A Cu(II) MOF with laccase-like activity for colorimetric detection of 2,4-dichlorophenol and p-nitrophenol

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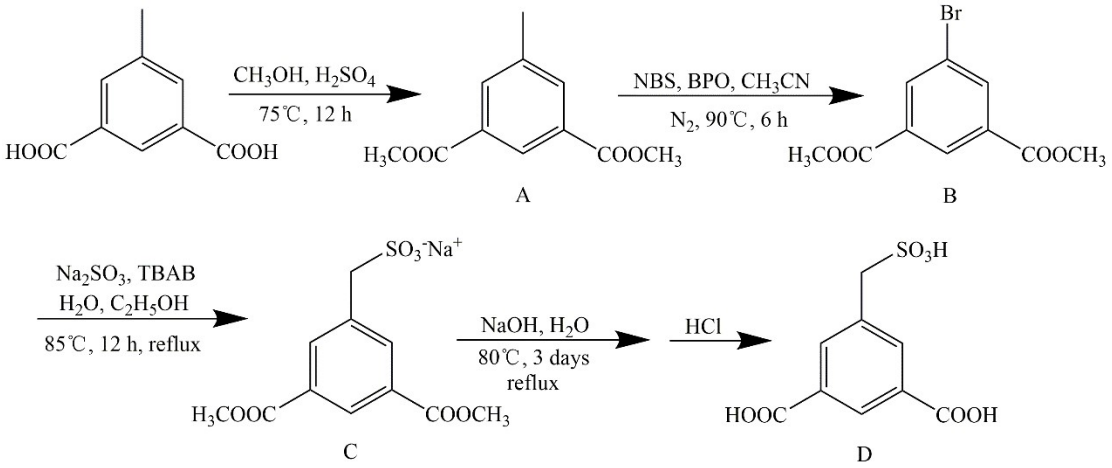

Fig. S1 Synthesis of 5-sulfomethyl isophthalic acid (5-SMIPA).

Compound **A** (5-methyl isophthalate): H_2SO_4 (4 mL) was slowly added to solution of 5-methylisophthalic acid (1.08 g, 6 mmol) in CH_3OH (20 mL) and resulting mixture stirred at 75 °C for 12 h. When the reaction was end and cooled to room temperature, 10 M NaOH (aq) was added to neutralize the solution. Compound A was extracted by CH_2Cl_2 (150 mL) and the CH_2Cl_2 was removed by rotary evaporation to obtain compound A (1.17 g, 94.1%). NMR spectrum was shown in Fig. S2 and Fig. S3.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.48 (s, 1H), 8.04 (s, 2H), 3.94 (s, 6H), 2.45 (s, 3H).

^{13}C NMR (400 MHz, Chloroform-d) δ 166.40, 138.67, 134.39, 130.47, 127.94, 52.27, 21.10.

Compound **B** (5-bromomethyl isophthalate): Compound A (0.832 g, 4 mmol) and NBS (0.783 g, 4 mmol) were dissolved in anhydrous CH_3CN (20 mL), then added the CH_3CN solution of BPO (0.09 g, 0.4 mmol). The mixture heated under reflux under N_2 and stirred for 6 h. After 6 h quenched BPO with water, and removed solvent. The residue was purified by flash chromatography (EtOAc : petroleum ether, 1:20) to obtain compound B(0.75 g, 65.7%). NMR spectrum was shown in Fig. S4 and Fig. S5.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.60 (s, 1H), 8.26 (s, 2H), 4.55 (s, 2H), 3.96 (s, 6H).

^{13}C NMR (400 MHz, Chloroform-d) δ165.55, 138.83, 134.18, 131.29, 130.51, 52.52, 31.50.

Compound **C** (5-sulfomethyl isophthalate): Added compound B (0.28 g, 1 mmol), Na_2SO_3 (0.15 g,

1.2 mmol), TBAB (0.008g, 0.025 mmol) to a mixture of H_2O and ethanol and stirred for 12 h. The solvent was evaporated to obtain a mixed solid.

Compound **D** (5-sulfomethyl isophthalic acid, 5-SMIPA): Added mixed solid, NaOH (0.64 g, 16 mmol) to water and stirred at 85 °C for 3 days. Then added HCl to adjust pH to neutral conditions, the white solid precipitated was compound D (0.16 g). NMR spectrum was shown in Fig. S6 and Fig. S7.

^{1}H NMR (600 MHz, MeOD), δ (TMS, ppm) 8.50 (1H, s), 8.07 (2H, s), 4,13 (2H, s).

^{13}C NMR (600 MHz, MeOD), δ (TMS, ppm) δ 173.82, 137.56, 132.76, 132.17, 128.92, 56.94.

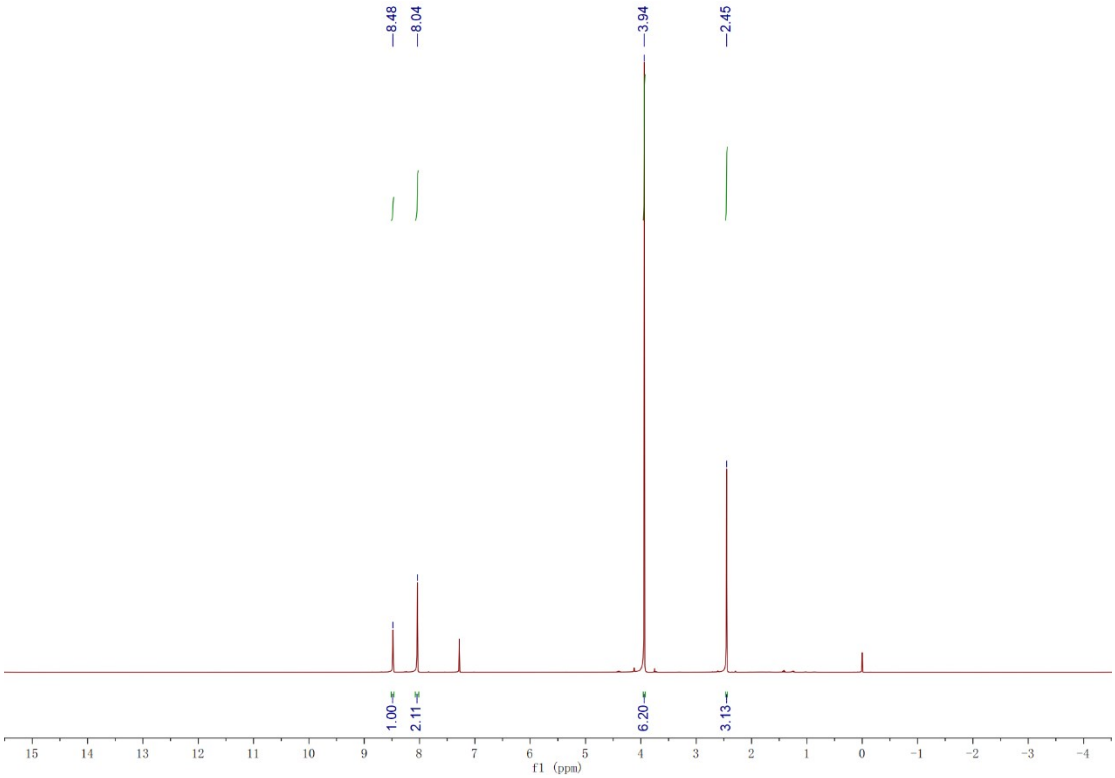

Fig. S2. ^{1}H NMR (400 MHz, Chloroform-d) spectrum of 5-methyl isophthalate.

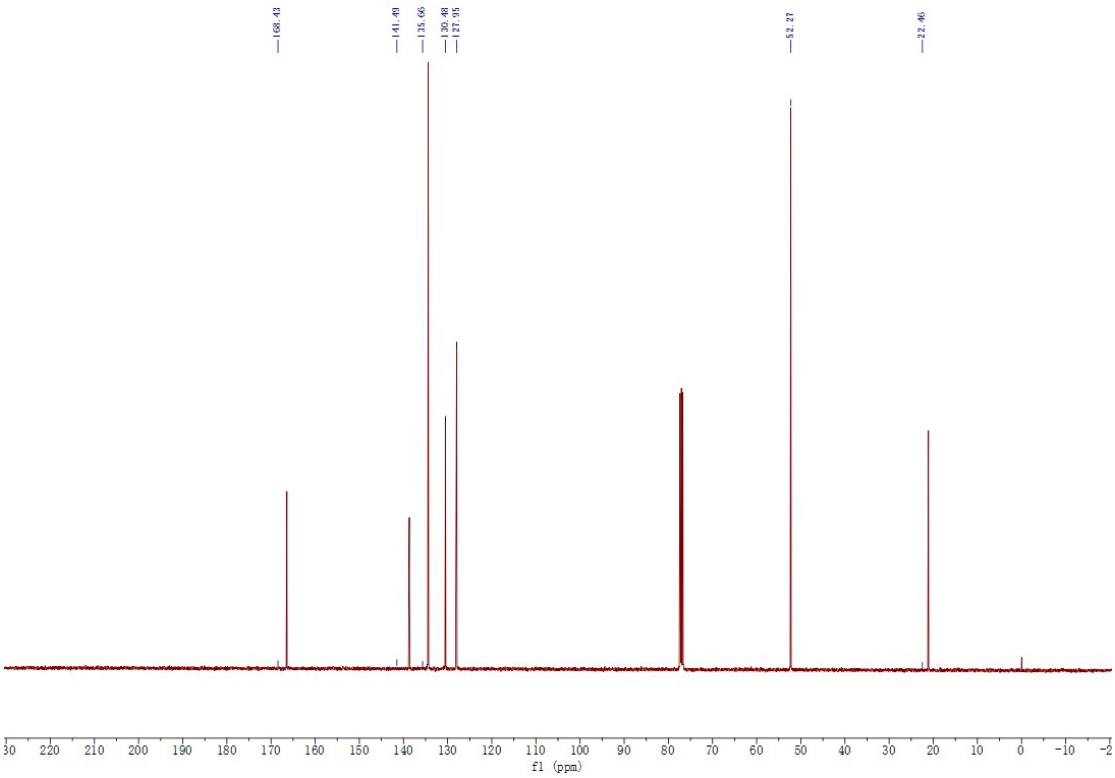

Fig. S3. ^{13}C NMR (400 MHz, Chloroform-d) spectrum of 5-methyl isophthalate.

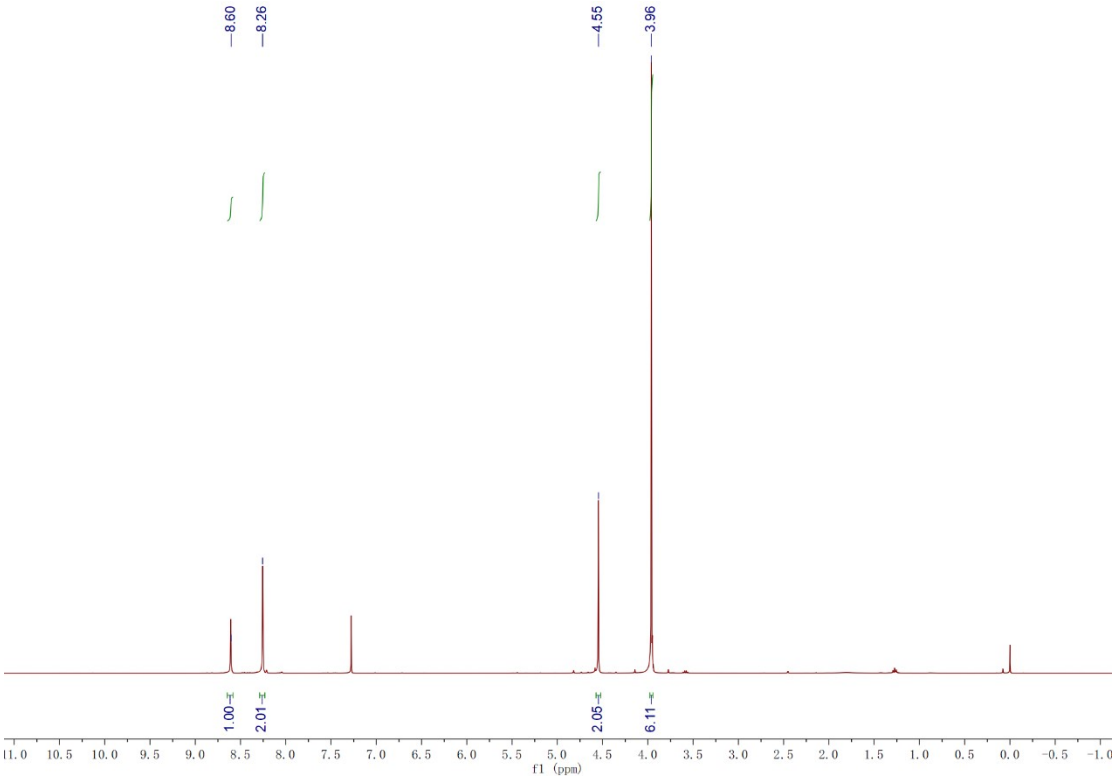

Fig. S4. ^{1}H NMR (400 MHz, Chloroform-d) spectrum of 5-bromomethyl isophthalate.

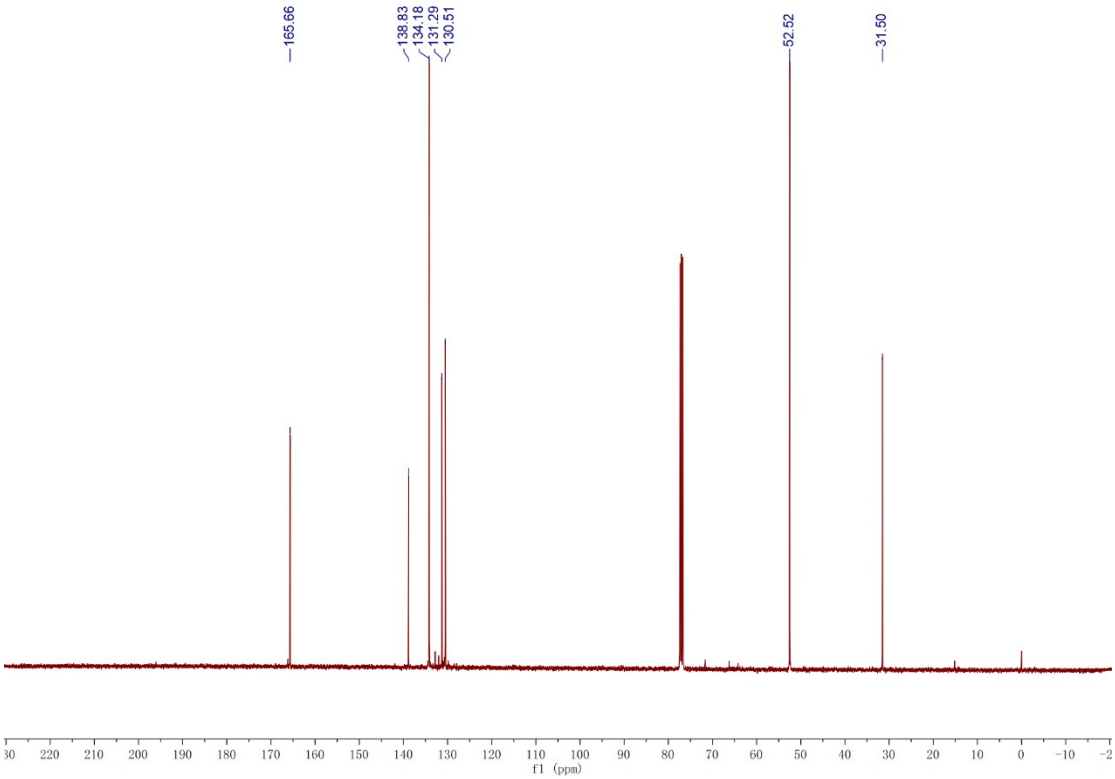

Fig. S5. ^{13}C NMR (400 MHz, Chloroform-d) spectrum of 5-bromomethyl isophthalate.

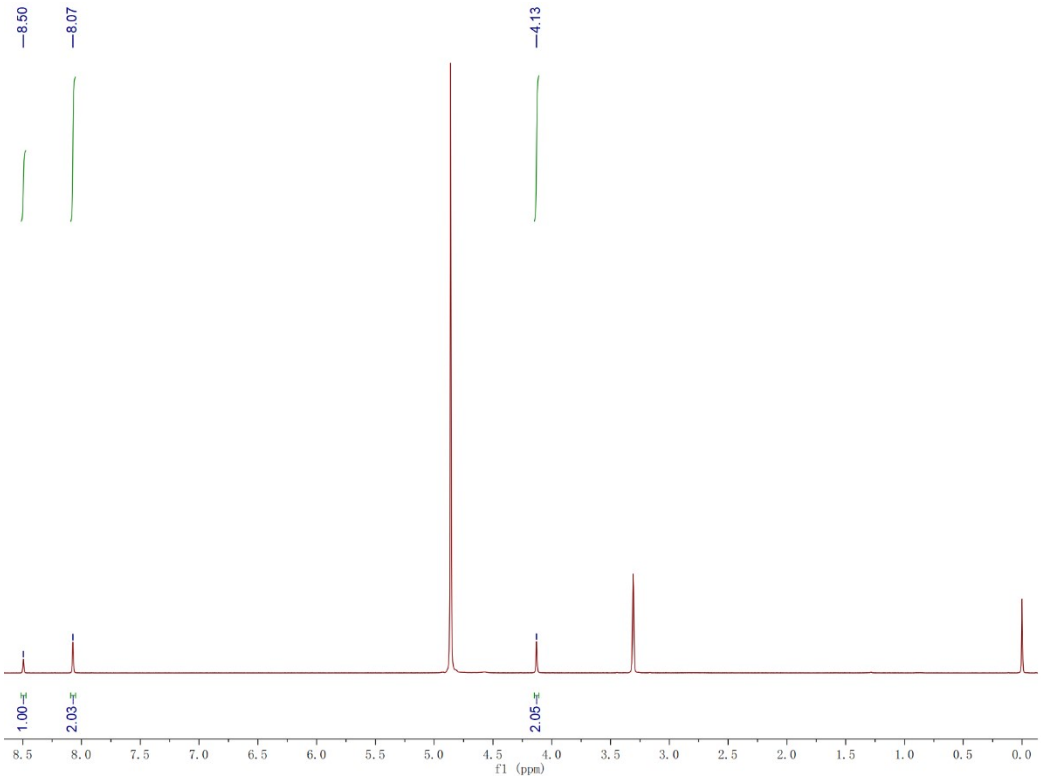

Fig. S6. ^{1}H NMR (600 MHz, MeOD) spectrum of 5-sulfomethyl isophthalic acid (5-SMIPA).

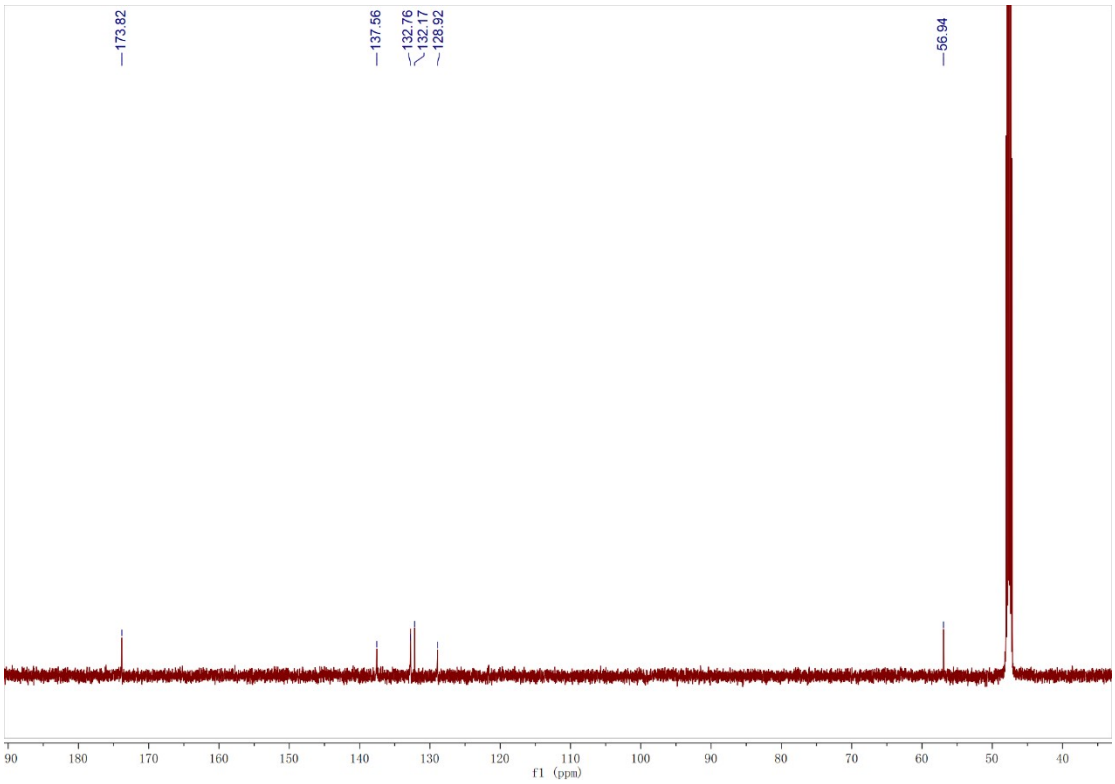

Fig. S7. ^{13}C NMR (600 MHz, MeOD) spectrum of 5-sulfomethyl isophthalic acid (5-SMIPA).

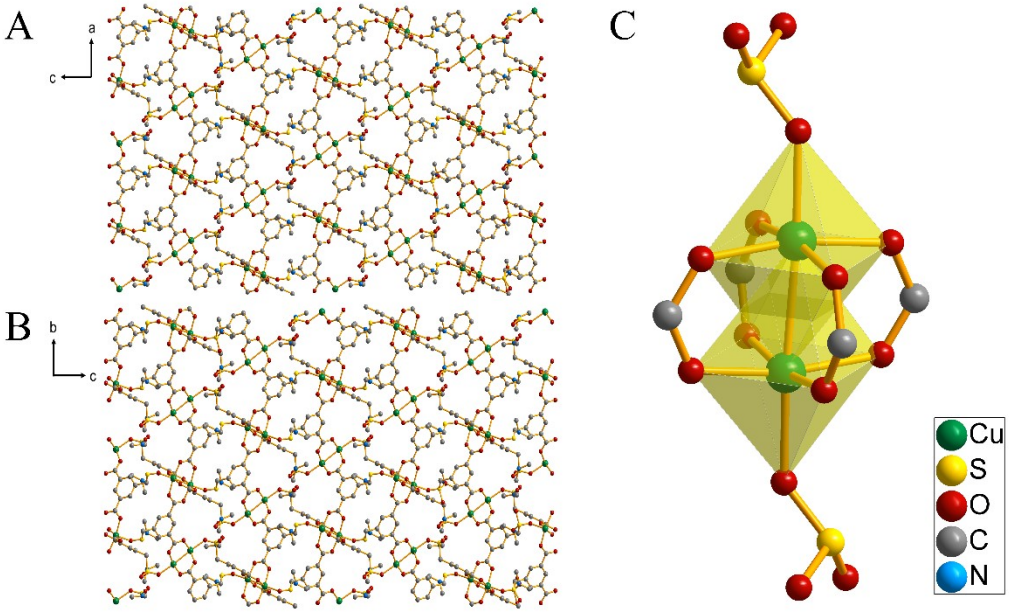

Fig. S8. (A) Crystal packing pattern along the b axis. (B) Crystal packing pattern along the a axis. (C) Specific coordination environment of Cu.

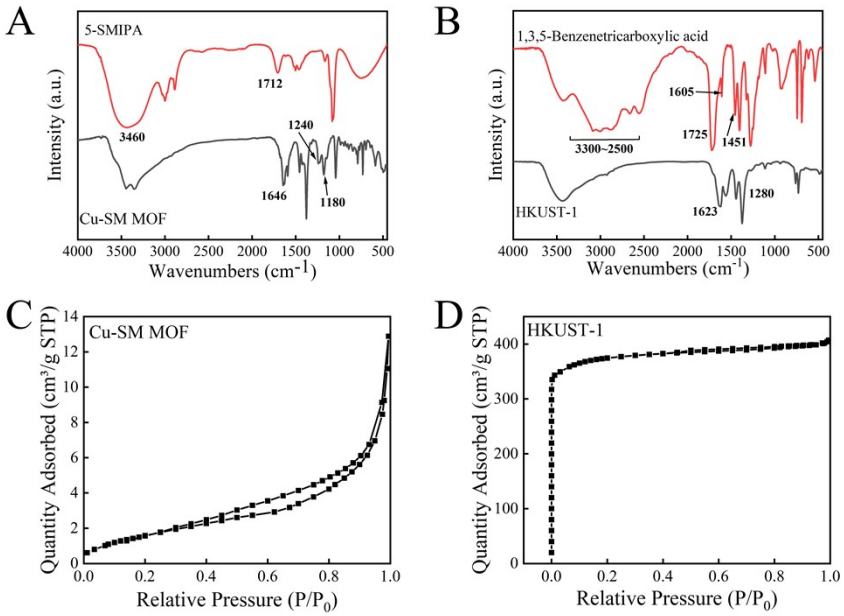

Fig. S9. (A) FTIR spectra of Cu-SM MOF and 5-SMIPA. (B) FTIR spectra of HKUST-1 and 1,3,5-benzenetricarboxylic acid. (C) N_2 adsorption isotherm of the Cu-SM MOF after drying to measure the specific surface area. (D) N_2 adsorption isotherm of the HKUST-1 after drying to measure the specific surface area.

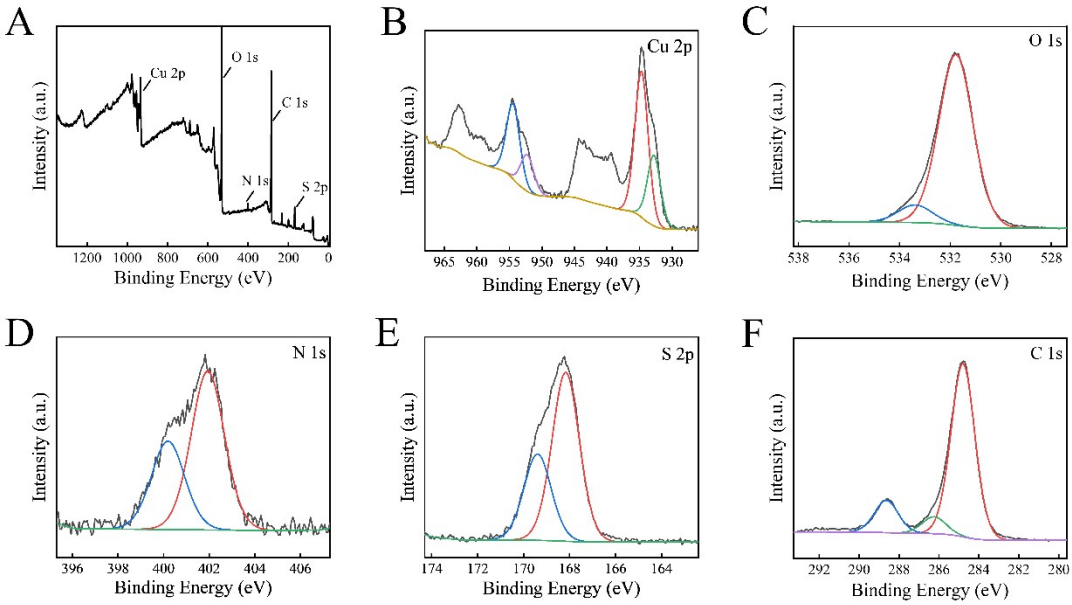

Fig. S10. (A) XPS spectra of Cu-SM MOF. High-resolution (B) Cu 2p, (C) O 1s, (D) N 1s, (E) S 2p, (F) C 1s.

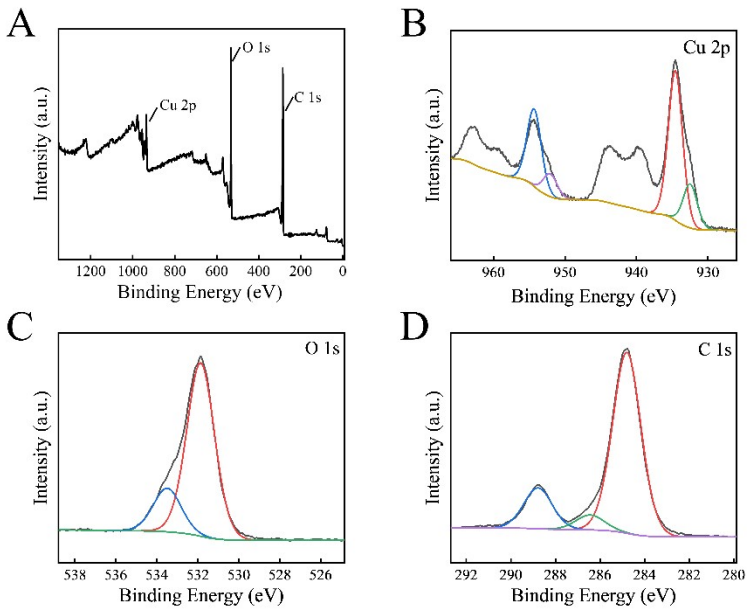

Fig. S11. (A) XPS spectra of HKUST-1. High-resolution (B) Cu 2p, (C) O 1s, (D) C 1s.

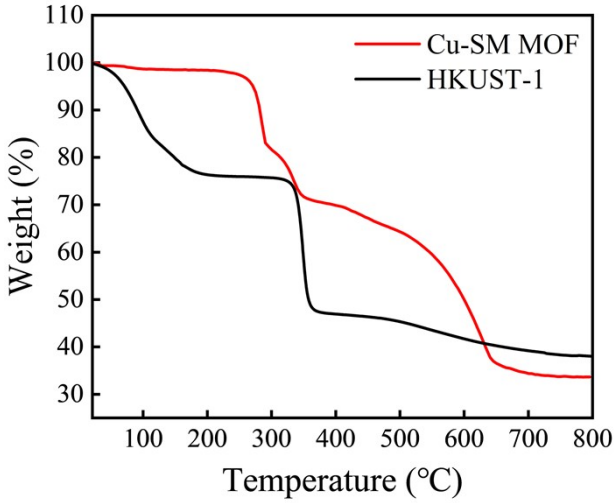

Fig. S12. TGA curves of Cu-SM MOF (red curve) and HKUST-1 (black curve).

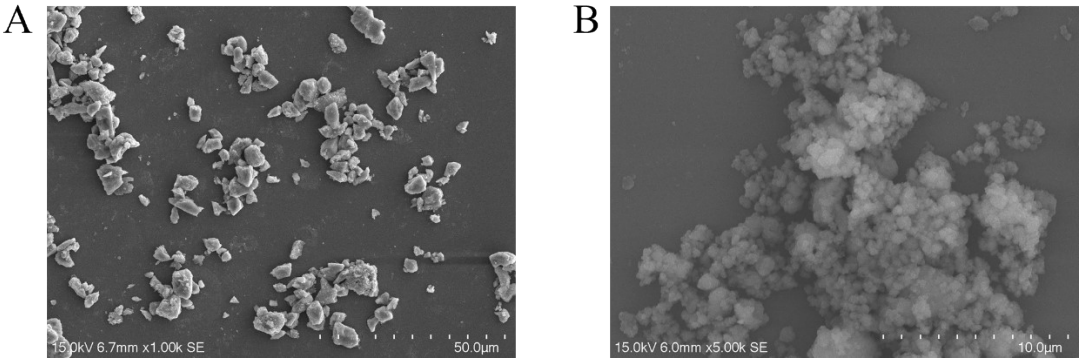

Fig. S13. SEM images of (A) Cu-SM MOF and (B) HKUST-1 after grinding.

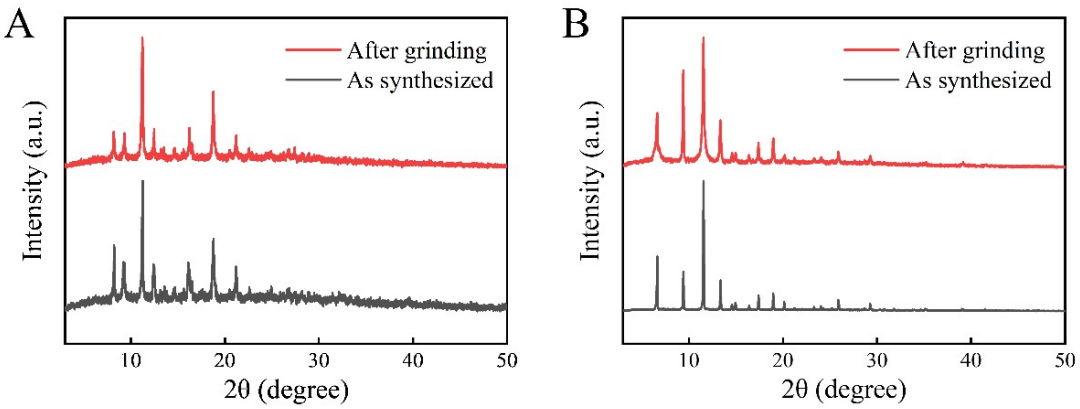

Fig. S14. PXRD patterns of (A) Cu-SM MOF and (B) HKUST-1 after grinding.

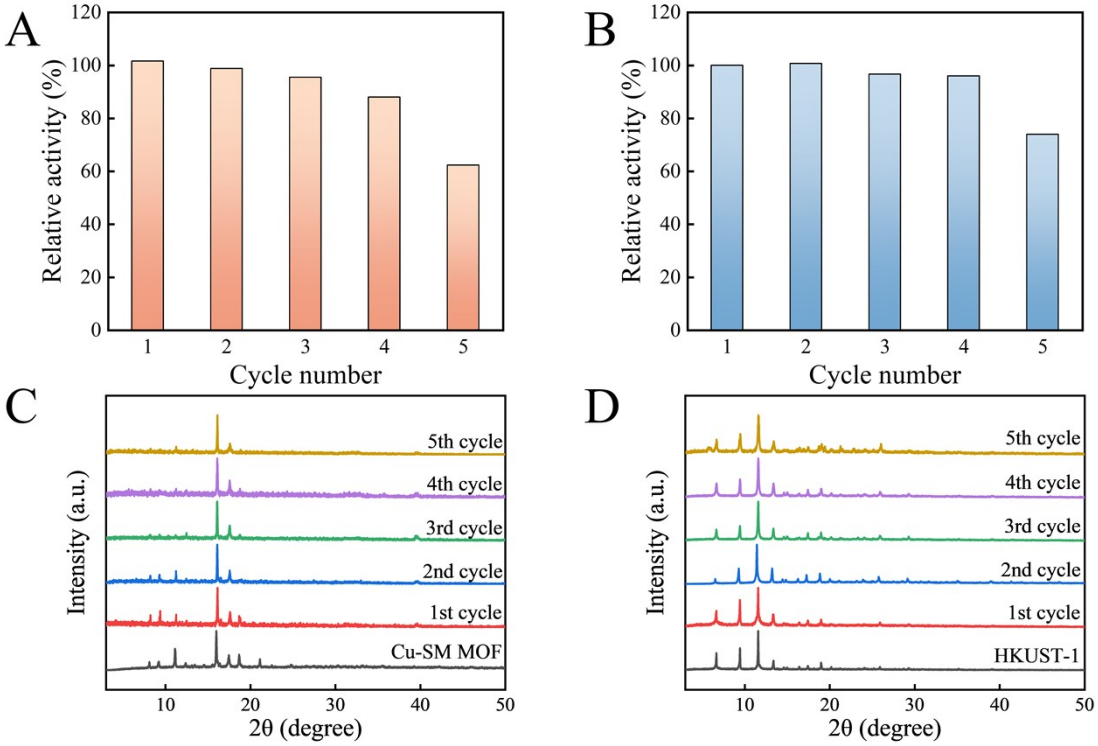

Fig. S15. Catalytic efficiency of (A) Cu-SM MOF and (B) HKUST-1 during the recycling experiment up to the 5th cycle. PXRD patterns of (C) Cu-SM MOF and (D) HKUST-1 during the recycling experiment up to the 5th cycle.

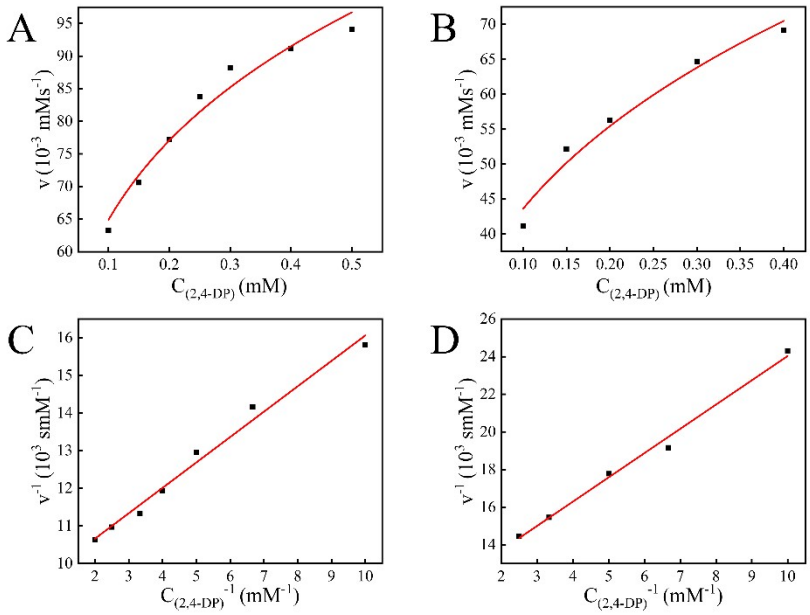

Fig. S16. Plot of absorbance at 510 nm obtained from the time-dependent kinetic data at various concentrations of 2,4-DP, (A) Cu-SM MOF, (B) HKUST-1. Lineweaver-Burk plot of (C) Cu-SM MOF, (D) HKUST-1.

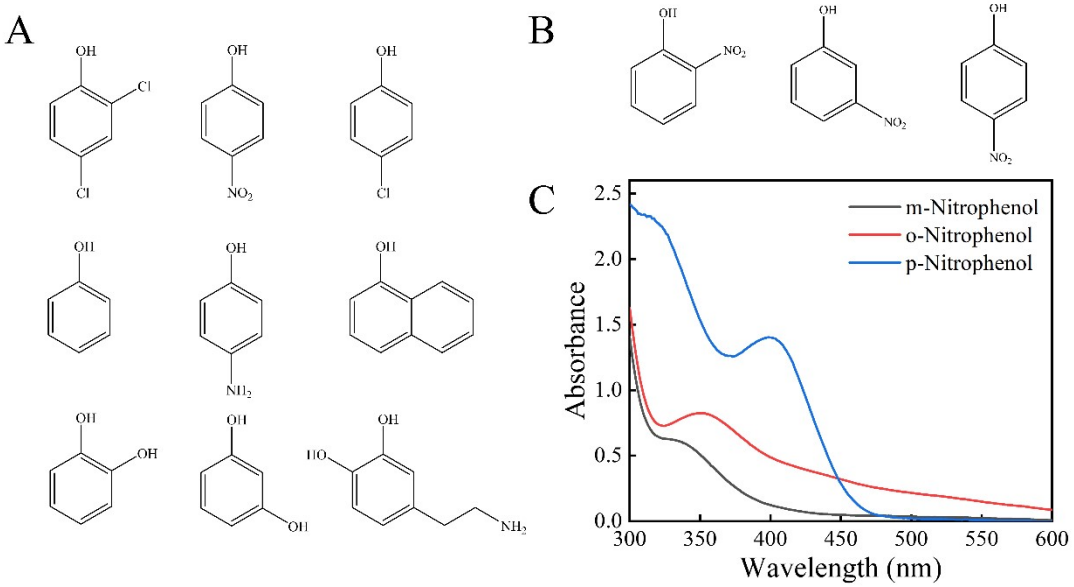

Fig. S17. (A) Structure of a variety of phenolic compounds. (B) Structure of three nitrophenols. (C) Oxidation of three nitrophenols catalyzed by Cu-SM MOF.

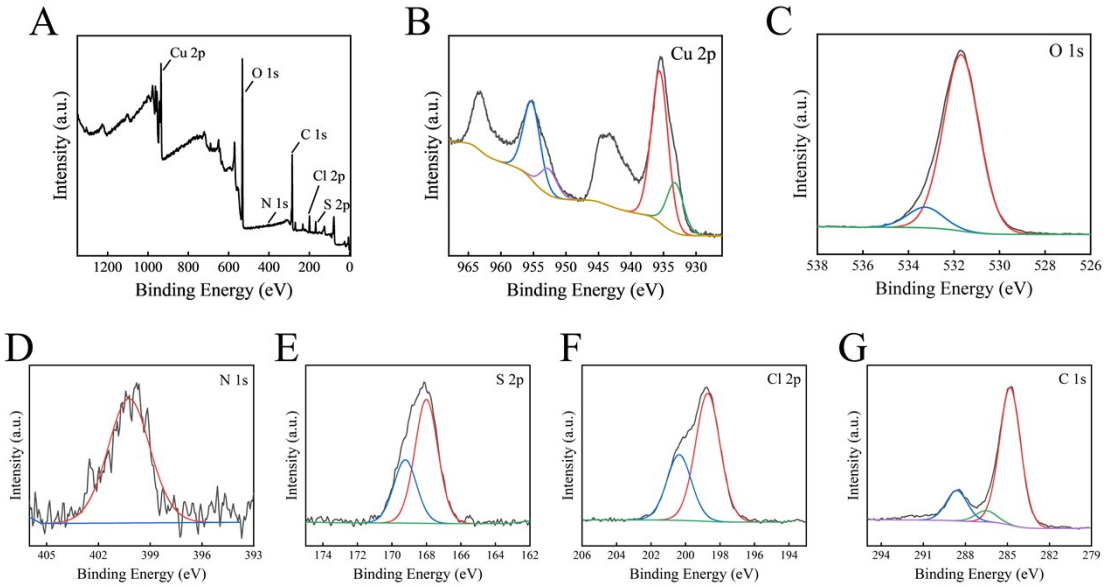

Fig. S18. (A) XPS spectra of Cu-SM MOF incubated with 2,4-DP. High-resolution (B) Cu 2p, (C) O 1s, (D) N 1s, (E) S 2p, (F) Cl 2p, (G) C 1s.

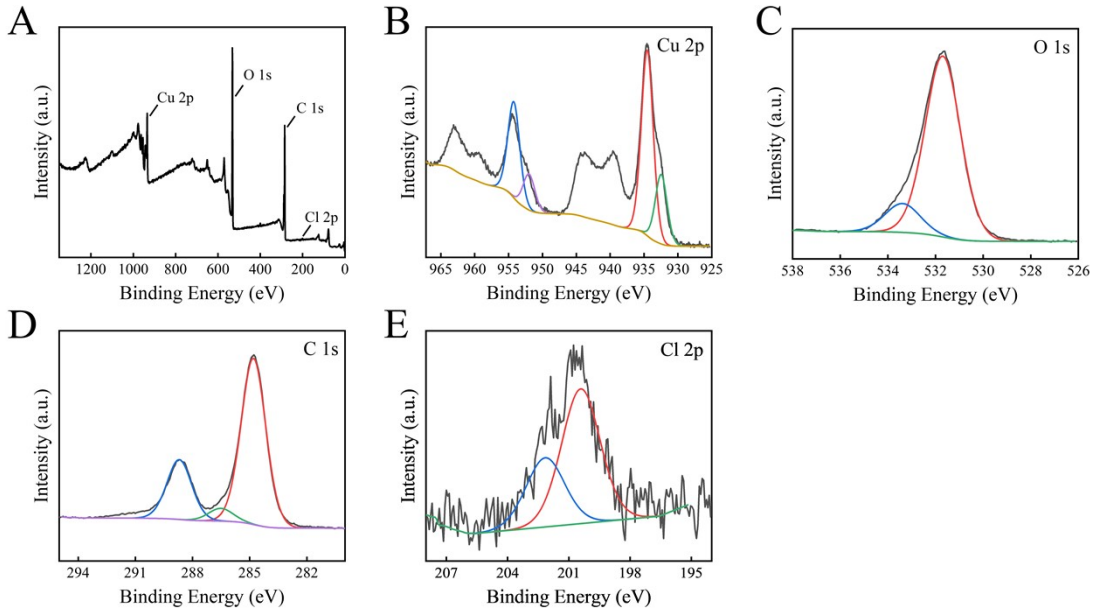

Fig. S19. (A) XPS spectra of HKUST-1 incubated with 2,4-DP. High-resolution (B) Cu 2p, (C) O 1s, (D) C 1s, (E) Cl 2p.

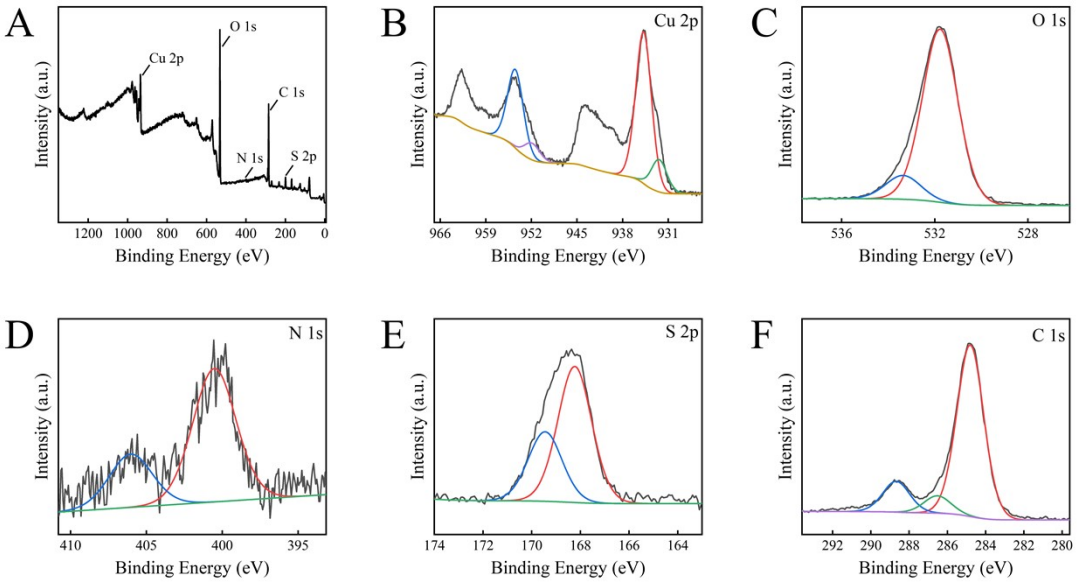

Fig. S20. (A) XPS spectra of Cu-SM MOF incubated with p-nitrophenol. High-resolution (B) Cu 2p, (C) O 1s, (D) N 1s, (E) S 2p, (F) C 1s.

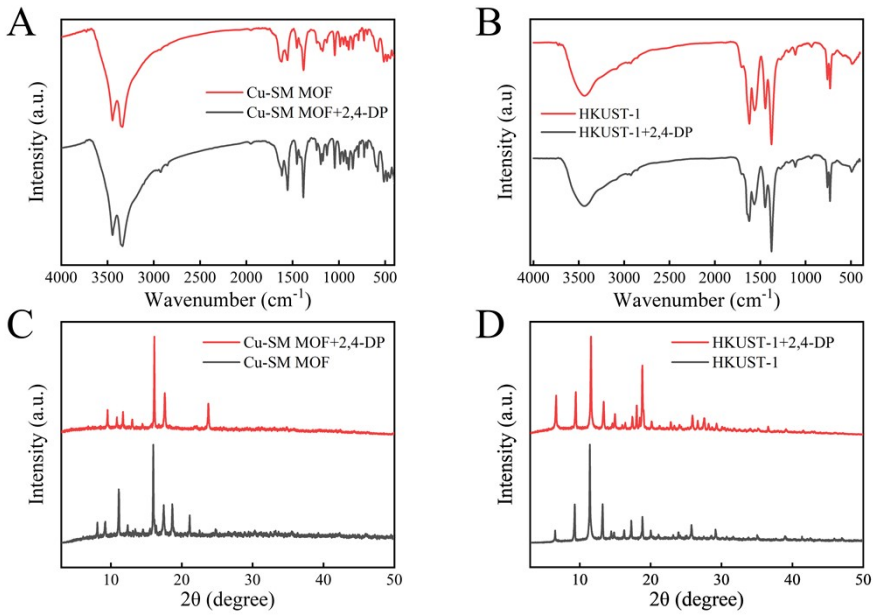

Fig. S21. FTIR spectrum of MOFs and that incubated with 2,4-DP. (A) Cu-SM MOF, (B) HKUST-1. PXRD patterns of MOFs and that incubated with 2,4-DP. (C) Cu-SM MOF, (D) HKUST-1.

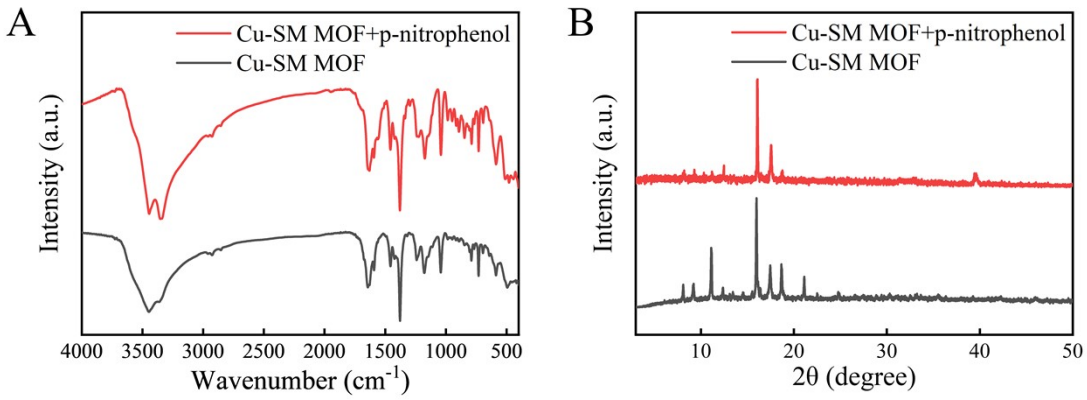

Fig. S22. (A) FTIR spectrum and (B) PXRD patterns of Cu-SM MOF incubated with p-nitrophenol.

Table S1. Experimental details regarding the LOD calculation for detection of 2,4-DP and p-nitrophenol.

	σ	***k***	**LOD=3σ/*k***
2,4-DP	0.002109	0.01203	0.53 μM
p-nitrophenol	0.004289	0.00796	1.62 μM

σ: standard deviation of blank, *k*: calibration curve slope from the linear relationships (Fig. 6).

Table S2. Detection of 2,4-DP.

Sample	**Addition (μM)**	**Found (μM)**	**Recovery (%)**	**RSD (%)**
River water	20	20.75	103.75	1.0
	50	50.62	101.24	0.8
	80	81.82	102.27	4.4
Lake water	20	21.05	105.25	0.4
	50	50.28	100.56	0.4
	80	80.33	100.41	2.0
Tap water	20	20.78	103.90	0.8
	50	51.21	102.42	1.3
	80	81.64	102.05	0.3

Table S3. Detection of p-nitrophenol.

Sample	**Addition (μM)**	**Found (μM)**	**Recovery (%)**	**RSD (%)**
River water	50	48.93	97.86	0.8
	100	99.58	99.58	1.4
	200	195.57	97.78	2.9
Lake water	50	51.29	102.58	0.8
	100	100.59	100.59	0.8
	200	202.28	101.14	0.7
Tap water	50	48.98	97.96	0.9
	100	100.88	100.88	0.1
	200	210.16	105.08	4.1

Table S4. Crystal data and structure refinements for Cu-SM MOF.

Compound	Cu-SM MOF
Formula	$C_{11}H_{13}CuNO_7S$
M	366.82
Temperature (K)	293 (2)
Crystal system	*trigonal*
Space group	R-3*m*
a, *b*, *c* (Å)	18.733 (7) 18.733 (7) 28.218 (8)
α, *β*, *γ* (°)	90 90 120
V ($Å^3$)	8576 (7)
Z	18
Dc (g/cm^3)	1.279
μ (mm^{-1})	1.279
F (000)	3366.0
Reflns collected	24754
Independent reflns	2428
R (int)	0.1366
Data / restraints / parameters	2428/517/220
GOF on F^2	1.052
$^bR_1[I>2\sigma(I)]$, wR_2	0.0789, 0.2173
R_1[all data], wR_2	0.1009, 0.2384

Table S5. Bond Lengths for Cu-SM MOF.

[1]1-X,-Y,-Z; [2]1+Y-X,+Y,+Z; [3]-Y+X,-Y,-Z; [4]-1/3-Y+X,-2/3+X,1/3-Z; [5]+X,-1+X-Y,+Z

Atom	Atom	Length/Å
Cu1	Cu1[1]	2.6250(17)
Cu1	O1[2]	1.955(4)
Cu1	O1	1.956(4)
Cu1	O2[3]	1.943(4)
Cu1	O2[1]	1.943(4)
Cu1	O5[4]	2.161(6)
S1	O5	1.441(6)
S1	O3	1.620(13)
S1	C6	1.758(9)
S1	O4	1.354(10)
O1	C1	1.255(6)
O2	C1	1.265(6)
C2	C3	1.383(6)
C2	C1	1.485(7)
C2	C4	1.385(7)
C5	C4	1.386(6)
C5	C4[5]	1.386(6)
C5	C6	1.488(11)
C10	N2	1.458(10)
C9	N2	1.459(10)
N5	C15	1.444(10)
N5	C16	1.454(10)
C13	N4	1.447(10)
N4	C14	1.445(10)
C7	N1	1.447(10)
N1	C8	1.448(10)
C12	N3	1.4848(4)
C11	N3	1.455(7)

Table S6. Bond Angles for Cu-SM MOF.

[1]1+Y-X,+Y,+Z; [2]1-X,-Y,-Z; [3]-1/3-Y+X,-2/3+X,1/3-Z; [4]-Y+X,-Y,-Z; [5]2/3+Y,1/3-X+Y,1/3-Z; [6]+X,-1+X-Y,+Z

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1[1]	Cu1	Cu1[2]	82.15(11)	C1	O1	Cu1	125.2(3)
O1	Cu1	Cu1[2]	82.15(11)	C1	O2	Cu1[2]	120.6(3)
O1[1]	Cu1	O1	89.8(2)	S1	O5	Cu1[5]	137.2(4)
O1[1]	Cu1	O5[3]	95.17(15)	C3	C2	C1	120.2(5)
O1	Cu1	O5[3]	95.17(15)	C3	C2	C4	119.2(5)
O2[4]	Cu1	Cu1[2]	86.49(12)	C4	C2	C1	120.4(5)
O2[2]	Cu1	Cu1[2]	86.49(12)	C2	C3	C2[6]	120.9(7)
O2[4]	Cu1	O1[1]	168.58(16)	C4[6]	C5	C4	119.1(7)
O2[4]	Cu1	O1	89.80(16)	C4	C5	C6	120.4(4)
O2[2]	Cu1	O1	168.58(16)	C4[6]	C5	C6	120.4(4)
O2[2]	Cu1	O1[1]	89.80(16)	O1	C1	O2	125.4(5)
O2[4]	Cu1	O2[2]	88.3(2)	O1	C1	C2	117.0(4)
O2[2]	Cu1	O5[3]	96.23(16)	O2	C1	C2	117.5(4)
O2[4]	Cu1	O5[3]	96.23(16)	C2	C4	C5	120.8(5)
O5[3]	Cu1	Cu1[2]	176.19(16)	C5	C6	S1	115.3(6)
O5	S1	O3	104.5(5)	C10	N2	C9	117.9(12)
O5	S1	C6	106.7(4)	C15	N5	C16	119.7(12)
O3	S1	C6	97.6(5)	C14	N4	C13	120.3(13)
O4	S1	O5	118.7(5)	C7	N1	C8	119.7(13)
O4	S1	O3	115.0(8)	C11	N3	C12	116.4(9)
O4	S1	C6	111.9(5)				