOF-3(Fe)

A mixture of Ni-TCPP (10 mg, 11.8 μmol), $Fe(NO_3)_3 \cdot 9H_2O$ (8 mg, 19.8 μmol), benzoic acid (400 mg, 3.28 mmol), trifluoroacetic acid (240 μL, 3.24 mmol) and H_2O (45 μL, 2.50 mmol) is ultrasonically dissolved in *N*,*N*-dimethylformamide (2 mL) in a 15 mL Teflon-lined autoclave. The

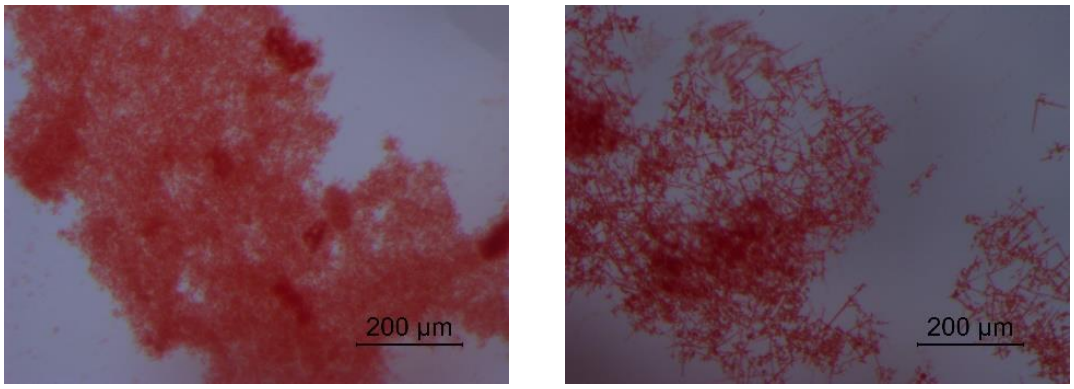
autoclave is afterwards placed in a programmable oven at 150 ℃ for 12 h with a heating rate of 1.5 ℃/min and a cooling rate of 0.3 ℃/min. After being cooled down to room temperature, the dark red crystals of Ni-PMOF-3(Fe) are obtained by filtration, and washed with DMF for five times with and acetone for three times.

Anal. Calcd. for Ni-PMOF-3(Fe) $\cdot 5(C_6H_5COOH) \cdot 2.1(CF_3COOH) \cdot 4H_2O$: C, 54.82; H, 3.36; N, 2.93. Found: C, 54.38; H, 5.74; N, 2.43. FTIR (cm^{-1}, ATR): 3431 (m), 2928 (w), 2350 (w), 1514 (s), 1414 (s), 1182 (w), 1001 (m), 773 (m), 712 (m), 556 (m), 516 (m), 463 (m).

Synthesis of Cu-PMOF-3(Fe)

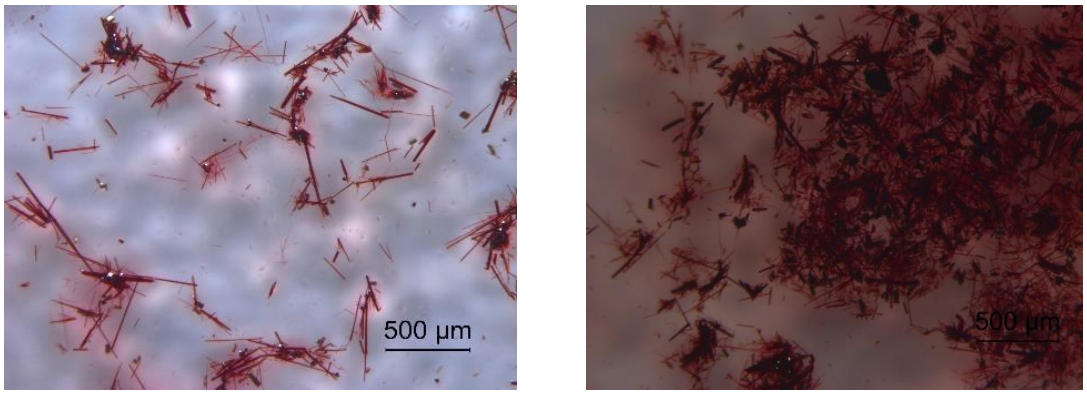
A mixture of Cu-TCPP (10 mg, 11.7 μmol), $Fe(NO_3)_3 \cdot 9H_2O$ (9 mg, 22.3 μmol), benzoic acid (400 mg, 3.28 mmol), trifluoroacetic acid (240 μL, 3.24 mmol) and H_2O (45 μL, 2.50 mmol) is ultrasonically dissolved in *N*,*N*-dimethylformamide (2 mL) in a 15 mL Teflon-lined autoclave. The autoclave is afterwards placed in a programmable oven at 150 ℃ for 12 h with a heating rate of 1.5 ℃/min and a cooling rate of 0.3 ℃/min. After being cooled down to room temperature, the dark red crystals of Cu-PMOF-3(Fe) are obtained by filtration, and washed with DMF for five times with and acetone for three times.

Anal. Calcd. for Cu-PMOF-3(Fe) $\cdot 1.8(CF_3COOH) \cdot 0.02DMF \cdot 3H_2O$: C, 55.83; H, 3.33; N, 3.02. Found: C, 55.55; H, 5.84; N, 2.57. FTIR (cm^{-1}, ATR): 3045 (w), 2928 (w), 1517 (s), 1411 (s), 1345 (s), 1182 (m), 998 (m), 773 (m), 713 (m), 605 (w) , 550 (m), 516 (m), 447 (m).



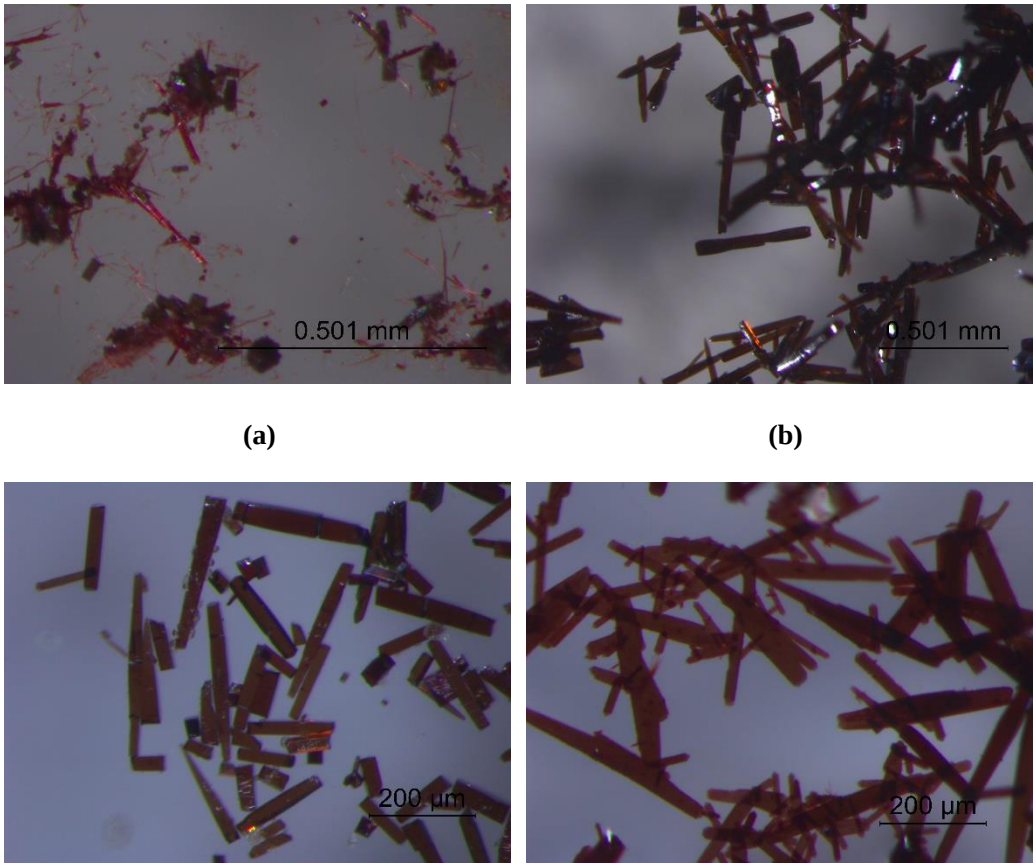
(a) **(b)**

Figure S1. The products that are prepared from the reaction of Ni-TCPP and $Fe(NO_3)_3$ $9H_2O$ in the absence of trifluoroacetic acid (Reaction conditions: (a) Ni-TCPP (10 mg, 11.8 µmol), $Fe(NO_3)_3$ $9H_2O$ (8 mg, 19.8 µmol), benzoic acid (400 mg, 3.28 mmol), H_2O (25 µL, 1.39 mmol), *N*,*N*-dimethylformamide (2 mL), 150 ℃, 12 h; (b) Ni-TCPP (10 mg, 11.8 µmol), $Fe(NO_3)_3$ $9H_2O$ (8 mg, 19.8 µmol), benzoic acid (700 mg, 5.73 mmol), H_2O (25 µL, 1.39 mmol), *N*,*N*-dimethylformamide (2 mL), 150 ℃, 12 h.



(a) **(b)**

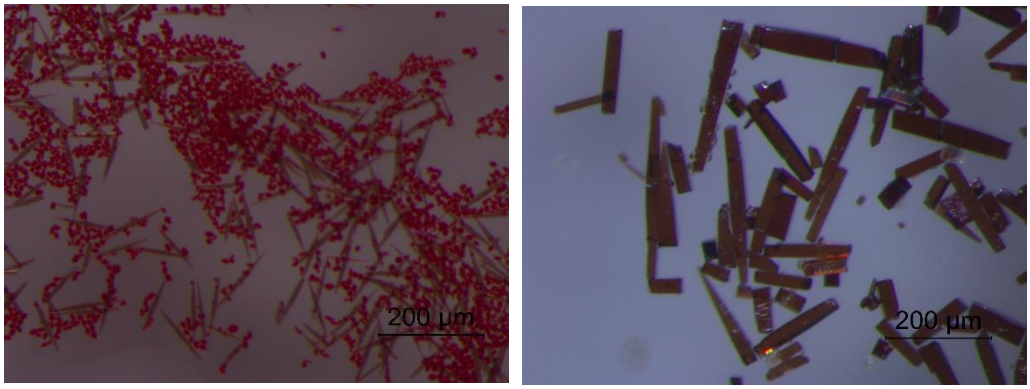
Figure S2. The products that are prepared from the reaction of Ni-TCPP and $Fe(NO_3)_3$ $9H_2O$ in the absence of benzoic acid (Reaction conditions: (a) Ni-TCPP (10 mg, 11.8 µmol), $Fe(NO_3)_3$ $9H_2O$ (8 mg, 19.8 µmol), trifluoroacetic acid (0.4 mL, 5.39 mmol), H_2O (25 µL, 1.39 mmol), *N*,*N*-dimethylformamide (2 mL), 150 ℃, 12 h; (b) Ni-TCPP (10 mg, 11.8 µmol), $Fe(NO_3)_3$ $9H_2O$ (8 mg, 19.8 µmol), trifluoroacetic acid (0.5 mL, 6.74 mmol), H_2O (25 µL, 1.39 mmol), *N*,*N*-dimethylformamide (2 mL), 150 ℃, 12 h.



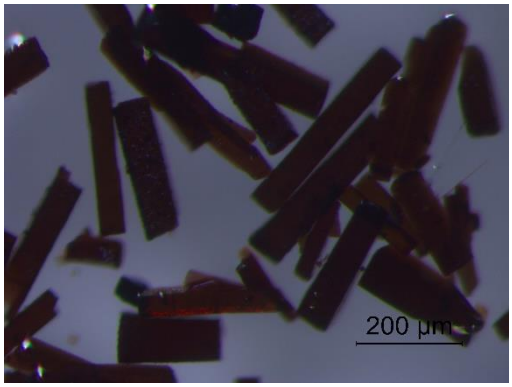
(a) **(b)**

(c) **(d)**

Figure S3. The products that are prepared from the reaction of Ni-TCPP and $Fe(NO_3)_3\ 9H_2O$ (Reaction conditions: Ni-TCPP (10 mg, 11.8 μmol), $Fe(NO_3)_3\ 9H_2O$ (8 mg, 19.8 μmol), trifluoroacetic acid (0.24 mL, 3.24 mmol), H_2O (25 μL, 1.39 mmol), *N*,*N*-dimethylformamide (2 mL), 150 ℃, 12 h) with different amount of benzoic acid: (a) 0 mg; (b) 200 mg (1.64 mmol); (c) 400 mg (3.28 mmol); (d) 600 mg (4.91 mmol).

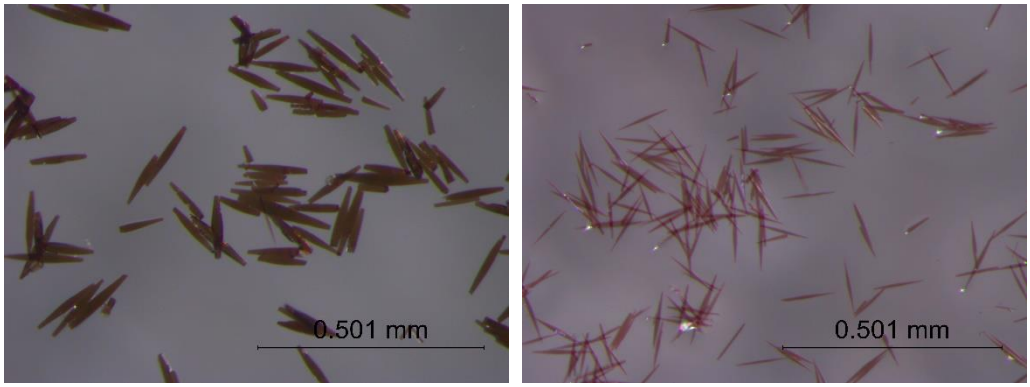


(a) **(b)**

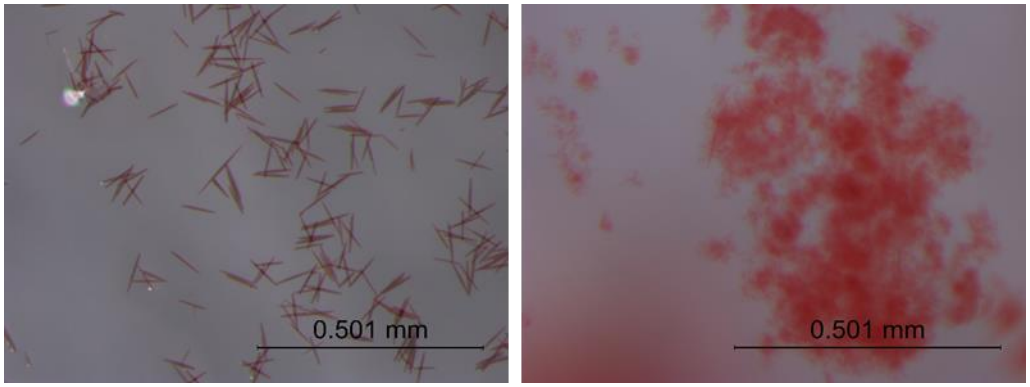


(c)

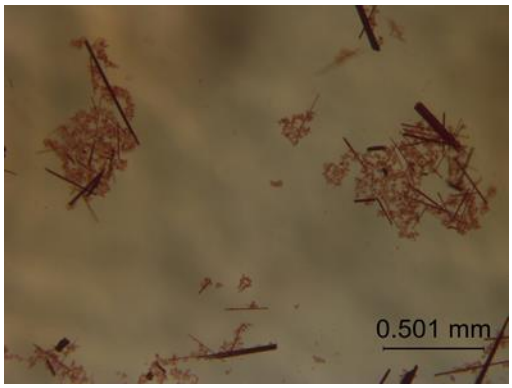
Figure S4. The products that are prepared from the reaction of Ni-TCPP and $Fe(NO_3)_3$ $9H_2O$ (Reaction conditions: Ni-TCPP (10 mg, 11.8 μmol), $Fe(NO_3)_3$ $9H_2O$ (8 mg, 19.8 μmol), benzoic acid (400 mg, 3.28 mmol), H_2O (25 μL, 1.39 mmol), *N*,*N*-dimethylformamide (2 mL), 150 ℃, 12 h) with different amount of trifluoroacetic acid: (a) 0.14 mL (1.89 mmol); (b) 0.24 mL (3.24 mmol); (c) 0.34 mL (4.58 mmol).



(a) **(b)**



(c) **(d)**



(e)

Figure S5. The products that are prepared from the reaction of Ni-TCPP and $Fe(NO_3)_3$ $9H_2O$ (Reaction conditions: Ni-TCPP (10 mg, 11.8 μmol), $Fe(NO_3)_3$ $9H_2O$ (8 mg, 19.8 μmol), benzoic acid (400 mg, 3.28 mmol), trifluoroacetic acid (0.24 mL, 3.24 mmol), *N*,*N*-dimethylformamide (2 mL), 150 ℃, 12 h) with different amount of water: (a) 25 μL (1.39 mmol); (b) 85 μL (4.72 mmol); (c) 125 μL (6.94 mmol); (d) 200 μL (11.1 mmol); (e) no water

2. Structure

Table S1. Summary of crystallographic data for Ni-PMOF-3(Fe) and Cu-PMOF-3(Fe).

Compound	Ni-PMOF-3(Fe)	Cu-PMOF-3(Fe)
Empirical formula	$C_{48}H_{24}N_4O_{10}Fe_2Ni$	$C_{48}H_{24}N_4O_{10}Fe_2Cu$
F_W	987.10	991.96
Color	Red	Red
Temperature	200 K	200 K
Crystal system	Orthorhombic	Orthorhombic
Space group	*Cmmm*	*Cmmm*
a (Å)	6.8484(3)	6.8469(3)
b (Å)	32.9205(14)	32.8843(16)
c (Å)	16.5679(8)	16.6801(15)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	3735.3(3)	3755.6(4)
Z	2	2
F(000)	1000.0	1002.0
$D_{calcd.}$ (g cm^{-3})	0.878	0.877
μ (mm^{-1})	0.670	3.703
h, k, l	8, 42, 21	8, 40, 20
Nref	2448	2169
T_{min},T_{max}	0.935, 0.967	0.915, 0.963
Theta(max)	27.499	73.383
Data completeness	0.996	0.958
R(reflections)	0.0450(1992)	0.0592(1775)
wR_2 (reflections)	0.1333(2437)	0.1983(2077)
GOF on F^2	1.080	1.125
R_1, wR_2 [$I > 2\sigma(I)$]	0.0450, 0.1279	0.0592, 0.1917
R_1, wR_2 (all data)	0.0565, 0.1333	0.0662, 0.1983

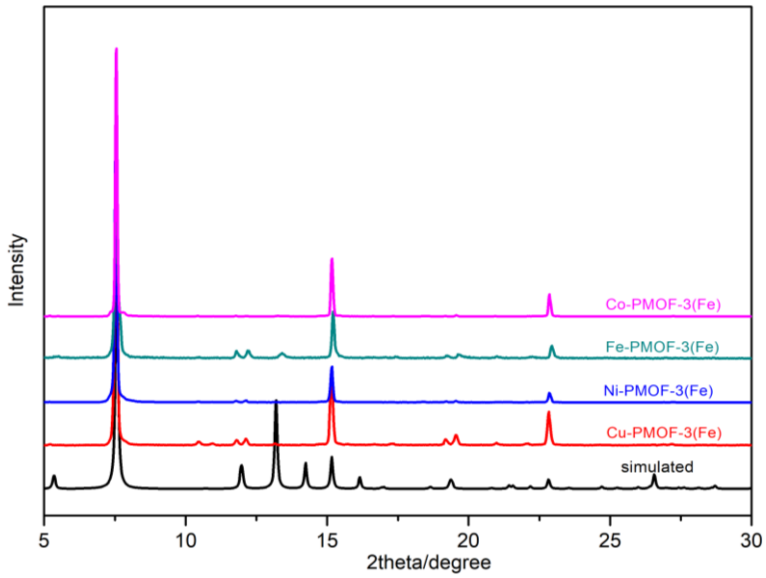


Figure S6. PXRD patterns of M-PMOF-3(Fe).

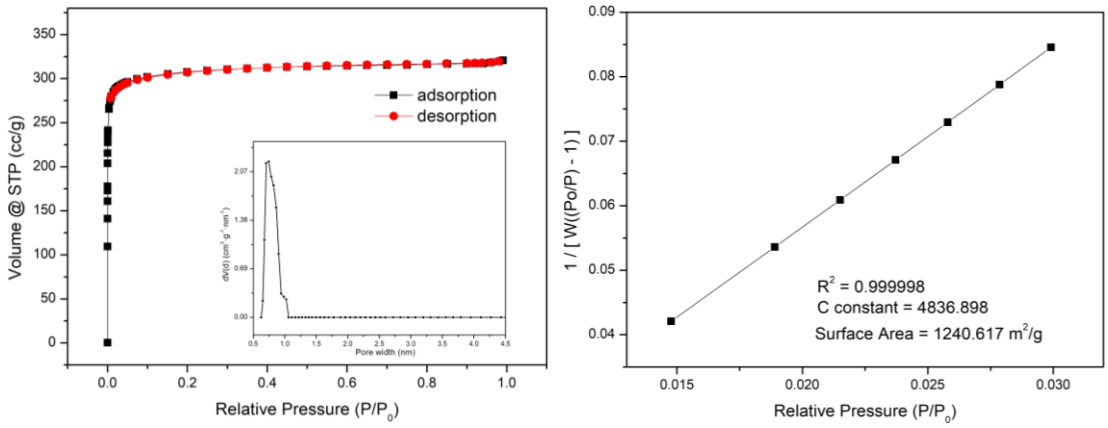


Figure S7. N_2 adsorption-desorption isotherm and BET surface area of Fe-PMOF-3(Fe).

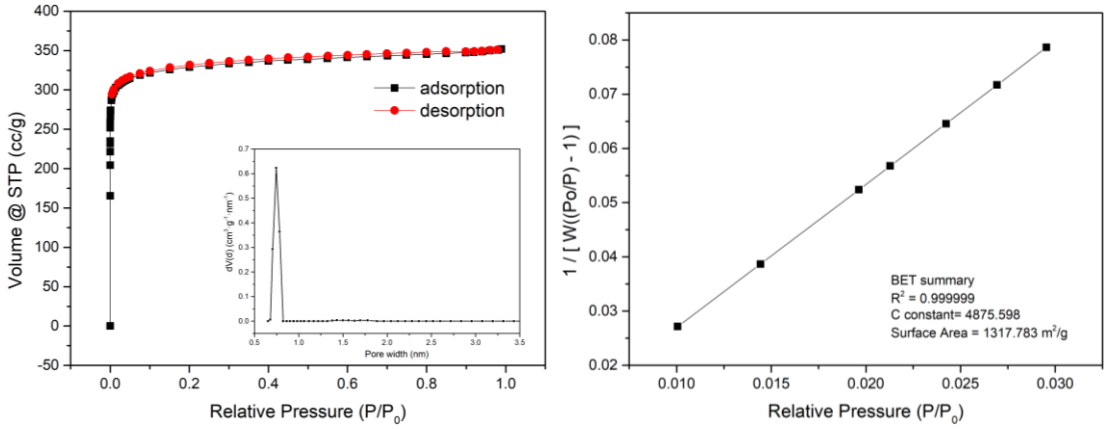


Figure S8. N_2 adsorption-desorption isotherm and BET surface area of Co-PMOF-3(Fe).

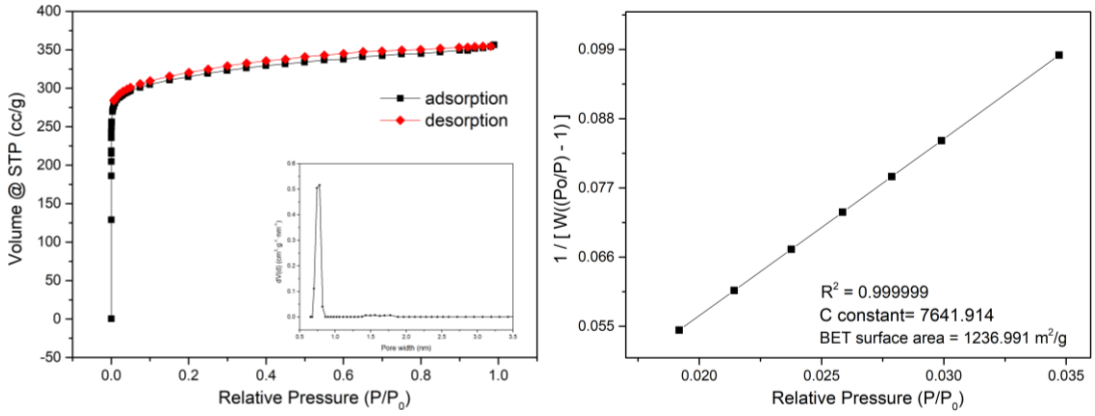


Figure S9. N_2 adsorption-desorption isotherm and BET surface area of Ni-PMOF-3(Fe).

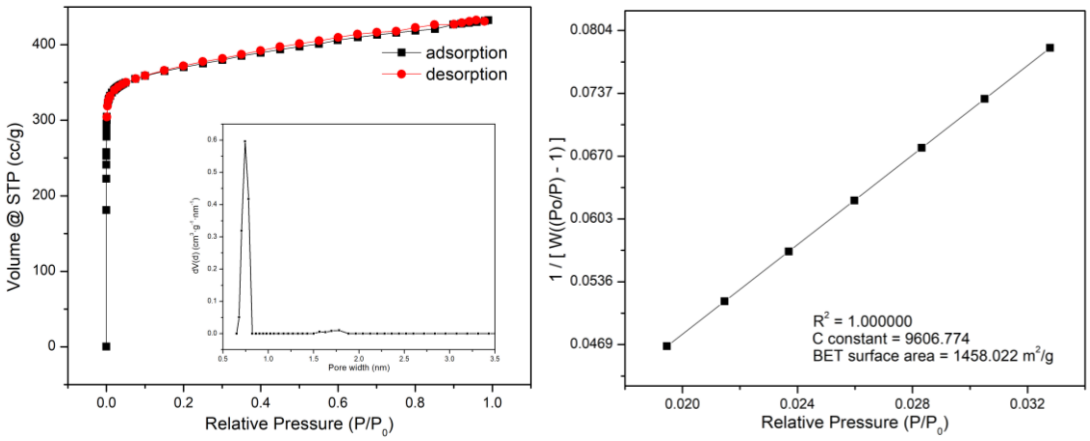


Figure S10. N_2 adsorption-desorption isotherm and BET surface area of Cu-PMOF-3(Fe).

Table S2. Summary of the data for the BET surface area and pore diameter.

	Fe-PMOF-3(Fe)	Co-PMOF-3(Fe)	Ni-PMOF-3(Fe)	Cu-PMOF-3(Fe)
BET surface area (m^2/g)	1240.6	1317.8	1236.9	1458.0
Pore diameter (Å)	7.4	7.4	7.8	7.4

3. Characterizations and stability

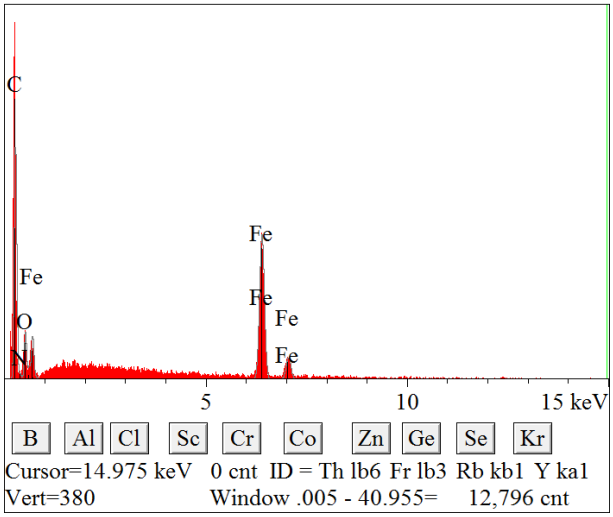


Figure S11. EDS spectrum of Fe-PMOF-3(Fe).

Table S3. Elemental analysis of Fe-PMOF-3(Fe) based on EDS experiment.

Element	Weight %	Atomic %
Fe	36.456	11.618

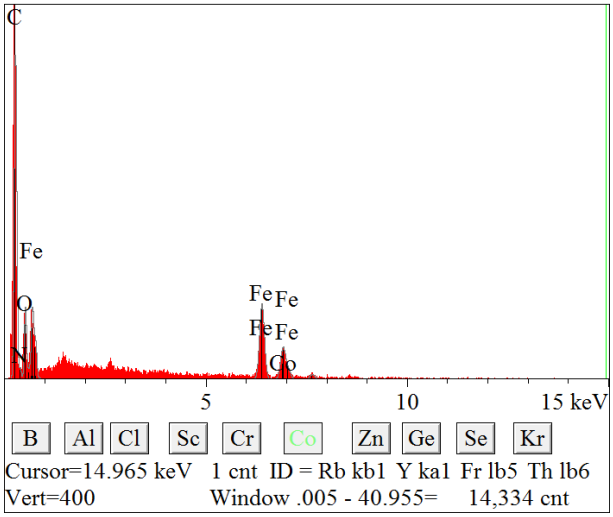


Figure S12. EDS spectrum of Co-PMOF-3(Fe).

Table S4. Elemental analysis of Co-PMOF-3(Fe) based on EDS experiment.

Element	Weight %	Atomic %
Fe	16.302	4.707
Co	8.543	2.338

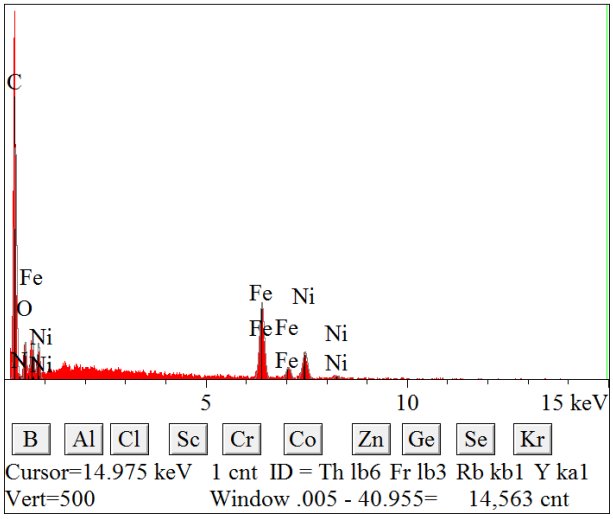


Figure S13. EDS spectrum of Ni-PMOF-3(Fe).

Table S5. Elemental analysis of Ni-PMOF-3(Fe) based on EDS experiment.

Element	Weight %	Atomic %
Fe	20.454	6.215
Ni	12.035	3.480

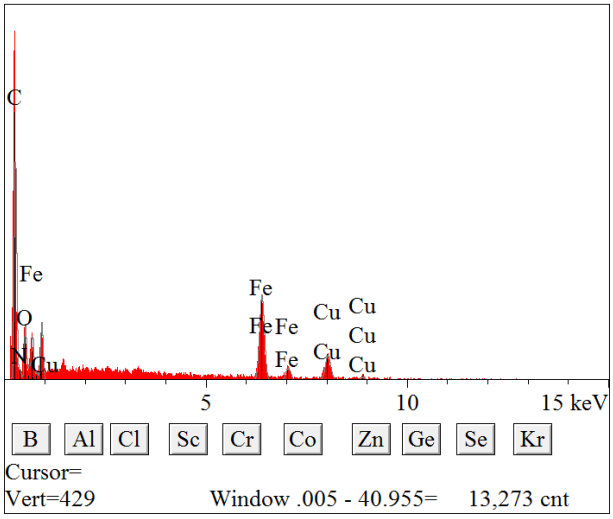


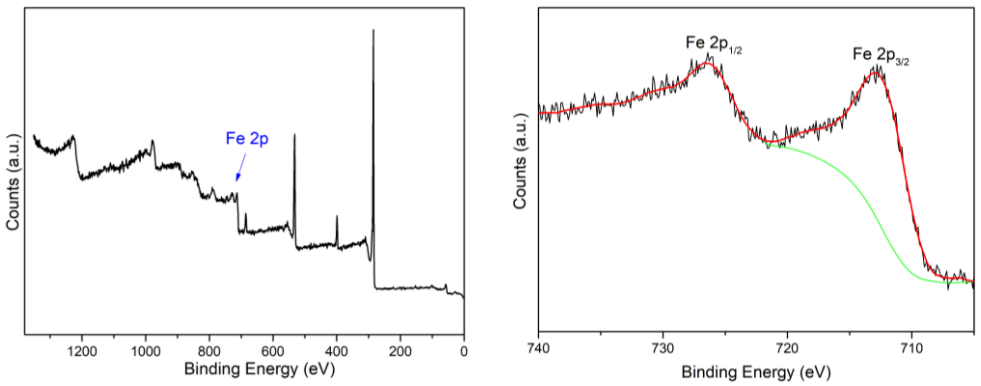
Figure S14. EDS spectrum of Cu-PMOF-3(Fe).

Table S6. Elemental analysis of Cu-PMOF-3(Fe) based on EDS experiment.

Element	Weight %	Atomic %
Fe	19.962	6.186
Cu	12.169	3.314

Table S7. The weight percentage (wt %) of the metal in M-PMOF-3(Fe) as disclosed by ICP-AES (Numbers in parentheses represent theoretical values).

	Fe-PMOF-3(Fe)	Co-PMOF-3(Fe)	Ni-PMOF-3(Fe)	Cu-PMOF-3(Fe)
Fe (wt %)	16.96 (16.48)	11.34 (10.85)	10.76 (11.35)	9.70 (11.29)
M (wt %)	/	5.97 (5.64)	5.20 (5.95)	5.36 (6.41)
Ratio of M to Fe	/	0.53 (0.52)	0.48 (0.52)	0.55 (0.57)

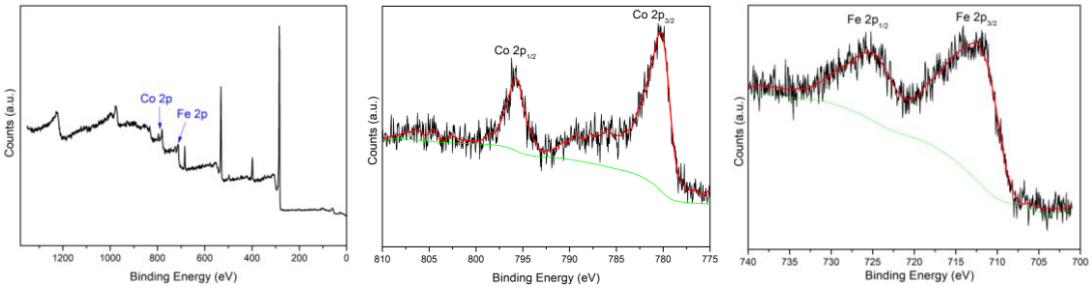


(a) **(b)**

Figure S15. XPS spectrum of Fe-PMOF-3(Fe) (a) and the peaks of Fe 2p (b).

Table S8. Bond energy of the metal elements in Fe-PMOF-3(Fe) based on the XPS spectrum.

Element	Peak	Bond Energy (eV)
Fe	$Fe\ 2p_{1/2}$	726
	$Fe\ 2p_{3/2}$	712.8

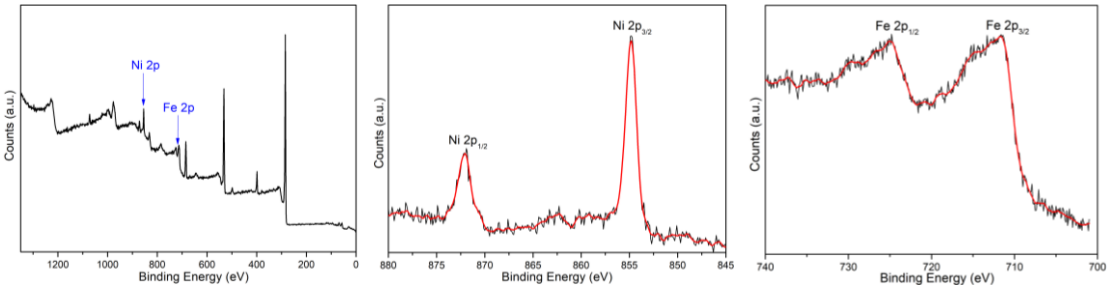


(a) **(b)** **(c)**

Figure S16. XPS spectrum of Co-PMOF-3(Fe) (a), and the peaks of Co 2p (b) and Fe 2p (c).

Table S9. Bond energy of the metal elements in Co-PMOF-3(Fe) based on the XPS spectrum.

Element	Peak	Bond Energy (eV)
Fe	$Fe\ 2p_{1/2}$	725.4
	$Fe\ 2p_{3/2}$	712.5
Co	$Co\ 2p_{1/2}$	795.7
	$Co\ 2p_{3/2}$	780.3

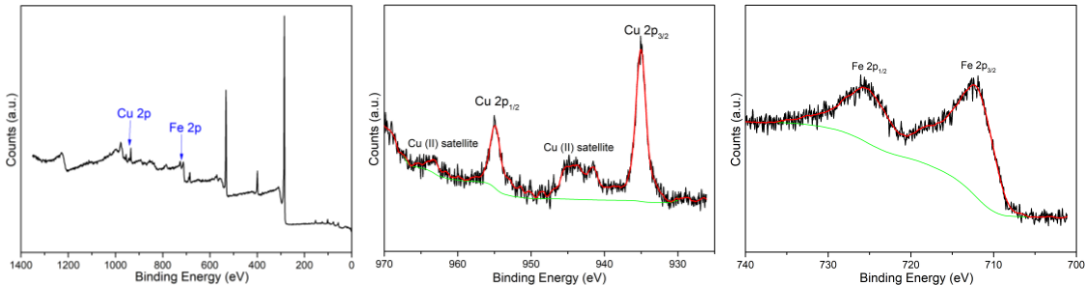


(a) **(b)** **(c)**

Figure S17. XPS spectrum of Ni-PMOF-3(Fe) (a), and the peaks of Cu 2p (b) and Fe 2p (c).

Table S10. Bond energy of the metal elements in Ni-PMOF-3(Fe) based on the XPS spectrum.

Element	Peak	Bond Energy (eV)
Fe	Fe $2p_{1/2}$	725.1
	Fe $2p_{3/2}$	711.8
Ni	Ni $2p_{1/2}$	872.1
	Ni $2p_{3/2}$	854.8



(a) **(b)** **(c)**

Figure S18. XPS spectrum of Cu-PMOF-3(Fe) (a), and the peaks of Cu 2p (b) and Fe 2p (c).

Table S11. Bond energy of metal elements in Cu-PMOF-3(Fe) based on the XPS spectrum.

Element	Peak	Bond Energy (eV)
Fe	Fe $2p_{1/2}$	725.5
	Fe $2p_{3/2}$	712.8
Cu	Cu $2p_{1/2}$	954.4
	Cu $2p_{3/2}$	934.5

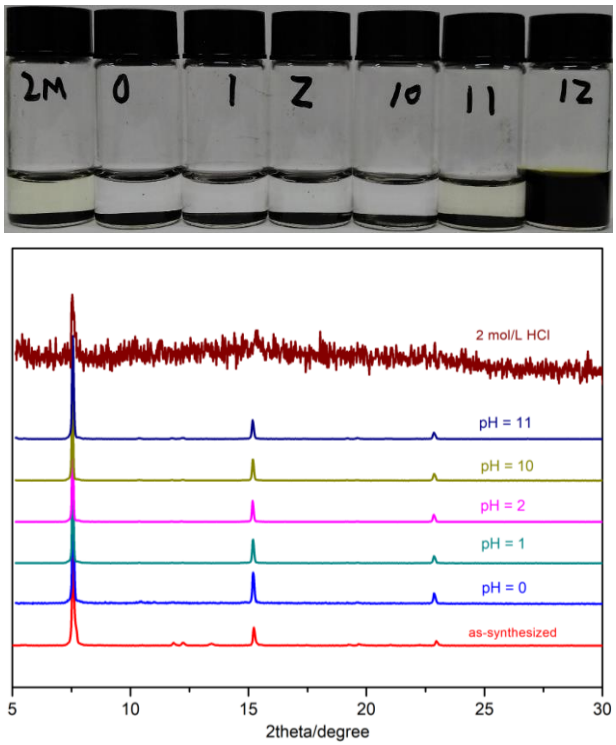


Figure S19. Stability test of Fe-PMOF-3(Fe) in aqueous solutions with the pH range of 0-12 and 2 M HCl for 48 h.

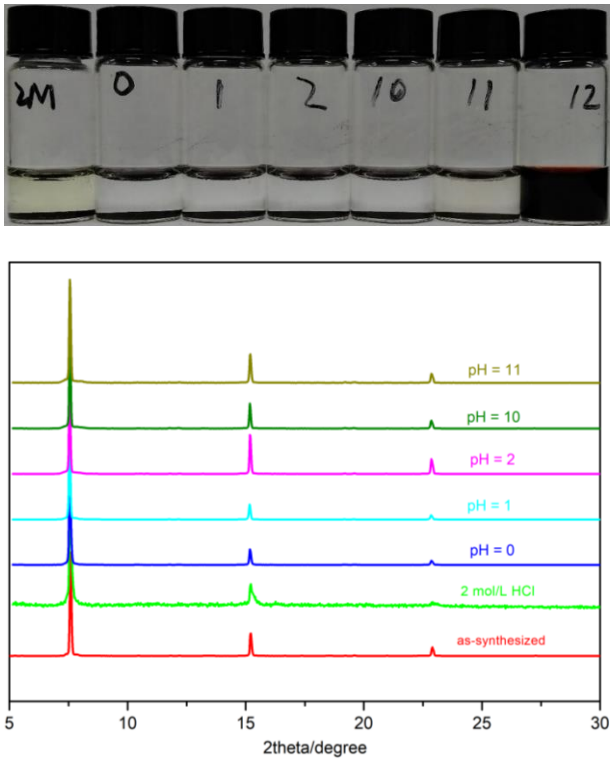


Figure S20. Stability test of Ni-PMOF-3(Fe) in aqueous solutions with the pH range of 0-12 and 2 M HCl for 48 h.

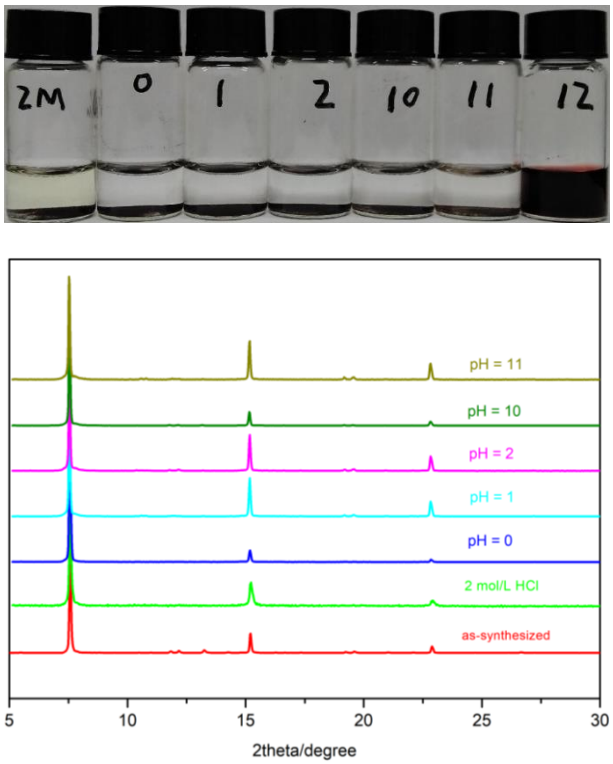


Figure S21. Stability test of Cu-PMOF-3(Fe) in aqueous solutions with the pH range of 0-12 and 2 M HCl for 48 h.

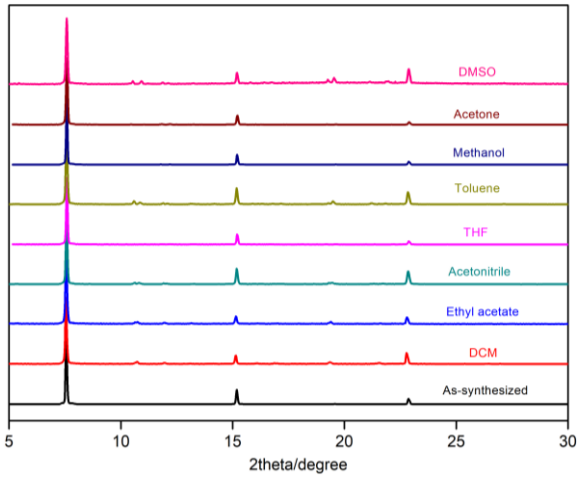


Figure S22. Stability test of Fe-PMOF-3(Fe) in different solvents for 7 days.

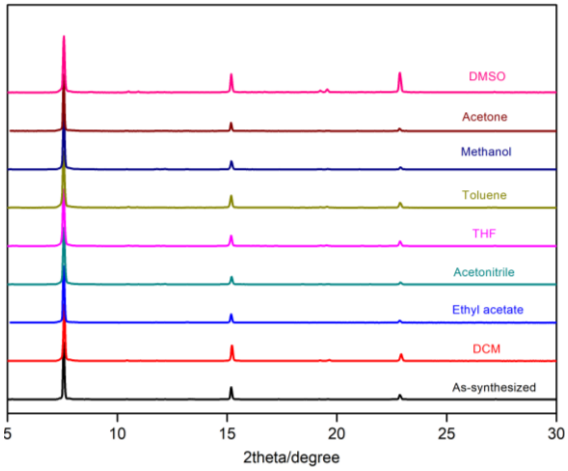


Figure S23. Stability test of Ni-PMOF-3(Fe) in different solvents for 7 days.

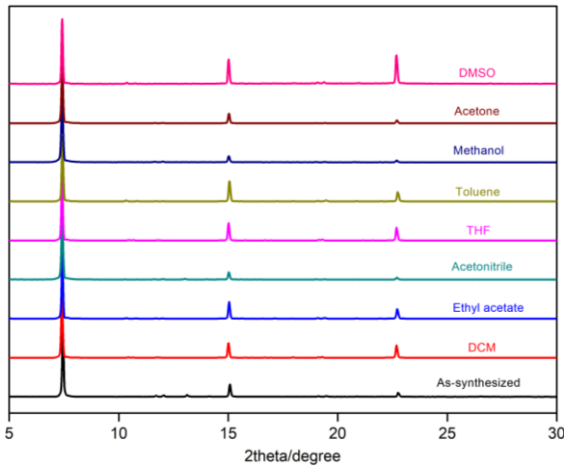
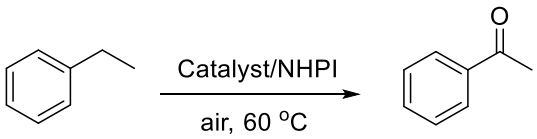


Figure S24. Stability test of Cu-PMOF-3(Fe) in different solvents for 7 days.

4. Catalysis

Table S12. Comparison of aerobic oxidation catalyzed by Cu-PMOF-3(Fe) and Cu-TCPP.[a]



Catalyst	Ethylbenzene (mmol)	Yield[b] (%)	Ketone Selectivity (%)	TON
Cu-PMOF-3(Fe)	4	33	97	330
Cu-TCPP	4	18	97	180

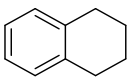
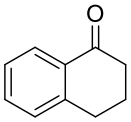
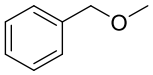
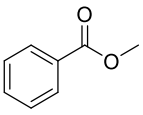
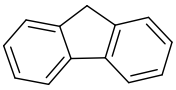
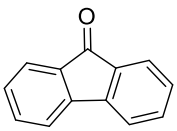
[a]Reaction conditions: A mixture of ethylbenzene (4 mmol), catalyst (0.004 mmol) and NHPI (0.037 mmol) in acetonitrile (2 mL) is stirred under atmospheric pressure at 60℃ for 48 h. [b]Determined by GC–MS.

Table S13. Catalytic performances of Cu-PMOF-3(Fe) in the solvent-free system.[a]

Time (d)	2	3	4	5	6	7
acetophenone (μmol)[b]	807	964	1113	1230	1313	1478
1-phenylethanol (μmol)[b]	235	289	340	389	426	495

[a]Reaction conditions: A mixture of ethylbenzene (2 mL, 16 mmol), catalyst (0.004 mmol) and NHPI (0.037 mmol) is stirred under atmospheric pressure at 60℃. [b]The amount of the product is determined by GC–MS using 1,2-dichlorobenzene as the internal standard.

Table S14. Aerobic oxidation of other benzyl C-H bonds.[a]

Entry	Substrate	Product	Yield (%)[b]	Ketone Selectivity (%)
1			99	>99%
2			96	>99%
3			58	>99%

[a]Reaction conditions: A mixture of alkylbenzene (0.2 mmol), Cu-PMOF-3(Fe) (4 mg, 0.004 mmol), and NHPI (6 mg, 0.037 mmol) is stirred in acetonitrile (2 mL) at 60℃ under atmospheric pressure for 24 h. [b]The yield is determined by GC-MS.

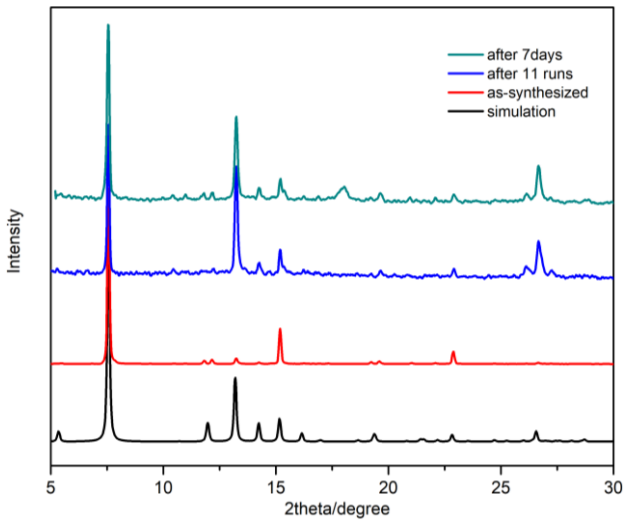


Figure S25. The PXRD patterns of Cu-PMOF-3(Fe) before and after catalysis.