

Supporting Information

Fabrication of Hydrazone-Linked Covalent Organic Frameworks Using Alkyl Amine as Building Block for High Adsorption Capacity of Metal Ions

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Experimental Section

Materials

The starting material of Tp was synthesized according to protocols reported by MacLachlan²⁴. Hexamethylenetetramine and phloroglucinol were purchased from Aladdin Industrial Corporation (Shanghai, China). Acetic acid, 1,2-dichlorobenzene (o-DCB), N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMAc) were from J&K Scientific Ltd. (Beijing, China). ODH, TFB were obtained from Sigma (St Louis, MO, USA). 1,4-Dioxane, mesitylene and tetrahydrofuran (THF) were supplied by Tianjin Kermel Plant of Chemical Reagent (Tianjin, China). Water was purified with a Milli-Q system from Millipore (Milford, USA).

Synthesis of Tp

Tp was synthesized using previously reported methods. Briefly, a mixture of hexamethylenetetramine (15.098 g, 0.108 mol), dried phloroglucinol (6.014 g, 0.048 mol) and trifluoroacetic acid (45 mL) was added in a flask. The reaction temperature was slowly increased to 100 °C and stirred under nitrogen for 2.5 h. Then 3 M HCl was slowly added and further refluxed for another 1 h. Finally, the mixture was allowed to cool at room temperature and filtered through celite bed. Filtrate was extracted with dichloromethane (4 times) and dried over anhydrous Na₂SO₄. Once dry the dichloromethane was removed by rotary evaporation yielding an orange solid. This solid was washed with hot ethanol (3 × 100 mL) to yield a pale yellow free flowing power. This power was dried in oven overnight to yield the final product. ¹H NMR and ¹³C NMR (Fig. S1) indicated the purity nearly to 99%.

Preparation of COFs of TpODH and TFBODH

An ampoule bottle measuring 10×8 mm (o.d. × i.d.) was charged with ODH (18 mg, 0.15 mmol) and Tp (21 mg, 0.10 mmol), 500 μL of anhydrous dioxane and 500 μL of mesitylene, and then immersed in an ultrasonic bath for 15 min. After sonication for 30 min, 0.4 mL of aqueous acetic acid (6 M) were added. The bottle was rapid frozen at 77 K (liquid N₂ bath), evacuated to an internal pressure of below 5 Pa and sealed by flame. The length of the tube sealed was reduced to 10-15 cm. The reaction was heated at 120 °C for 72 h yielding a brown solid, which was isolated by filtration and

washed with anhydrous DMF and THF, the resulting powder was immersed in anhydrous THF for 24 h and dried under vacuum at 100 °C overnight. Yield: 30 mg, 77% for C₈H₈N₄O₅. Elemental analysis calculated: C, 40.00%; H, 3.33%; N, 23.33%. Found: C, 40.96%; H, 4.02%; N, 18.98%.

Similarly, TFBODH was synthesized by TFB (0.01 mmol) and ODH (0.15 mmol) in a same style ampoule bottle. Yield: 26 mg, 76% for C₈H₈N₃O₄. Elemental analysis calculated: C, 46.15%; H, 3.85%; N, 26.92%. Found C, 48.16%; H, 4.88%; N, 20.81%.

Characterizations and application

The powder X-ray diffraction (XRD) patterns were recorded at room temperature with a PANalytical X'Pert Pro Multipurpose Diffractometer using Cu K α radiation at 40 kV and 40 mA. Helium ion microscopy (HIM) images were taken using a ORION NANOFAB helium microscopy (Zeiss, Germany). Fourier-transform infrared spectroscopy (FT-IR) characterization was carried out by a FT-IR spectrometer using KBr pellets (Nicolet, USA). Nitrogen adsorption/desorption measurements were performed on a Micrometrics Surface area analyzer (Micrometrics, USA). The samples were outgassed under vacuum for at least 8 h at 120 °C before measurements. Surface area was calculated using the Brunauer-Emmett-Teller (BET) model. Solid-state ¹³C NMR was recorded on an Advance III-500MHz spectrometer (Bruker, Switzerland). Thermogravimetric analysis from 20-800 °C was carried out on a STA449F3 Thermogravimetric Analyzer in nitrogen atmosphere with a heating rate of 10 °C min⁻¹ (Netzsch, Germany). X-ray photoelectron spectroscopy (XPS) characterization was taken using ESCALAB 250Xi XPS spectrometer with an Al K α X-ray source (Thermo Scientific, USA).

The stability of TpODH and TFBODH was investigated by a dissolution experiment. Three portions of the materials (10 mg for each) were immersed into 10 mL of 9 M HCl, boiling water and 9 M NaOH solutions, respectively, for two days. Then, the mixture was centrifuged and washed with anhydrous THF overnight. The product was dried at 100 °C for XRD analysis.

Batch adsorption experiments

The adsorption properties of the COF for metal ions were tested under non-competitive conditions by immersing COF into a solution containing one type of metal ion.

Adsorption isotherms were conducted at 298 K. A 10 mg sample of dried COF was placed in a series of flasks containing different initial concentrations of each metal ions. Each flask was agitated at 150 rpm for 24 h. The filtrate was collected for the determination of the metal ion concentrations. The amount of metal ion adsorbed was calculated according to equation (1). The adsorption isotherm of metal ion was obtained by plotting Q_e against C_e .

$$Q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where Q_e is the equilibrium adsorption capacity (mg g^{-1}), C_o and C_e are the initial and equilibrium metal ion concentrations (mg L^{-1}), V is the solution volume (L), and W is the mass of the dry COF (g). Such extraordinarily high adsorption amount for TpODH can be ascribed to the high concentration of chelating groups together with well-defined pore channels adequate to facilitate the diffusion of Cu(II) ions. These results underscore the superiority of the utilization of COFs as promising candidates in accomplishing copper removal from the water.

A 10 mg sample of dried TpODH was placed in a series of flasks containing 50 mL of each metal ion solution (2 mmol L^{-1}). Each flask was collected for the determination of the metal ion concentrations. The kinetic curve was obtained by plotting the adsorption capacities of the metal ions vs. the adsorption time. The experimental results were fitted with the pseudo-second-order kinetic model using the equation of

$$t/q_t = (k_2 q_e^2)^{-1} + t/q_e \quad (2)$$

where k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the pseudo-second-order rate constant of adsorption, q_t (mg g^{-1}) is the amount of Cu(II) adsorbed at time t (min), and q_e (mg g^{-1}) is the amount of Cu(II) adsorbed at equilibrium.

One measure of a sorbent's affinity for a target metal ion is the distribution

coefficient (K_d) measurement. The equation is defined as:

$$K_d = (C_i - C_f)V/C_f m \quad (3)$$

where C_i is the initial metal ion concentration, C_f is the final equilibrium concentration of metal ion, V is the volume of the treated solution (mL), m is the amount of adsorbents. The K_d indicate an vital aspect of any adsorbent's performance metrics of metal ion adsorption.

TpODH (10 mg) was added to a Erlenmeyer flask (250 mL) containing a 100 mL aqueous solution of CuCl_2 , $\text{Hg}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3$ and $\text{Cd}(\text{NO}_3)_2$ with each concentration at 10 ppm. The mixture was stirred at room temperature, and at appropriate time intervals, 2 mL were taken from the mixture, and the adsorbents were separated by syringe filter (0.22 μm membrane filter). The concentrations of ions in the resulting solutions were analyzed by ICP-OES or ICP-MS. The percentage removal of metal ions was calculated as follows:

$$\text{Capacity efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (4)$$

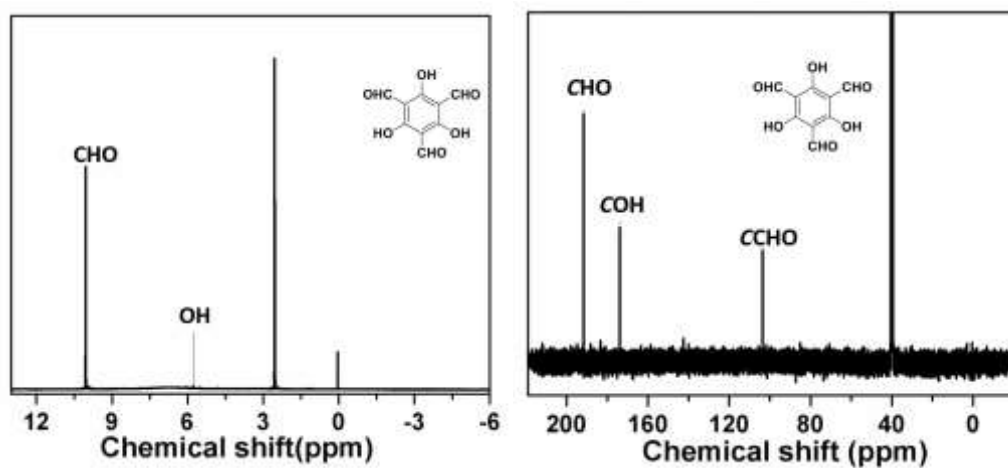


Fig. S1. ^1H NMR and ^{13}C NMR spectra of synthesized Tp.

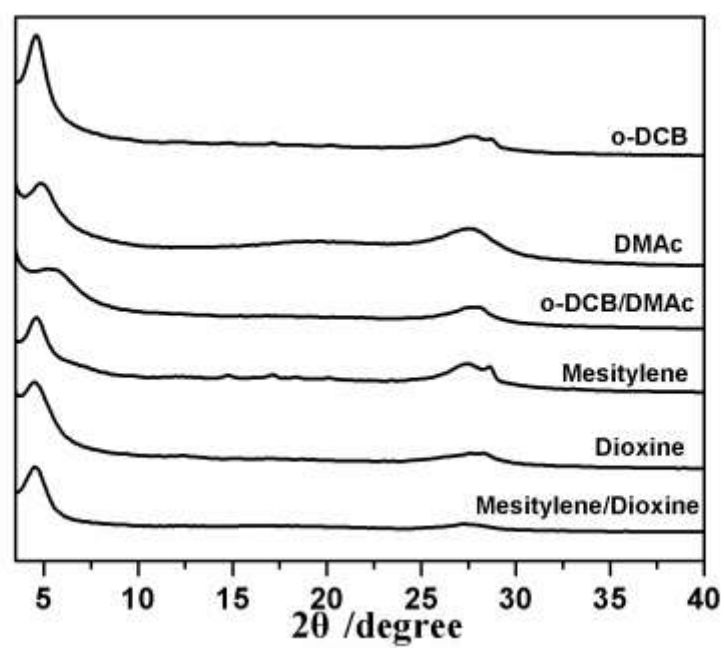


Fig. S2. PXRD patterns of TpODH at different solvents.

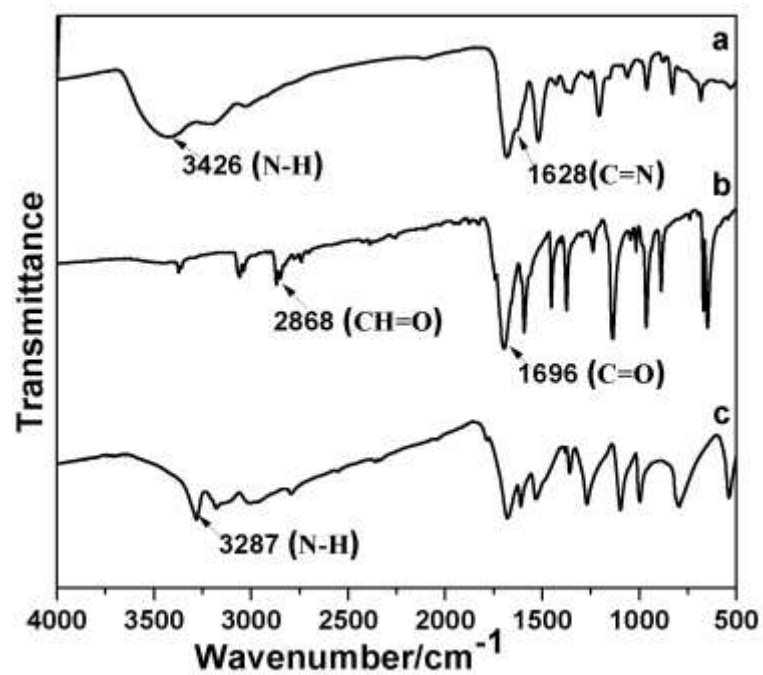


Fig. S3. High-resolution FT-IR spectra of (a) TFBODH, (b) TFB and (c) ODH.

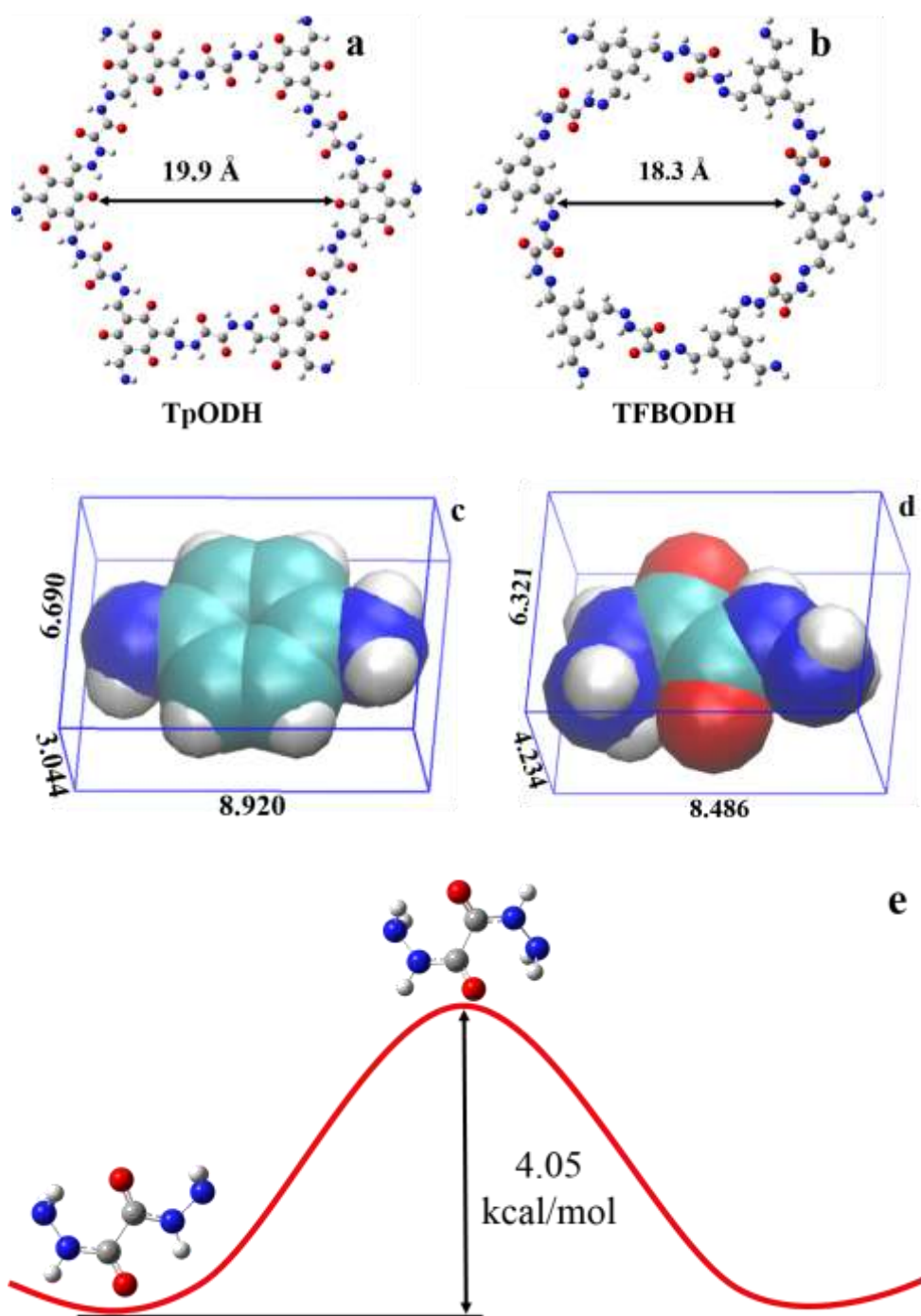


Fig. S4. The unit cells of (a) TpODH and (b) TFBODH, the molecular size of (c) *p*-phenylenediamine (PDA) and (d) ODH, (e) calculated gas-phase rotational barrier of C–N bond of ODH.

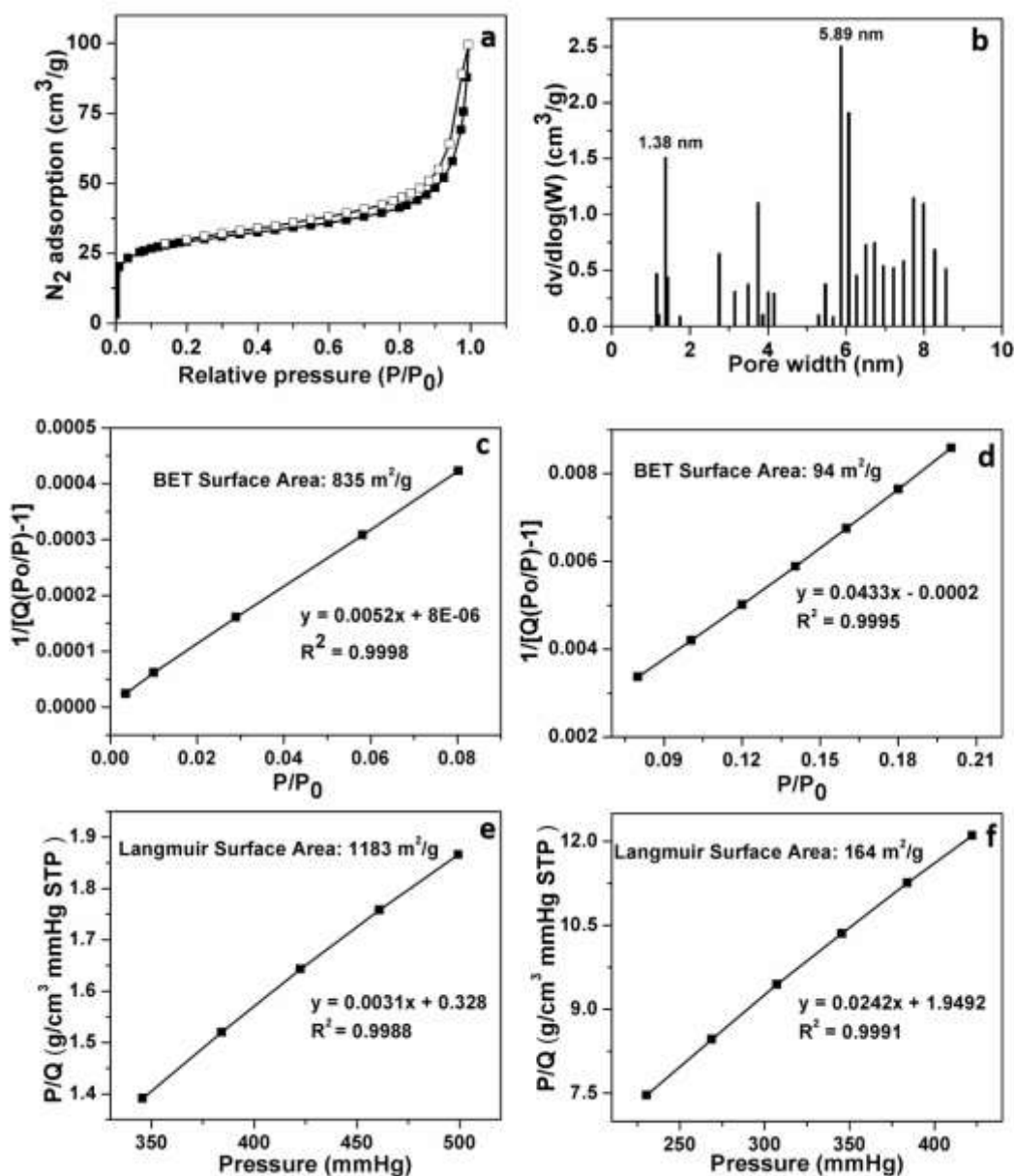


Fig. S5. (a) N₂ adsorption–desorption isotherms (77 K), (b) pore size distribution, (c, d) BET, (e, f) Langmuir surface area plots of TpODH (c, e) and TFBODH (a, b, d, f).

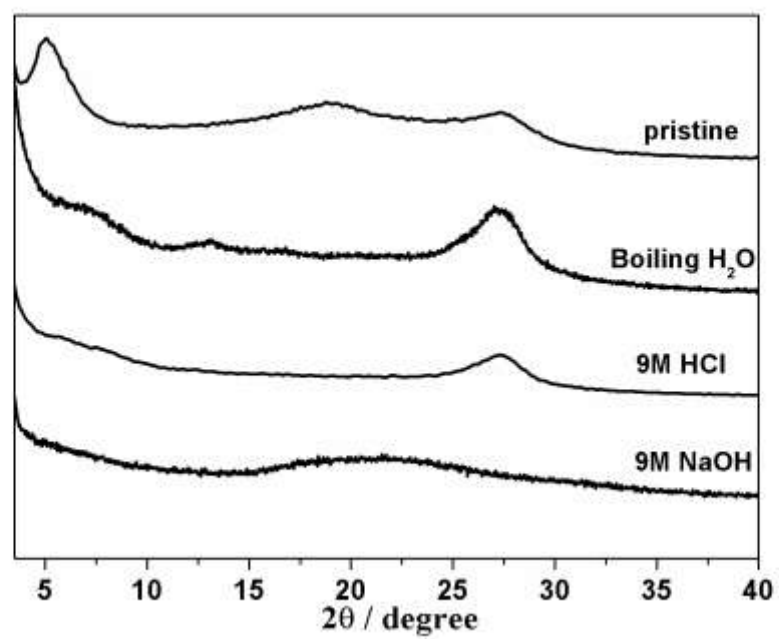


Fig. S6. PXRD patterns of TFBODH after 48 h treatment in boiling water, 9 M HCl (aq) and 9 M NaOH (aq).

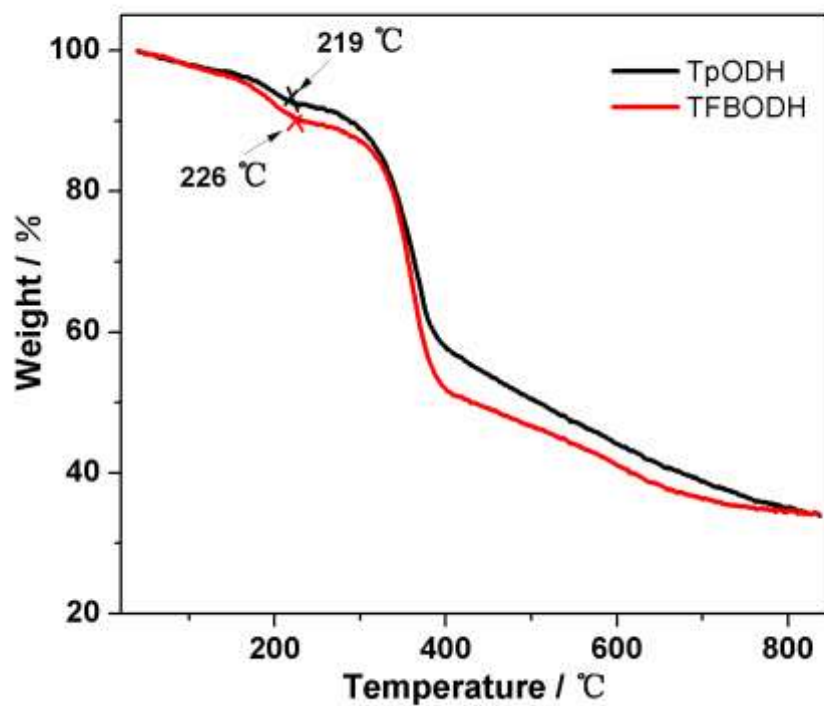


Fig. S7. TGA analysis result of as-synthesized COFs under N₂ atmosphere.

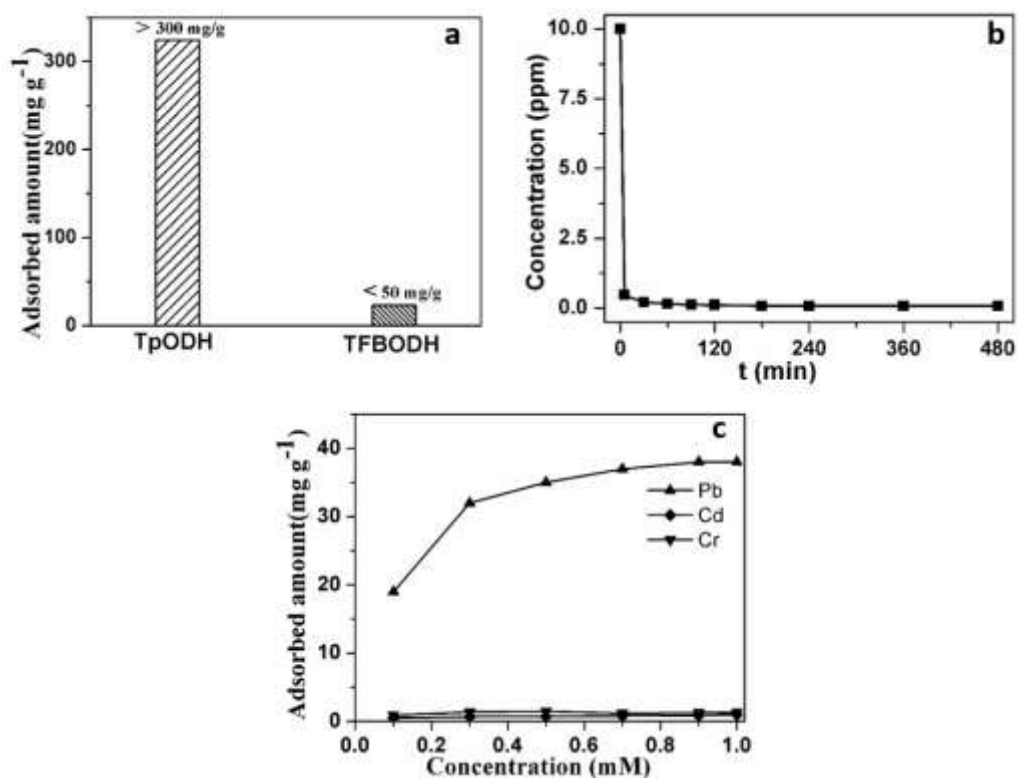


Fig. S8. (a) Cu(II) adsorbed amounts of different adsorbents at room temperature. (b) Cu(II) sorption kinetics under the initial Cu(II) concentration of 10 ppm. (c) Pb(II), Cd(II) and Cr(II) adsorption isotherms of TpODH at room temperature.

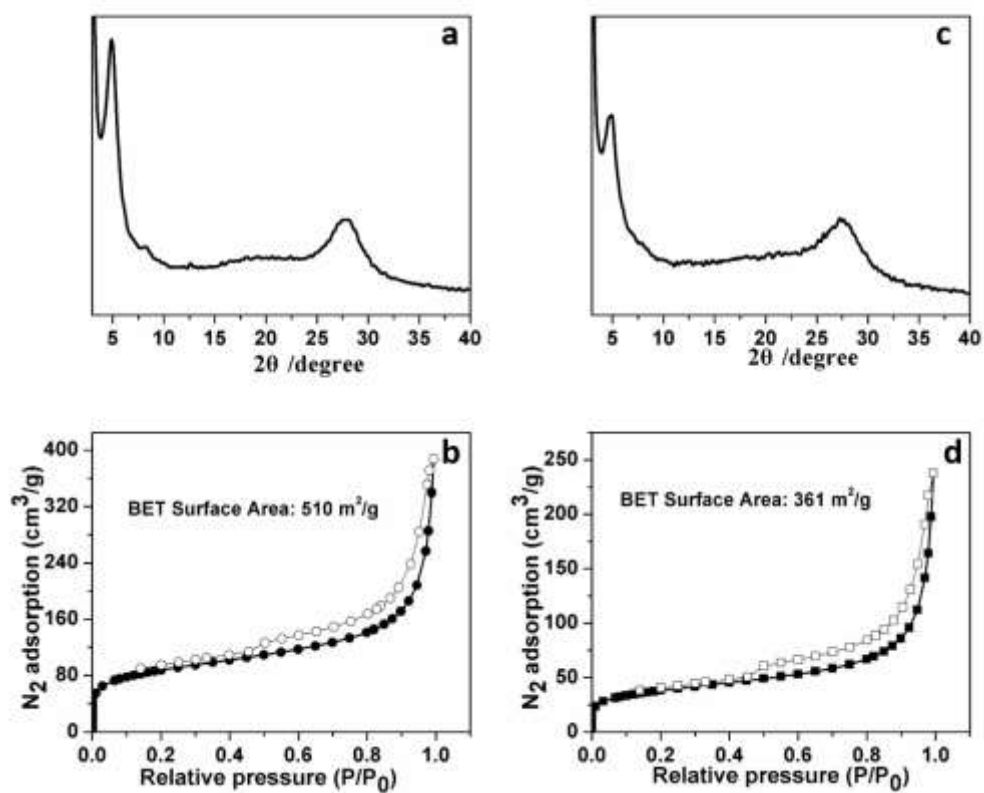


Fig. S9. (a, c) PXRD pattern and (b, d) N_2 adsorption–desorption isotherms (77 K) of TpODH_Cu (a, b) and TpODH_Hg (c, d).

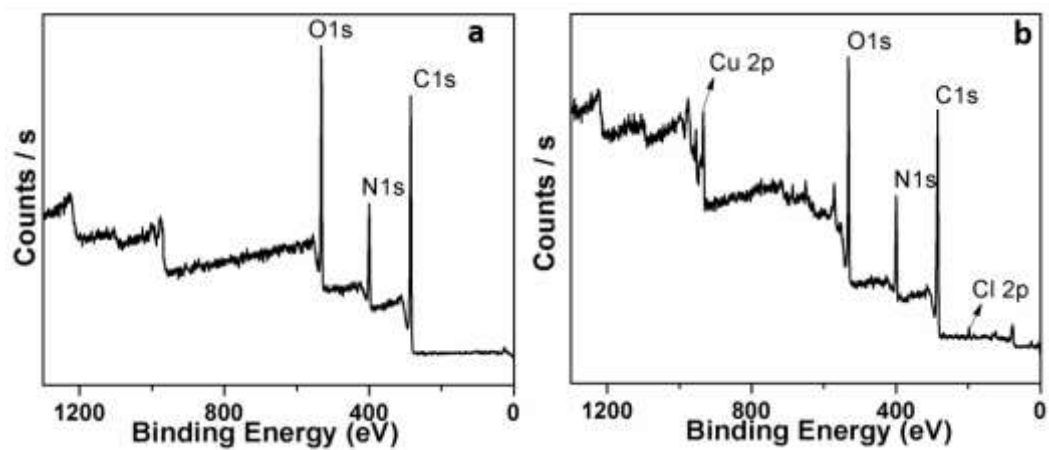


Fig. S10. Low-resolution XPS survey wide scans spectra of (a) TpODH and (b) TpODH_Cu.

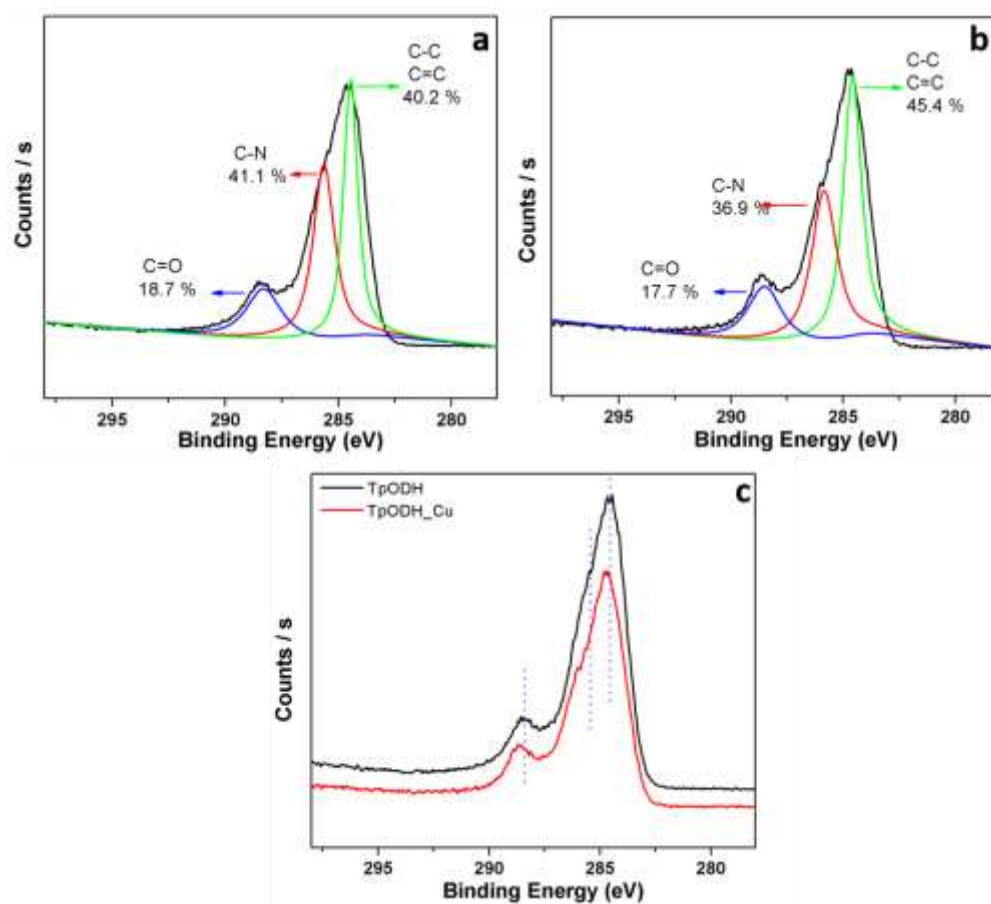


Fig. S11. High-resolution XPS C1s spectra of (a) TpODH and (b) TpODH_Cu and (c) comparison of XPS C1s high-resolution of TpODH and TpODH_Cu.

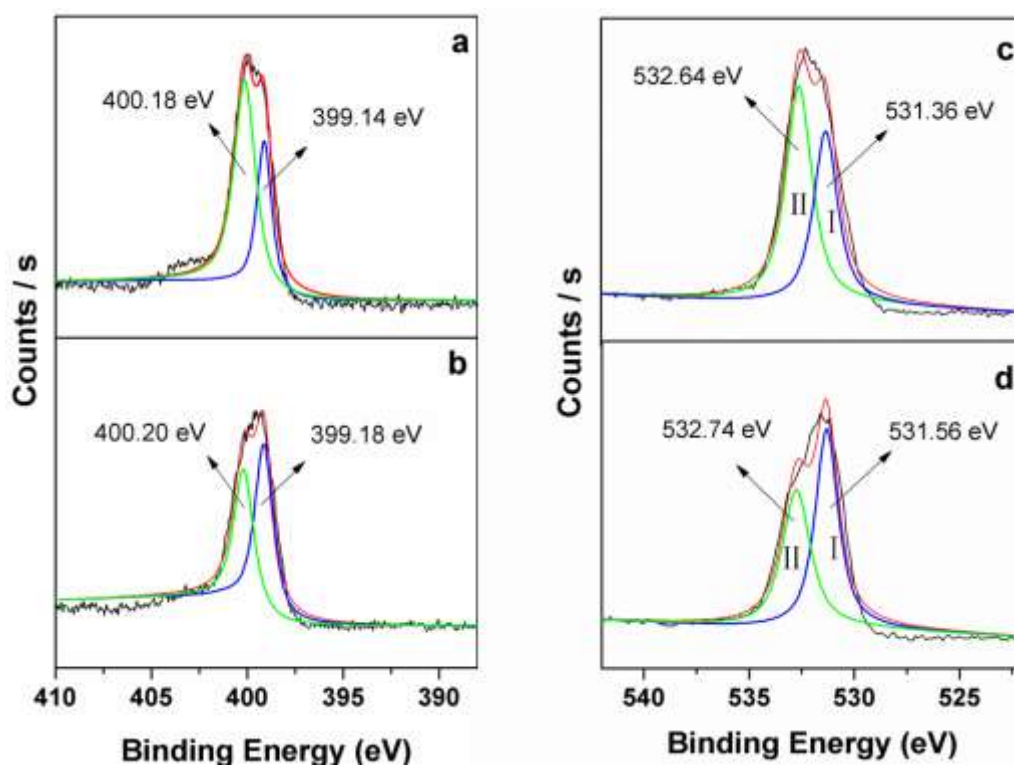


Fig. S12. XPS N 1s high-resolution spectrum of (a) TpODH and (b) TpODH_Cu. O 1s high-resolution spectrum of (c) TpODH and (d) TpODH_Cu.

Table S1 Elemental composition of the TpODH and TpODH_Cu sample based upon analysis of the survey spectra.

Peak	Peak BE/eV	At. % (TpODH)	At. % (TpODH_Cu)
O 1S	531.57	23.01	22.43
C 1S	284.99	61.49	57.12
N 1S	399.8	15.15	16.61
Cu 2p3	934.26	0	2.13
Cl 2P3	198.05	0	1.72