Supplementary Information

A Cryptand-Based Covalent Organic Framework for Efficient Gold Recovery from Electronic Waste

Xuyuan Jin [a,b,#], Anting Ding [a,#], Shuainan Ni [a,b*], Chenchen Zhu [a,b], Zhiwei Liu [a,b], Chengliang Xiao [a,b*]

[a]*College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310058, China*

[b]*Institute of Zhejiang University-Quzhou, Quzhou 325000, China*

*Corresponding author: C.L. Xiao. E-mail address: xiaoc@zju.edu.cn. S.N. Ni. E-mail address: nsn@zju.edu.cn.

1.1 Instrumentation

Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku SmartLab SE X-ray diffractometer equipped with a Cu Kα source (λ = 0.15418 nm). Brunauer-Emmett-Teller (BET) surface areas and pore size distributions were determined from N_2 adsorption/desorption isotherms collected at 77 K using a Micromeritics/3FLEX and the testing samples were degassed at 120 °C under vacuum for 8 h before measurement. Fourier-transform infrared spectra (FT-IR) were recorded on an INVENIO R. Scanning electron microscopy (SEM) images were recorded on a HITACHI Regulus 8230. Transmission electron microscopy (TEM) were recorded on a FEI Talos F200X. ^{13}C solid-state cross-polarization magic angle spinning nuclear magnetic resonance (13C CP/MAS NMR) spectra were recorded on a Bruker AVANCE NEO 600WB. Proton nuclear magnetic resonance spectrum (^1H NMR) were recorded on a Bruker AVANCE NEO 500. Mass spectrometry testing were recorded on a SHIMADZU LCMS-IT-TOF. Thermogravimetric analyses (TGA) were performed on a TG309 Li bra Classic. X-ray photoelectron spectroscopy (XPS) analyses were performed using an AXIS Supra+. All binding energies were calibrated against the C 1s peak at 284.8 eV of neutral hydrocarbons. Inductively coupled plasma mass spectrometry (ICP-MS) analyses were performed on a Thermo Scientific ICAP PRO.

1.2 Calculation method

All calculations were performed using Gaussian 16 (Revision C.01). The hybrid PBE0 functional was employed for all computations, incorporating Grimme's D3 dispersion correction with Becke-Johnson damping (DFT-D3BJ). Geometry optimizations and frequency analyses were conducted with the 6-31G(d,p) basis set and the Polarizable Continuum Model (PCM) for water. Subsequent single-point energy calculations utilized the larger 6-311+G(d,p) basis set along with the Solvation Model based on Density (SMD) to represent aqueous solvation effects. The structures were fully relaxed until the maximum force on each atom was less than 0.02 eV/Å, meanwhile the energy convergent standard was 10^{-5} eV. Molecular visualization was carried out using VMD software. The structure of Cryptand-COF was fully relaxed and reached the minimum energy principle during the structure optimization process. The electrostatic potential (ESP) surfaces and electron localization function (ELF) analyses were generated and processed with the Multiwfn program.

1.3 Adsorption experiments

1.3.1. Effect of pH value

$NaAuCl_4 \cdot 2H_2O$ was used for preparing Au(III) solutions. The influence of solution pH on the adsorption of Au(III) by Cryptand-COF was evaluated by dissolving $NaAuCl_4 \cdot 2H_2O$ in hydrochloric acid solutions of pH values ranging from 2 to 7, after which the COF was then added at a solid-to-liquid ratio of 1 g L^{-1}. Specifically, 5 mg of the COF was combined with 5 mL of the Au(III) solution and agitated for 1.5 hours. After filtration through a 0.1 μm membrane, the residual Au(III) concentration in the filtrate was determined by inductively coupled plasma mass spectrometry (ICP-MS).

1.3.2. Au(III) adsorption capacity study

All adsorption tests were conducted at 25°C with an adsorbent/liquid ratio of 1 g L^{-1}. Cryptand-COF was dispersed in pH 2 hydrochloric acid solutions spiked with Au(III) at initial concentrations varying from approximately 5 to 4000 mg L^{-1}. The mixtures were sonicated briefly and then shaken for 1.5 hours. Following this, the adsorbent was separated by filtration through a 0.1 μm membrane, and the equilibrium concentration of Au(III) in the filtrate was measured by ICP-MS.

The equilibrium adsorption capacity for Au(III) (q_e, mg g^{-1}) was determined using the formula provided below:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

The Langmuir adsorption isotherm was modeled by applying the following mathematical equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{2}$$

In the equation, C_0 and C_e denote the initial and equilibrium concentrations (mg L^{-1}) of Au(III), respectively, V is the solution volume (L), and m represents the mass (g) of the adsorbent used. The parameter q_m (mg g^{-1}) corresponds to the theoretical maximum adsorption capacity for Au(III), while K_L is the Langmuir equilibrium constant associated with adsorption affinity.

1.3.3. Au(III) adsorption kinetics study

To investigate the adsorption kinetics of Au(III), Cryptand-COF was introduced into an aqueous Au(III) solution (~500 mg L^{-1}, pH 2 adjusted with HCl) at an adsorbent/liquid ratio of 1 g L^{-1}. The mixture was stirred at 1000 rpm, and samples were withdrawn at 10-minute intervals. Each aliquot was immediately filtered through a 0.1 μm membrane, and the residual Au(III) concentration in the filtrate was analyzed by ICP-MS.

The Au(III) uptake kinetics data were fitted by a pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{K_2 q2_{e,cal}} + \frac{t}{q_{e,cal}} \tag{3}$$

Within this kinetic formulation, the parameter k_2 (g (mg·min)$^{-1}$) defines the adsorption rate constant of pseudo-second-order kinetic model, $q_{e,cal}$ signifies the predicted maximum adsorption uptake of Au(III), whereas q_t stands for the measured adsorption capacity (mg g^{-1}) at any given time point t.

1.3.4. Reusability study

Following the Au(III) adsorption tests, the spent Cryptand-COF was regenerated by immersion in a 0.5 mol L^{-1} thiourea/0.5 mol L^{-1} HCl eluent (5 mL) for 2 hours. The material was then rinsed thoroughly with ethanol and distilled water, dried under vacuum at 55 °C, and subsequently reused in the next cycle of Au(III) adsorption experiments.

1.3.5. mixed metal ions study

For the selectivity study, 10 mg of Cryptand-COF was introduced into a multi-ion solution (pH 2, adjusted with HCl) containing Au(III) and competing ions (Fe(III), Cu(II), Co(II), Ni(II), Zn(II), Cr(II), Mn(II), Na(I), Al(III)) at approximately 10 mg L^{-1} each, with an adsorbent/liquid ratio of 1 g L^{-1}. The suspension was sonicated, agitated for 1.5 h, and then filtered through a 0.1 μm membrane. The equilibrium concentrations of all metal ions in the filtrate were analyzed by ICP-MS.

1.3.6. Leaching experiment of disposed CPUs for Au(III) recovery by COF

Disposed CPUs were cleaned with distilled water and dried in an oven. Subsequently, the CPUs were placed on a hot plate and heated to 200 °C, after which the gold-plated pins were carefully peeled off and allowed to cool to room temperature. The obtained gold-plated pins were immersed in aqua regia for approximately 2 hours, and the supernatant liquid was collected, diluted 100-fold, and subjected to compositional analysis via ICP-MS. Then Cryptand-COF was dispersed in the supernatant liquid at an adsorbent/liquid ratio of 1 g L^{-1}. The newly prepared suspensions were subjected to brief sonication followed by agitation for 1.5 hours. After this period, the adsorbent was separated by filtration through a 0.1 μm membrane, and the concentration of Au(III) in the resulting filtrate was determined by ICP-MS.

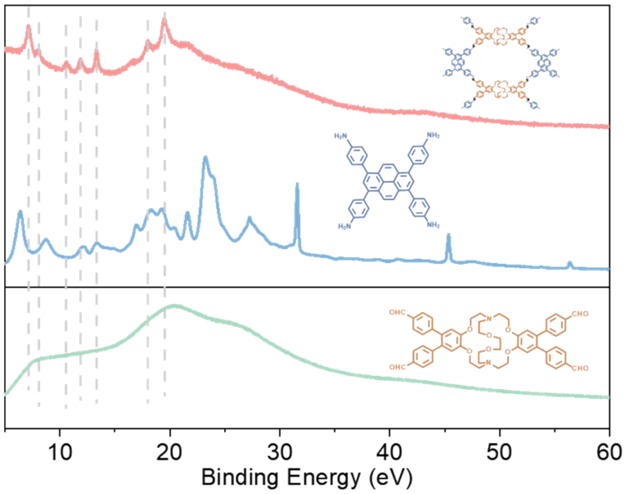


Figure S1 PXRD pattern of TFPPy, cryptand aldehyde-based ligand and Cryptand-COF .

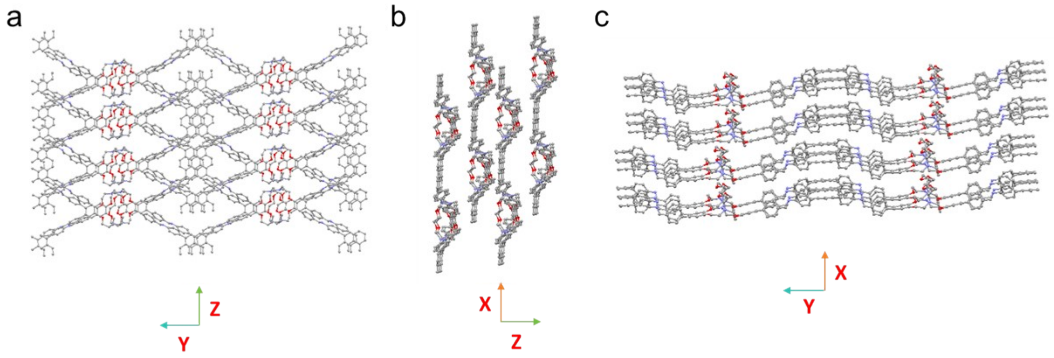


Figure S2 The simulated crystalline structures of Cryptand-COF with AB stacking mode along the x (a), y (b), and z (c) directions.

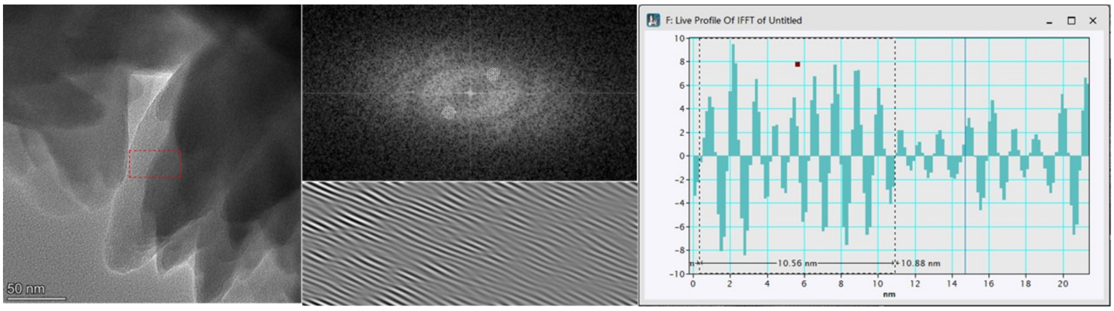


Figure S3 Enlarged HR-TEM images, corresponding FFT, and line profile along the indicated area in TEM image.

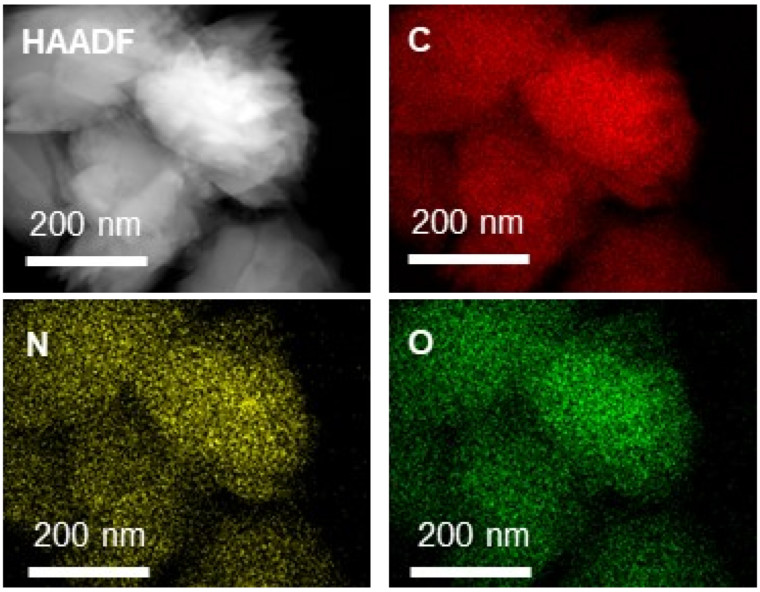


Figure S4 HAADF-STEM image and corresponding EDS mapping of C, N and O.

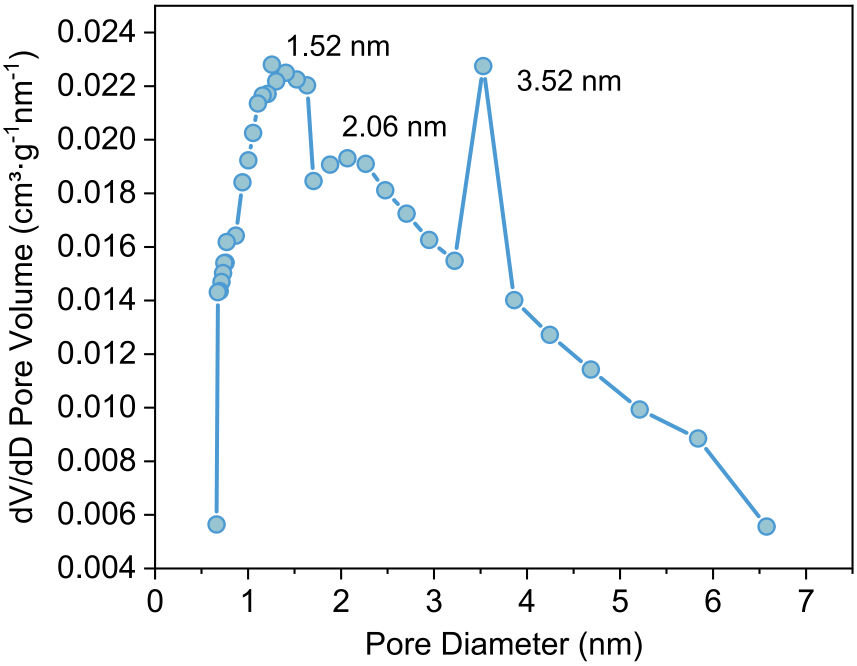


Figure S5 Pore size distributions of Cryptand-COF at 77 K.

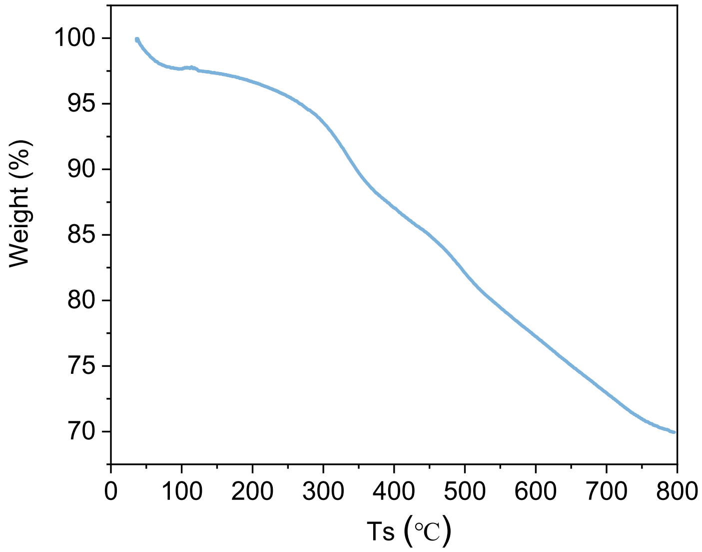


Figure S6 TGA of Cryptand-COF.

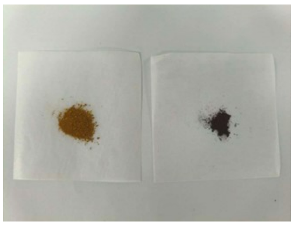


Figure S7 Color change of Cryptand-COF before (left) and after (right) gold adsorption.

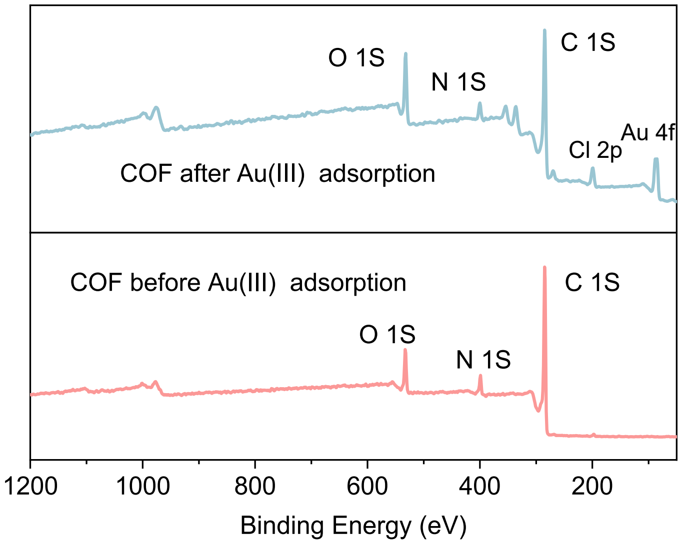


Figure S8 The full XPS spectra of Cryptand-COF before (pink curve) and after (blue curve) Au(III) adsorption.

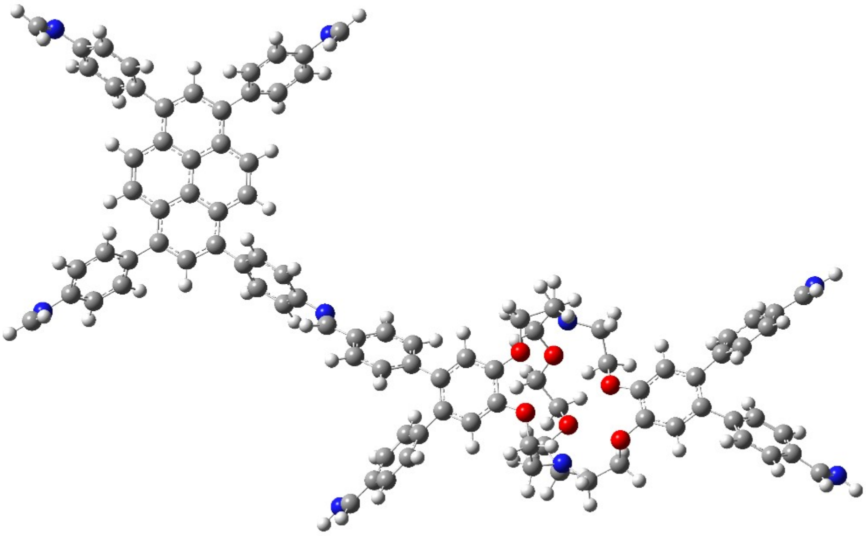


Figure S9 The optimized structures model of Cryptand-COF.

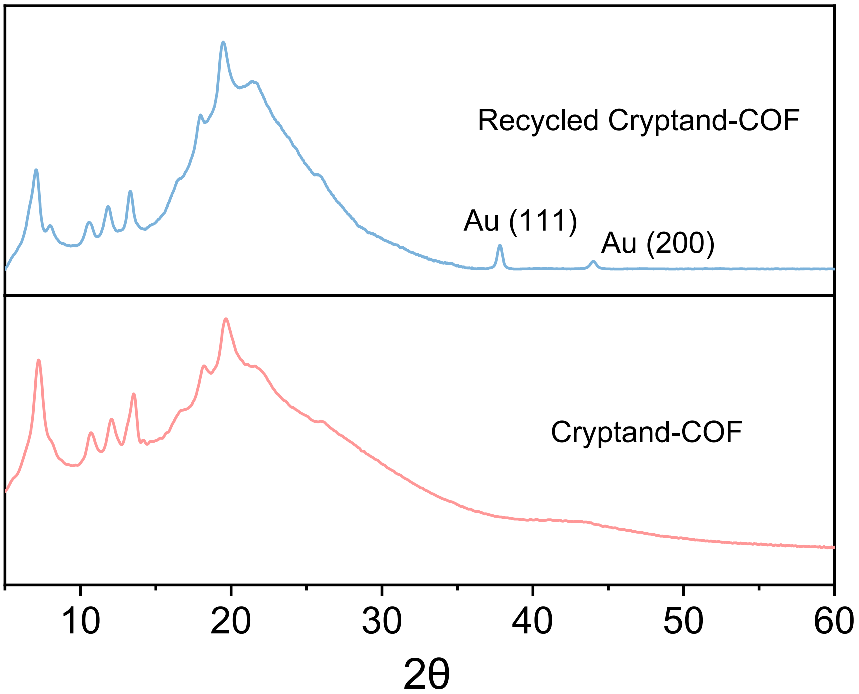
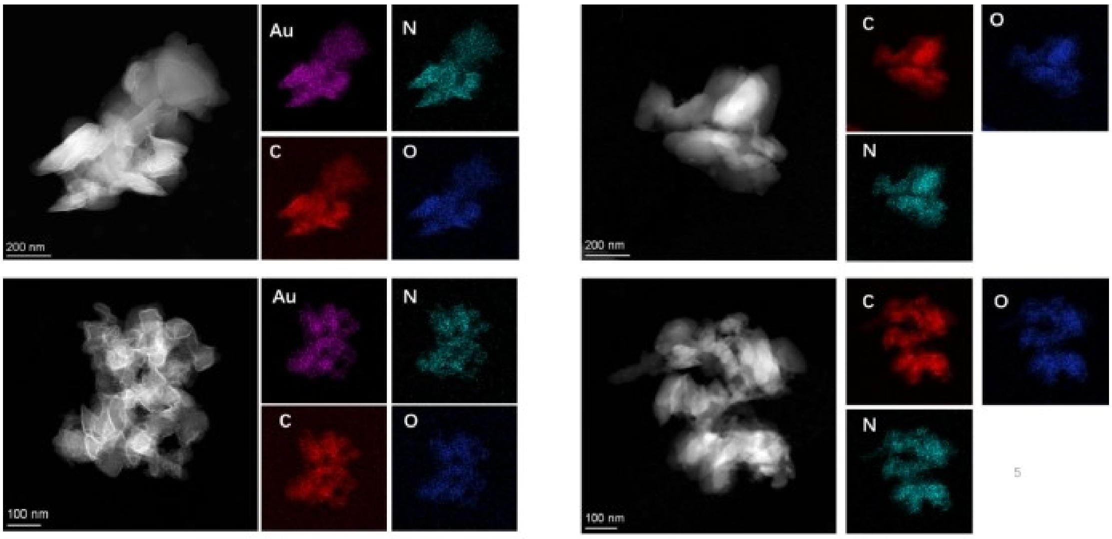


Figure S10 PXRD patterns of Cryptand-COF and recycled Cryptand-COF.



Au-adsorbed Cryptand-COF

Recycled Cryptand-COF

Figure S11 TEM patterns of Au-adsorbed Cryptand-COF (left) and recycled Cryptand-COF (right).

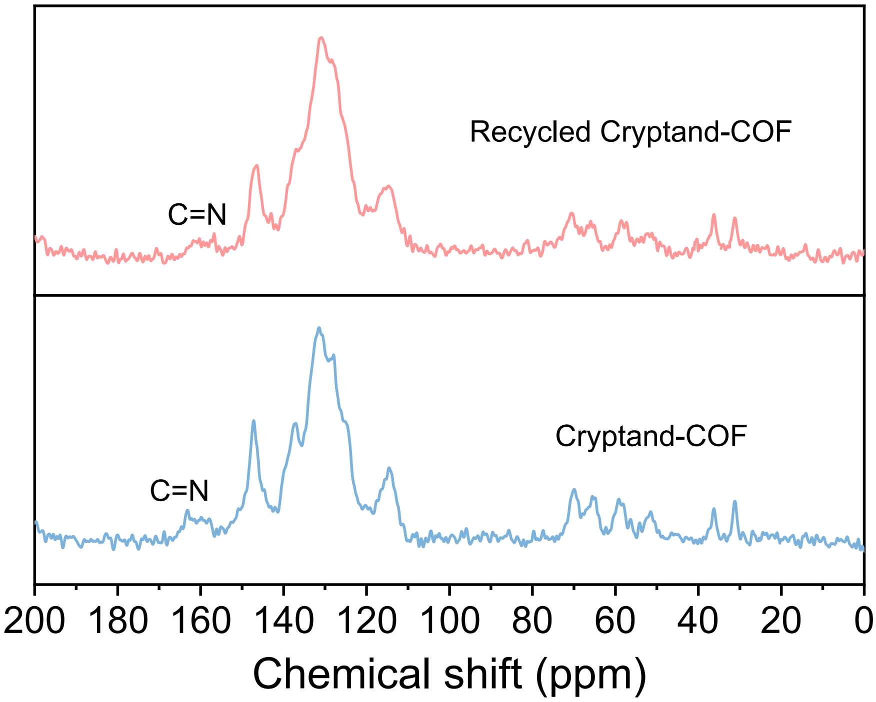


Figure S12 ^{13}C CP/MAS NMR spectra of Cryptand-COF and recycled Cryptand-COF.

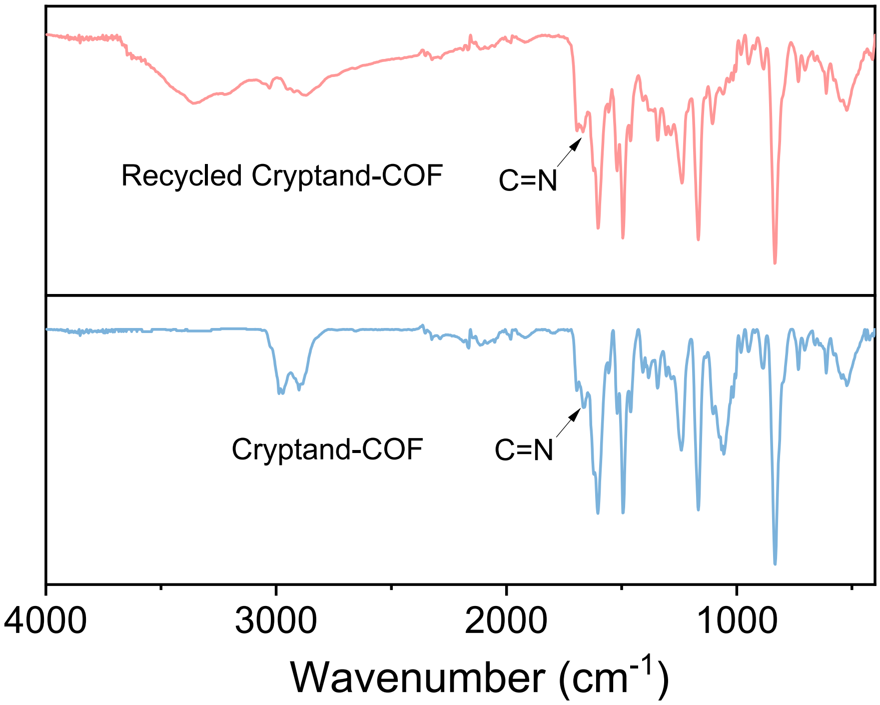
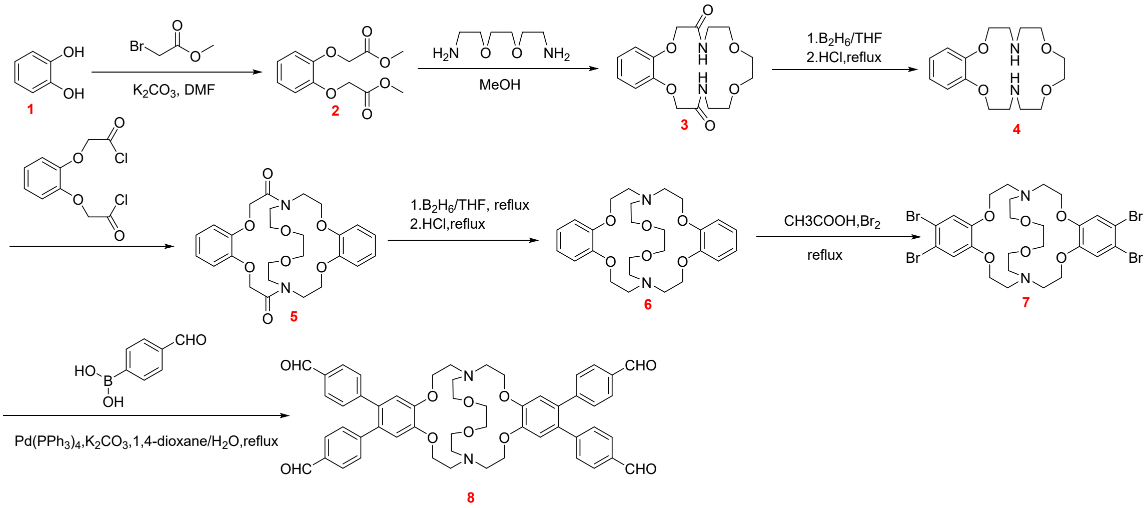


Figure S13 FT-IR spectra of Cryptand-COF and recycled Cryptand-COF.

1.4 Synthesis of Ligands



Scheme 1 Synthesis and characterization of cryptand-based aldehyde ligand.

2,2'-[(1,2-phenylene)bis(oxy)]bis[acetic acid] dimethyl ester (2). To a stirred solution of benzene-1,2-diol (10 g, 91.8 mmol) in dry DMF (500 mL) was added K_2CO_3 (2.8 g, 20.34 mmol) and methyl 4-bromobutyrate (1.93 mL, 15.26 mmol). The reaction mixture was then heated to 70 °C for 16 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. CH_2Cl_2 was added and the mixture was washed with water. The aqueous layer was extracted in CH_2Cl_2 and the combined organic layers were washed twice with water and brine. The solvent was removed under reduced pressure and the crude product was transferred to a 250 mL round-bottom flask. Then 200 mL MeOH was add and the round-bottom flask was flash frozen at 77 K until a significant quantity of white product precipitated. The white product was filtered and washed twice quickly with 20 mL MeOH to gave **2** as a white solid, which was used without further purification; Yield: 13.2 g (48.5 mmol, 53.5%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.97-6.92 (m, 2H), 6.90-6.86 (m, 2H), 4.74-4.70 (s, 4H), 3.81-3.76 (s, 6H).

4,7,13,16-tetraoxa-1,10-diaza-5,6-benzocyclooctadecane-2,9-dione (3). To a stirred solution of **2** (13.2 g, 48.5 mmol) in dry MeOH (500 mL) was added 3,6-dioxa-1,8-diaminooctane (7.178 g, 48.5 mmol). The reaction mixture was stirred and kept at room temperature for a week. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography of the residue (CH_2Cl_2-MeOH) gave **3** as a white solid. Yield: 12.8 g (37.8 mmol, 71%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.17-7.11 (m, 2H, N-H), 7.00-7.96 (m, 2H), 6.92-6.88 (m, 2H), 4.60-4.56 (s, 4H), 3.60-3.53 (m, 12H).

Benzodiaza-18-crown-6 (4). Borane THF complex (1 M in THF, 300 mL, 300 mmol) was added under an atmosphere of Argon to **3** (12.8 g, 37.8 mmol) at 0 °C. The solution was then stirred and kept at room temperature for 12 h. After reaction, 30 mL distilled water was added slowly and the solvent was removed under reduced pressure. 1.2 M HCl (100 mL) was then added and solution was then heated back to reflux for 8 h then cooled to room temperature. The pH of solution was adjusted to 11 by adding NaOH. The product was extracted with CH_2Cl_2 three times and solvent was removed under reduced pressure to gave **4** as a pink soild. Yield: 8.3 g (26.8 mmol, 61%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.89-6.83 (m, 4H), 4.13-4.06 (t, 4H), 3.68-3.58 (m, 8H), 3.06-3.02 (t, 4H), 2.87-2.83 (t, 4H).

N-(3,6-Dioxaoctamethylen)-N’-(1,2-phenylendioxydiethylen)-2,2’-(1,2-phenylendioxy)-diacetamid (5). The [2-(2-chloro-2-oxoethoxy)phenoxy]acetyl chloride (4.5 g, 19.3 mmol) was dissolved in anhydrous toluene (50 mL). A separate solution of the **4** (6.0 g, 19.3 mmol) and NEt_3 (10 mL) in anhydrous toluene (50 mL) and anhydrous CH_2Cl_2 (10 mL) was also prepared. Both solutions were added simultaneously over 2 h to a vigorously stirred solution of anhydrous toluene (300 mL) at 0 °C. Once the addition was complete the reaction mixture was warmed to room temperature and stirred for overnight. The solvent was then removed under reduced pressure. Flash chromatography of the residue gave **5** as a white solid. Yield: 4.2 g (8.5 mmol, 44%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.05-6.76 (m, 8H), 5.44-5.30 (dd, 2H), 4.87-4.79 (d, 1H), 4.65-4.53 (m, 2H), 4.37-3.89 (m, 7H), 3.74-3.31 (m, 9H), 3.14-2.98 (m, 2H), 2.88-2.76 (m, 1H).

5,6,14,15-Dibenzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (6). Borane THF complex (1 M in THF, 100 mL, 100 mmol) was added under an atmosphere of Argon to **5** (4.2 g, 8.5 mmol) at 0 °C. The solution was then stirred and kept at room temperature for 12 h. After reaction, 30 mL distilled water was added slowly and the solvent was removed under reduced pressure. 1.2 M HCl (100 mL) was then added and solution was then heated back to reflux for 8 h then cooled to room temperature. The pH of solution was adjusted to 11 by adding NaOH. The product was extracted with CH_2Cl_2 three times and solvent was removed under reduced pressure to gave **6** as a brown viscous liquid. Yield: 3.5 g (7.4 mmol, 61%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.94-6.89 (m, 4H), 6.84-6.79 (m, 4H), 4.18-4.10 (m, 4H), 4.01-3.95 (m, 4H), 3.61-3.56 (m, 4H), 3.46-3.40 (m, 4H), 3.05-2.96 (m, 4H), 2.87-2.74 (m, 8H).

bis(3,4-dibromobenzene)-5,6,14,15-Dibenzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (7). To a stirred solution of **6** (3.5 g, 7.4 mmol) in dry acetic acid, 5 mL bromine was added under an atmosphere of Argon at room temperature. The solution was then heated to 70 °C for 48 h. After reaction, the mixture was filtered to obtain a crude orange product with adhered bromine. The product was ultrasonically washed repeatedly with CH_2Cl_2, diethyl ether, and acetone until it turned into a white solid as a product **7**. Yield: 2.3 g (2.9 mmol, 39%). ^{1}H NMR (500 MHz,

$(CD_3)_2SO$, δ): 7.17-7.14 (s, 4H), 4.18-4.10 (m, 8H), 3.54-3.43 (m, 12H), 3.25-3.18 (m, 8H).

Bis ((1,1':2',1''-terphenyl)-4,4''-dicarbaldehydebenzene)- 5,6,14,15-Dibenzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (8). To a stirred solution of **7** (2.3 g, 2.9 mmol) in 40 mL 1,4-Dioxane and 10 mL distilled water, $Pd(PPh_4)_4$ (0.15 g, 0.15 mmol), 4-formylphenylboronic acid (3.6 g, 24 mmol), K_2CO_3 (3.6 g, 24 mmol) were added under an atmosphere of Argon at room temperature. The solution was then stirred and heated to 90 °C for 36 h. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography of the residue (CH_2Cl_2-MeOH) gave **8** as a white solid. Yield: 0.8 g (0.9 mmol, 31%). ^1H NMR (500 MHz, $CDCl_3$, δ): 9.98-9.94 (s, 4H), 7.75-7.69 (d, 8H), 7.30-7.22 (m, 8H), 6.95-6.84 (m, 4H), 4.32-4.10 (m, 8H), 3.62-3.52 (m, 4H), 3.44-3.31 (m, 8H), 2.90-2.67 (m, 8H). HRESIMS (m/z): $[M+H]^+$ calcd for 889.36; found, 889.37.

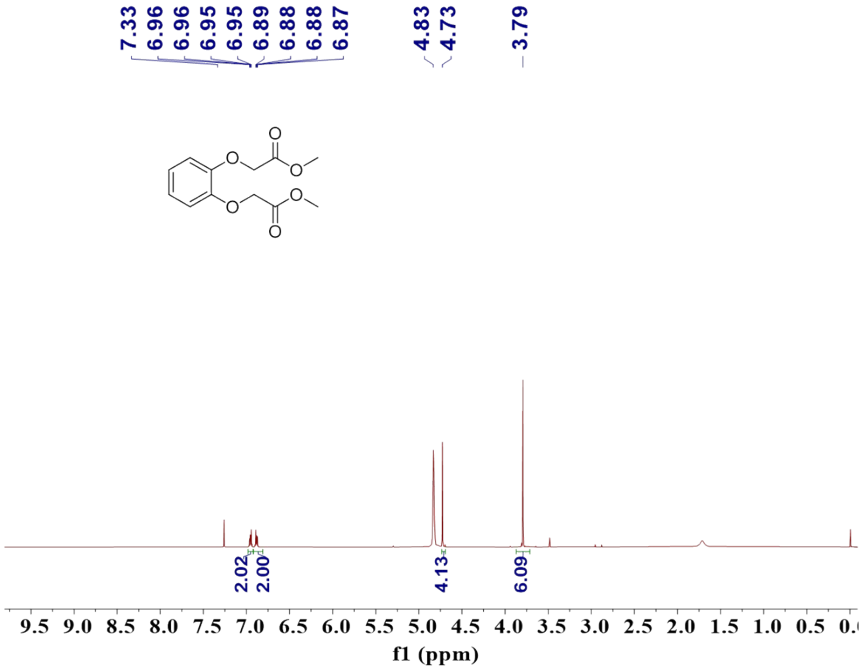


Figure S14 The ^1H NMR spectrum of compound **2**.

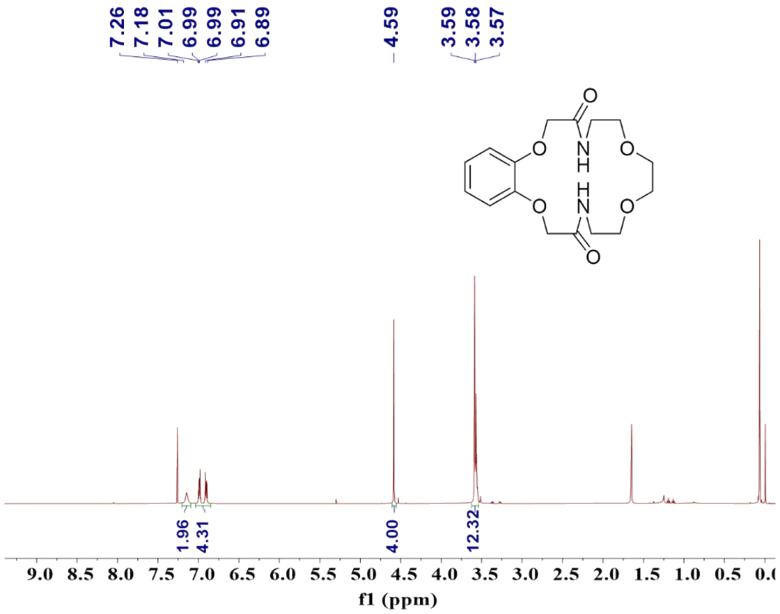


Figure S15 The ^{1}H NMR spectrum of compound **3**.

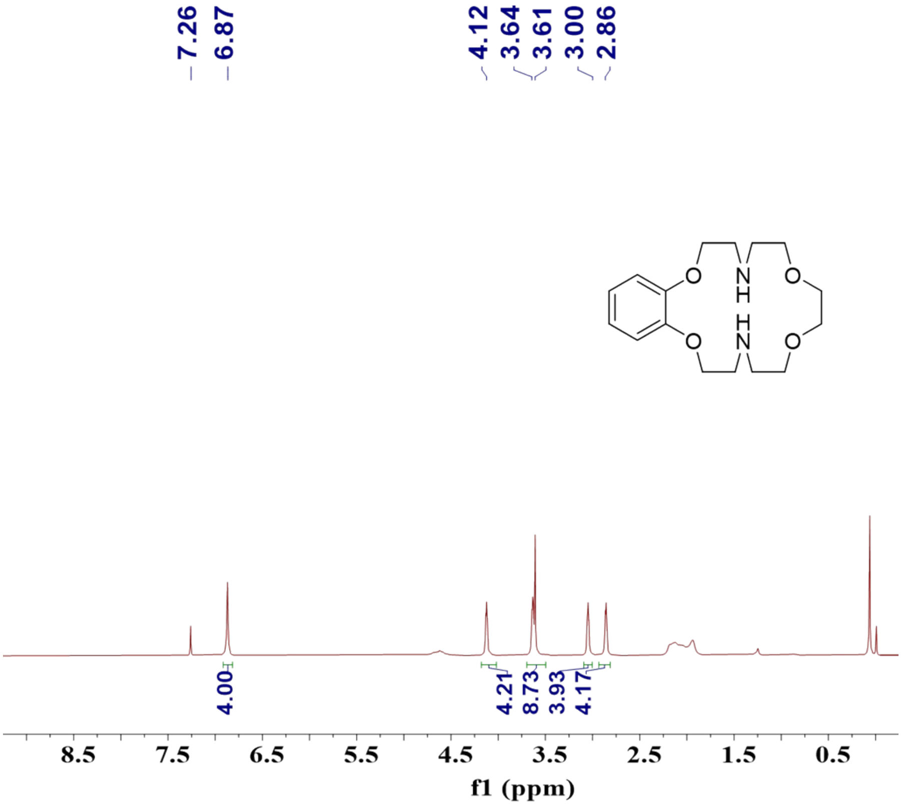


Figure S16 The ^{1}H NMR spectrum of compound **4**.

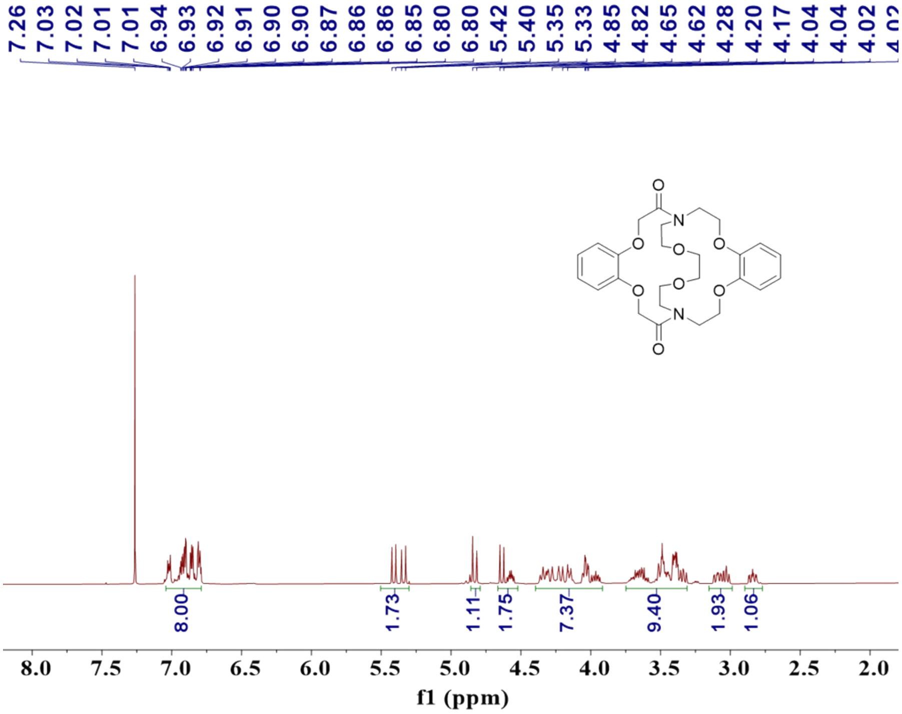


Figure S17 The ^{1}H NMR spectrum of compound **5**.

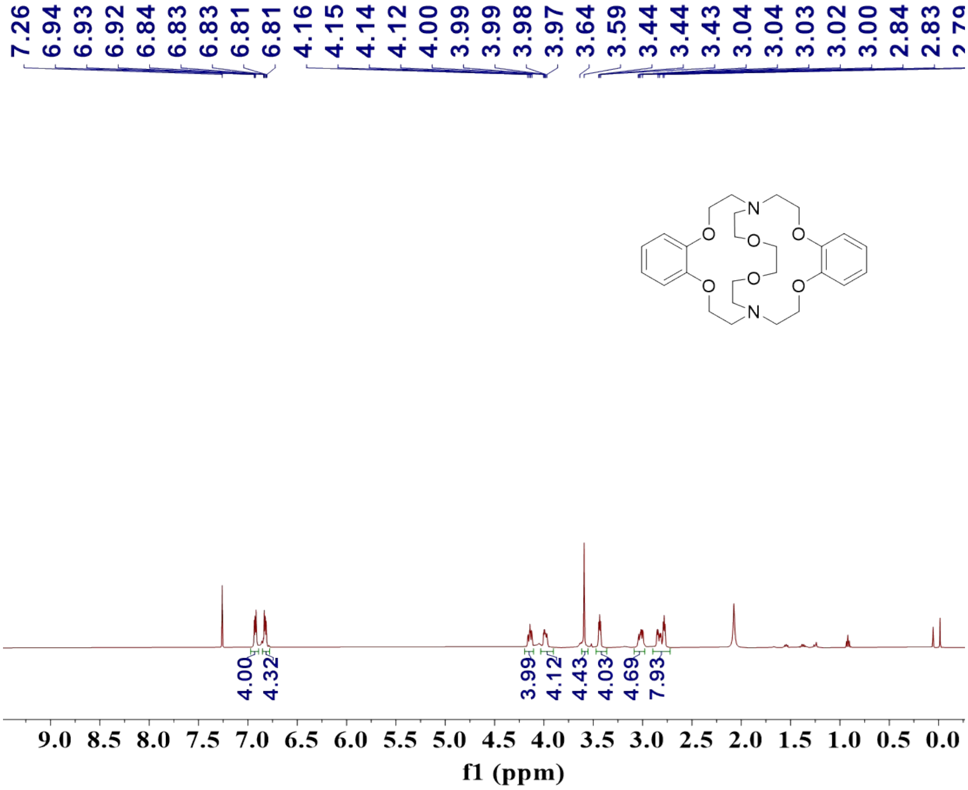


Figure S18 The ^{1}H NMR spectrum of compound **6**.

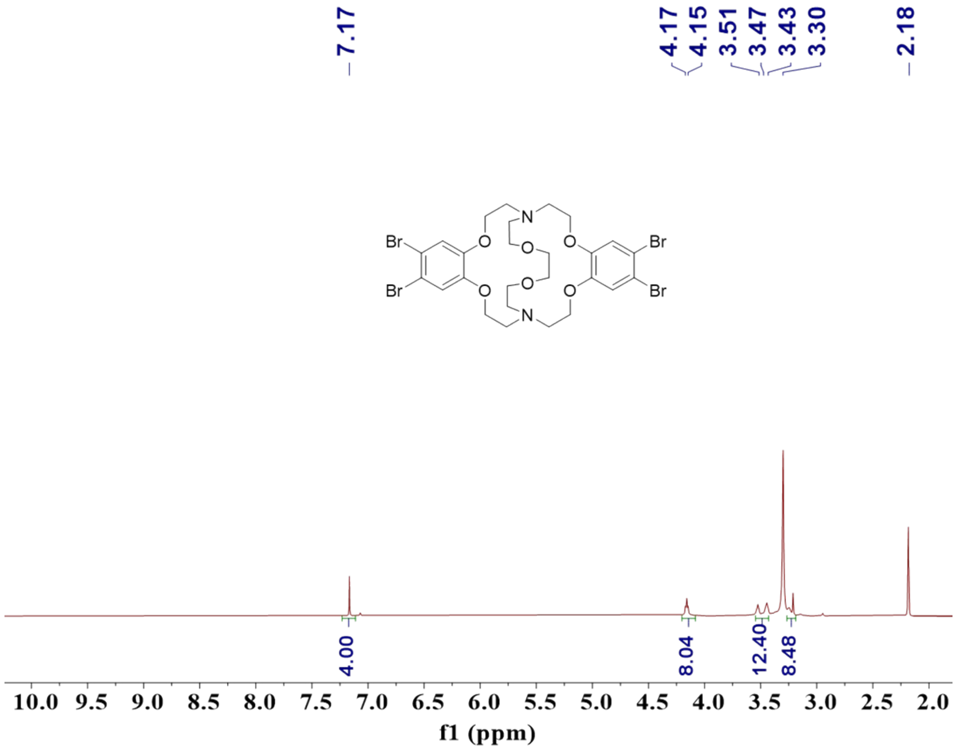


Figure S19 The ^{1}H NMR spectrum of compound **7**.

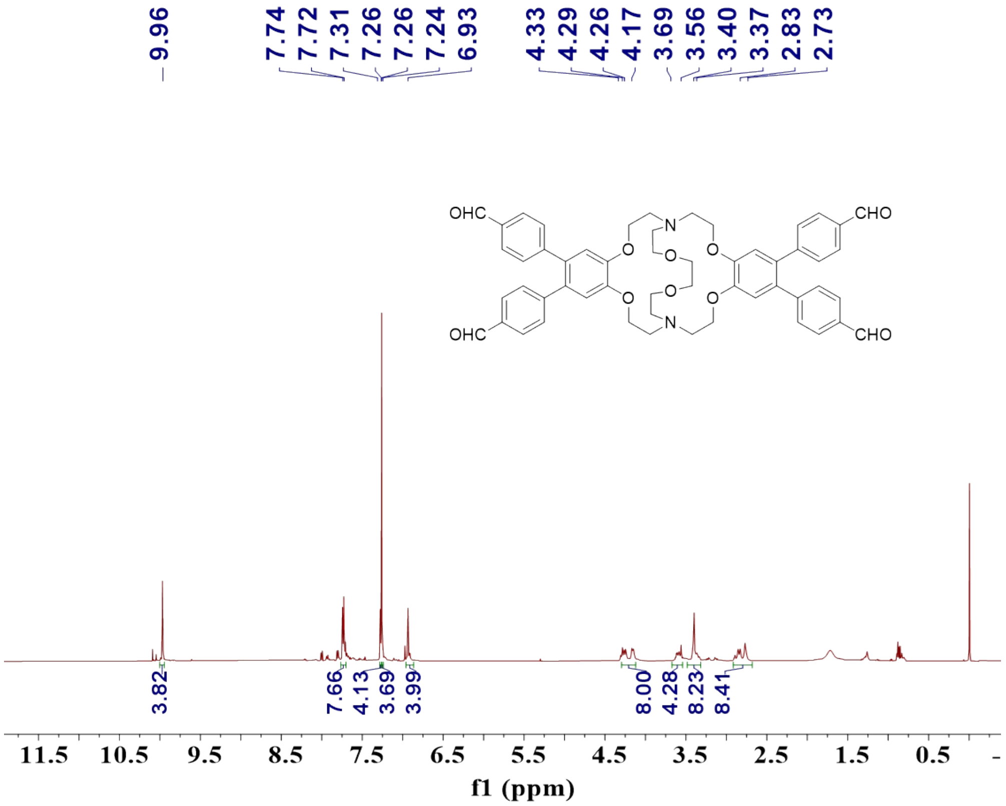


Figure S20 The ^{1}H NMR spectrum of compound **8**.

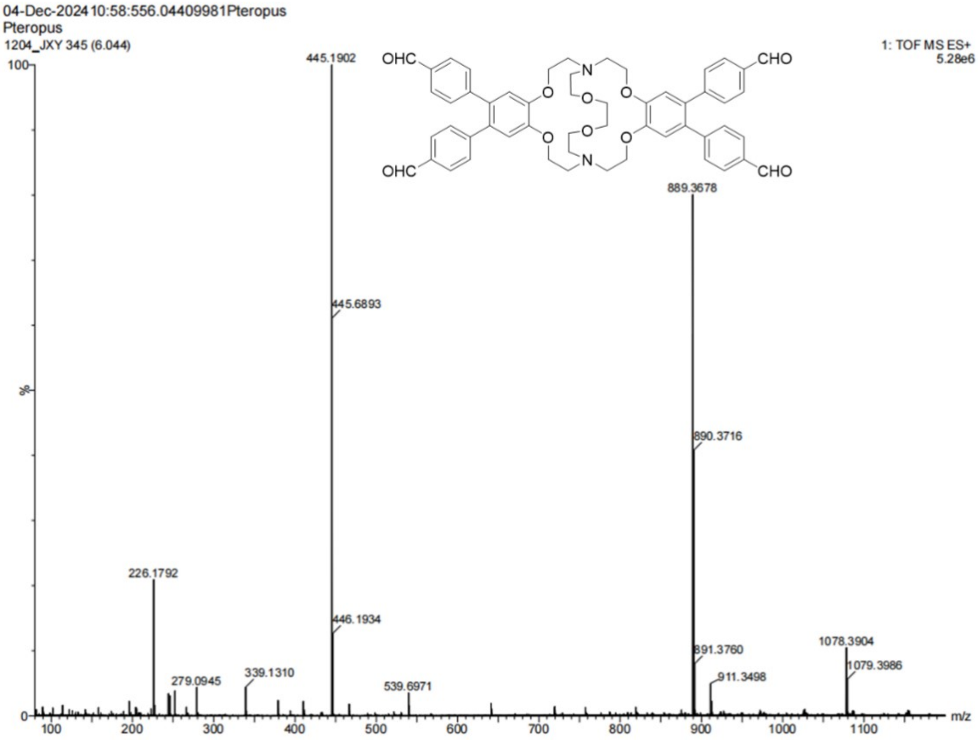


Figure S21 The mass spectrum of compound **8**.

Table S1 Changes in ion concentration in disposed CPU Leachate before and after adorption by Cryptand-COF (Diluted 100-fold).

	Before adsorption (mg L^{-1})	After adsorption(mg L^{-1})
Cu	72.343	72.267
Ni	4.206	4.105
Zn	0.241	0.239
Fe	1.697	1.658
Au	0.638	-0.001

Table S2 Energy calculation data for Cryptand-COF and other molecules.

	energy [a.u.]	binding energy [a.u.]	binding energy [eV]
Neutral COF fragment	-4686.3356445		
H_2O	-76.3577058		
H_3O^+	-76.7502821		
Protonated COF fragment	-4687.2398533	-0.5116325	-13.93
Protonated COF fragment---$2AuCl_4^-$	-8639.7653409	-0.0400664	-1.09