

Supplementary Information

Gram-scale green synthesis of a highly stable cationic covalent organic framework for efficient and selective removal of $\text{ReO}_4^-/^{99}\text{TcO}_4^-$

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1. Experimental methods

1.1. Characterization methods

Wide-angle powder X-ray diffraction (XRD) patterns were carried out on a PANalytical EMPYREAN powder diffractometer equipped with the PIXcel^{3D} detector (Malvern PANalytical, United Kingdom) in reflection geometry (Bragg–Brentano HD) using Cu K $\alpha_{1/2}$ radiation, operated at a voltage of 45 kV and a tube current of 40 mA, with a fixed divergence slit of 0.05 mm. The measurements were performed in the continuous mode with a step size 2θ of 0.013° and a data time per step of 300 s. Nitrogen physisorption isotherms were measured at –196 °C on an Anton Paar Quantatech Inc. iQ2 instrument (Boynton Beach, FL, USA). The sample was degassed under vacuum at 150 °C for 15 h before the measurement. The specific surface area (S_{BET}) was calculated by using Brunauer-Emmett-Teller (BET) method on the adsorption isotherm. The pore size distribution plot was obtained from the adsorption branch of isotherms by the quenched solid density functional theory (QSDFT) model (slit/cylindrical pores, N₂ at 77 K on carbon). The CO₂ sorption measurement was performed at 25 °C on a Micromeritics 3FLEX (USA) sorption analyser. The sample was degassed under vacuum at 120 °C for 12 h before the measurement. Scanning electron microscopy (SEM) analyses were performed on a Zeiss Supra 55 VP electron microscope equipped with an EDS detector. The accelerating voltages are 5 kV and 20 kV for images and EDS mappings, respectively. Fourier transform infrared (FT-IR) spectra were measured on a Bruker VERTEX 70v FT-IR Spectrometer equipped with Specac Golden Gate ATR accessory. Thermogravimetric analysis (TGA) was recorded on a Netzsch instrument (STA 449-F3 Jupiter) from 25 to 800 °C at a heating rate of 10 °C min⁻¹ in air atmosphere (20 mL min⁻¹). Solid-state magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) spectra were performed on a Bruker Avance NEO 500 wide bore system (Bruker BioSpin, Rheinstetten, Germany). A 4 mm triple resonance magic angle spinning (MAS) probe was used. Cross-polarization (CP) was employed using a ramped contact pulse, thereby sweeping the proton radio frequency field from 50 to 100%. The resonance frequency for ¹³C NMR was 125.78 MHz, the MAS rotor spinning was set to 14 kHz, and the CP contact time to 3 ms. The ReO₄⁻ concentrations in the solution were determined on an Agilent 7800 inductively coupled plasma mass spectrometer (ICP-MS).

1.2. Materials synthesis

1.2.1. Synthesis of Tp

108 mmol hexamethylenetetramine (15.1 g), 49 mmol phloroglucinol (6.0 g), and 90 mL trifluoroacetic acid were refluxed at 100 °C for 2.5 h under N₂. 150 mL HCl (3 M) was added slowly and the solution was heated at 100 °C for another 1 h. After cooling down, the solution was filtered through Celite and extracted with 350 mL of dichloromethane. After that, the solution was evaporated under reduced pressure to afford ~2.4 g of an off-white powder. Purification was carried out by sublimation.

1.2.2. Synthesis of the COF

PTSA (2.5g) and 856 mg DB were ground well, then 5 mL of water was added drop by drop. The mixture was ground thoroughly, then transferred into a bottle and 15 mL of water was added. The mixture was shaken well in a vortex shaker for 5 min. Then, 315 mg of Tp was added and the mixture was shaken for another 20 min. The red mixture was transferred into the autoclave with another 5 mL of water and kept in the oven at 125 °C for 24 h. Then, the red precipitate was filtered and sequentially washed with 3M HNO₃ and water. Finally, the collected solid was Soxhlet extracted with THF and dried at 100 °C to get TpDB-COF in ~96% yield.

2. Adsorption experiments

2.1. Batch experiments

All the experiments were conducted at room temperature (~25 °C) using the batch sorption method. The removal percentage (%) and the sorption capacity at equilibrium q_e (mg g⁻¹) were calculated by the following equations:

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100\%$$

$$q_e = \frac{C_0 - C_e}{m} \times V$$

in which C_0 (mg g⁻¹) and C_e (mg g⁻¹) are the initial and equilibrium concentrations of adsorbate, V (mL) is the volume of solution, and m (g) is the mass of sorbent.

2.2. Sorption kinetics

10 mg of TpDB-COF was added to 10 ml of aqueous solution containing 28 ppm of ReO_4^- . The mixture was shaken for 30 s, 1 min, 3 min, 5 min, and 10 min, respectively. The suspension was separated using a 0.22 μm nylon membrane filter. The concentrations of metals remaining in the filtered solution were then analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

2.3. Sorption isotherms

The ReO_4^- sorption isotherm experiments for TpDB-COF were conducted by varying the initial concentrations of ReO_4^- ranging from 28 to 2500 ppm with the solid/liquid ratio of 1 g L^{-1} . After being shaken for 14 h, the suspension was separated with a 0.22 μm nylon membrane filter and the concentrations of remaining ReO_4^- were determined by ICP-MS.

The adsorption isotherms were analyzed by applying the Langmuir isotherm model. The Langmuir isotherm model was expressed according to the following equation:

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

where q_m is the maximum adsorption capacity of adsorbent (mg g^{-1}) and K_L is the Langmuir constant (L mg^{-1}). By fitting each isotherm with this model, values of q_m and K_L were obtained.

2.4. pH effect study

The solution pH was tuned by adding negligible volumes of diluted HNO_3 or NaOH . The effect of pH for the ReO_4^- uptake was carried out by ranging pH values from 1 to 13. 10 mg of TpDB-COF was added to 10 ml of an aqueous solution containing 200 ppm of ReO_4^- . After being shaken for 14 h, the resulting mixture was separated with a 0.22 μm nylon membrane filter and the concentrations of remaining ReO_4^- were determined by ICP-MS.

2.5. Anion competition study

The effect of competing ions was studied and carried out at the solid/liquid ratio of 1 g L^{-1} , room temperature. The effect of H_2PO_4^- , SO_4^{2-} , ClO_4^- , CO_3^{2-} , NO_3^- , or Cl^- was studied by loading 0.5 mM

NaH₂PO₄, Na₂SO₄, NaClO₄, Na₂CO₃, NaNO₃, or NaCl solution into a 0.5 mM ReO₄⁻ solution, respectively. The influence of excessive NO₃⁻ was screened by adding different concentrations of NaNO₃ (0.15 mM, 0.75 mM, 1.5 mM, 3 mM, and 15 mM) into a 0.15 mM ReO₄⁻ solution. The influence of excessive SO₄²⁻ was investigated by adding different concentrations of Na₂SO₄ (0.08 mM, 0.8 mM, 8.0 mM, 80 mM, and 480 mM) into a 0.08 mM ReO₄⁻ solution. After being shaken for 14 h, the suspensions were separated with a 0.22 μm nylon membrane filter and the concentrations of the remaining ReO₄⁻ were determined by ICP-MS.

2.6. Batch experiments in 1M NaOH and 1M HNO₃ system

2 mg, 4 mg, 10 mg, 20 mg or 40 mg of TpDB-COF were added into 2 ml of 1M NaOH or 1M HNO₃ solution containing 200 ppm of ReO₄⁻, respectively. After shaking it for 14 h, the suspension was separated with a 0.22 μm nylon membrane filter and the concentrations of remaining ReO₄⁻ were determined by ICP-MS.

2.7. Recyclability study

The recyclability was measured in a neutral aqueous solution with an initial ReO₄⁻ concentration of 28 ppm and a 1 M HNO₃ aqueous solution containing 200 ppm ReO₄⁻, respectively. In the first cycle, 60 mg TpDB-COF was immersed into the ReO₄⁻ aqueous solution and shaken for 14 h. The concentrations of the remaining ReO₄⁻ were determined by ICP-MS. After that, the adsorbed material was eluted using 60 ml of 1 M NaBr solution at room temperature overnight, followed by washing with distilled water three times. The regenerated material was used for the next cycling test.

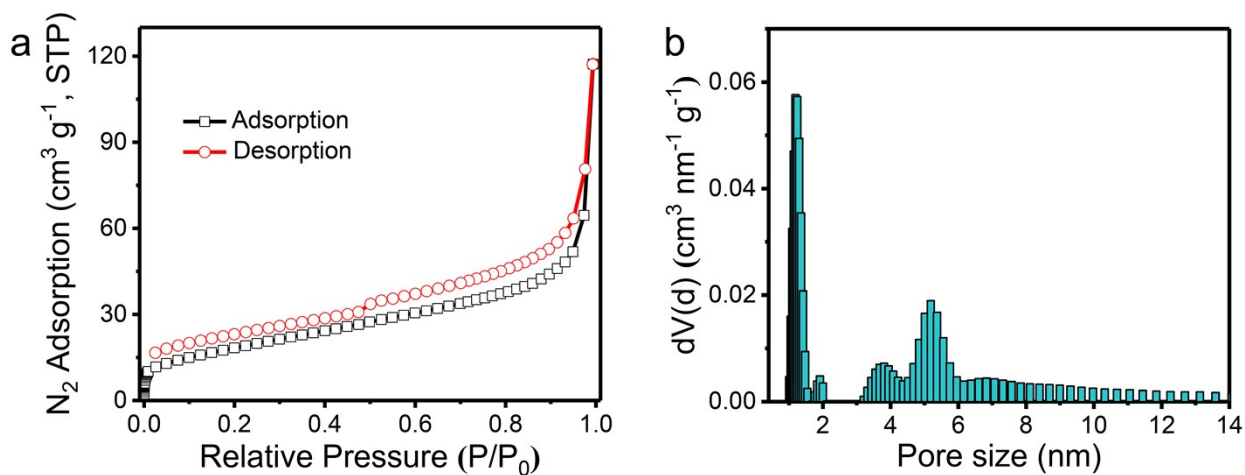


Figure S1. (a) N_2 adsorption-desorption isotherm ($-196\text{ }^\circ\text{C}$) and (b) QSDFT pore size distribution of TpDB-COF.

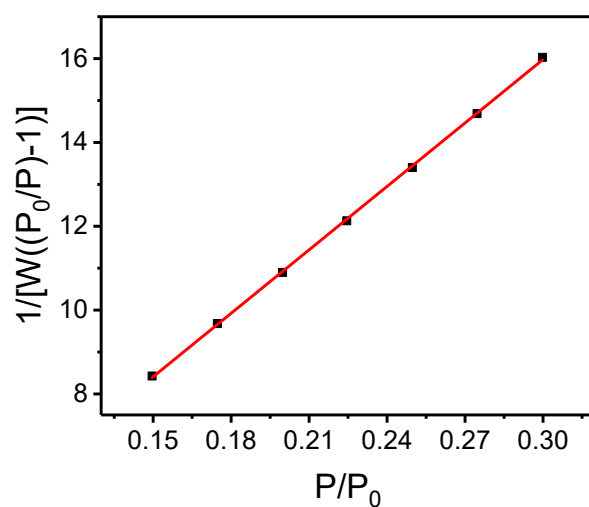


Figure S2. Linear range of the BET specific surface area plot calculated for the TpDB-COF N_2 physisorption isotherm.

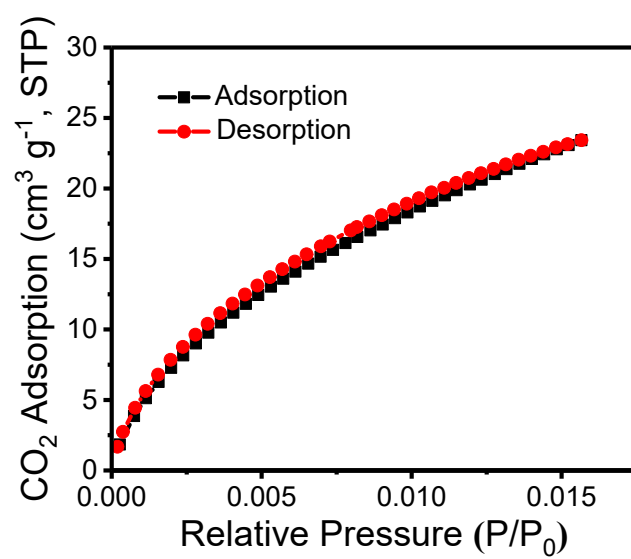


Figure S3. CO₂ adsorption-desorption isotherm of TpDB-COF measured at 25 °C.

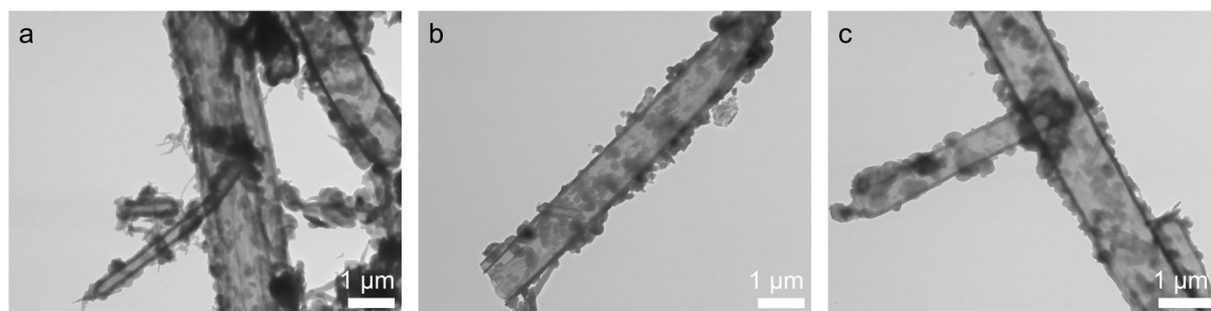


Figure S4. TEM images of (a) TpDB-COF, and TpDB-COF after treatment with (b) 3 M HNO₃ for 14 days and (c) 3 M NaOH for 4 days.

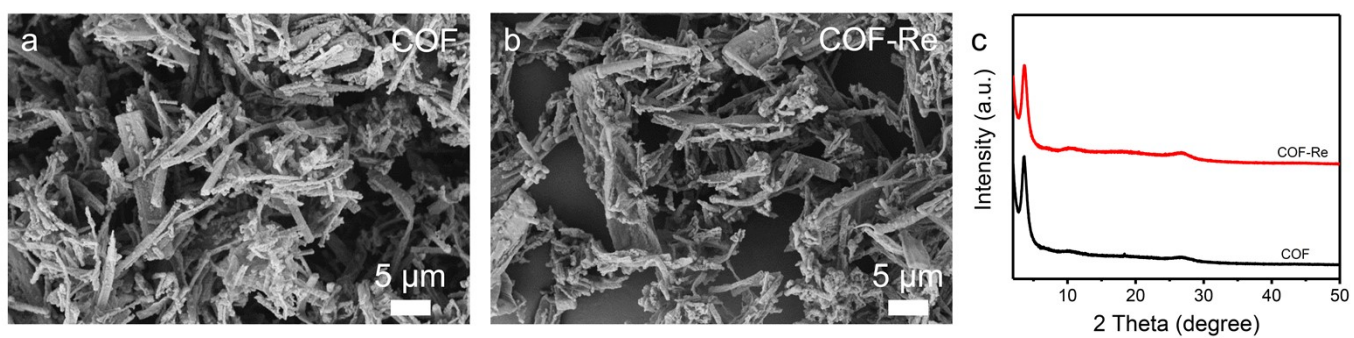


Figure S5. SEM images of (a) TpDB-COF, (b) TpDB-COF-Re, and (c) powder XRD patterns of COF and COF-Re.

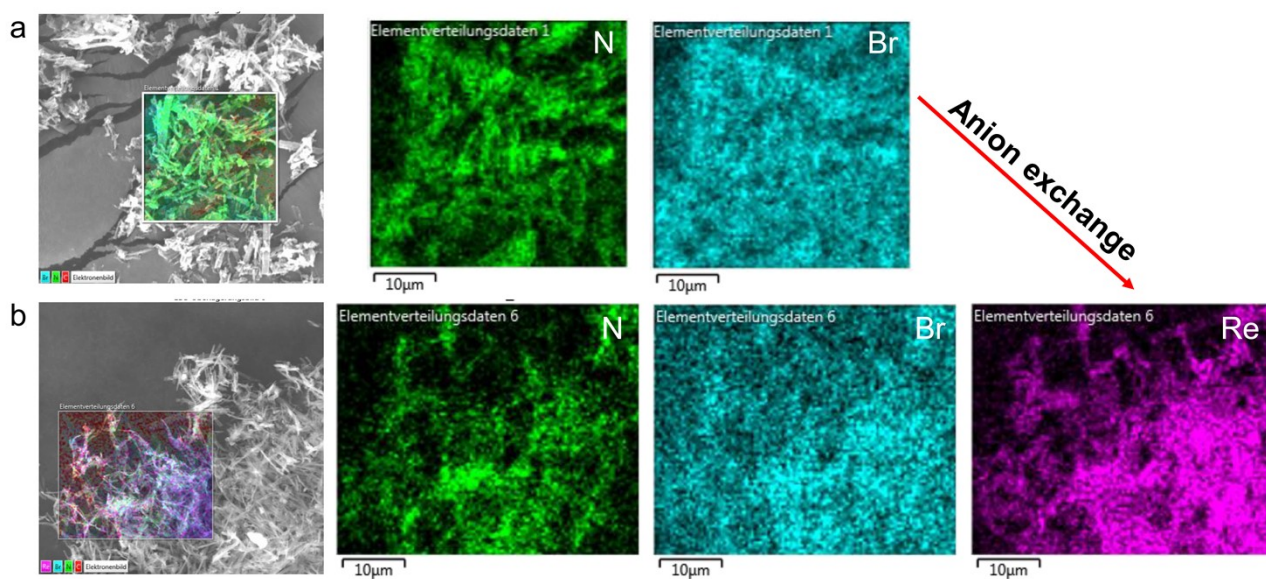


Figure S6. SEM and EDS mapping images of (a) TpDB-COF and (b) TpDB-COF-Re.

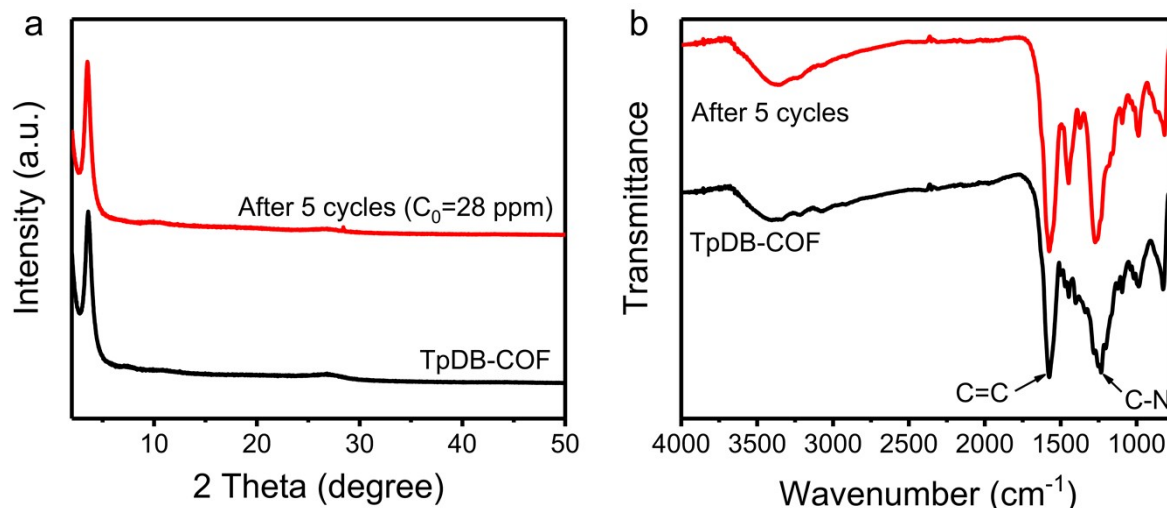


Figure S7. (a) Powder XRD patterns and (b) FT-IR spectra of fresh TpDB-COF and the sample after 5 cycles with initial concentration of $\text{ReO}_4^- \sim 28$ ppm (solid/liquid ratio of 1 mg mL^{-1}).

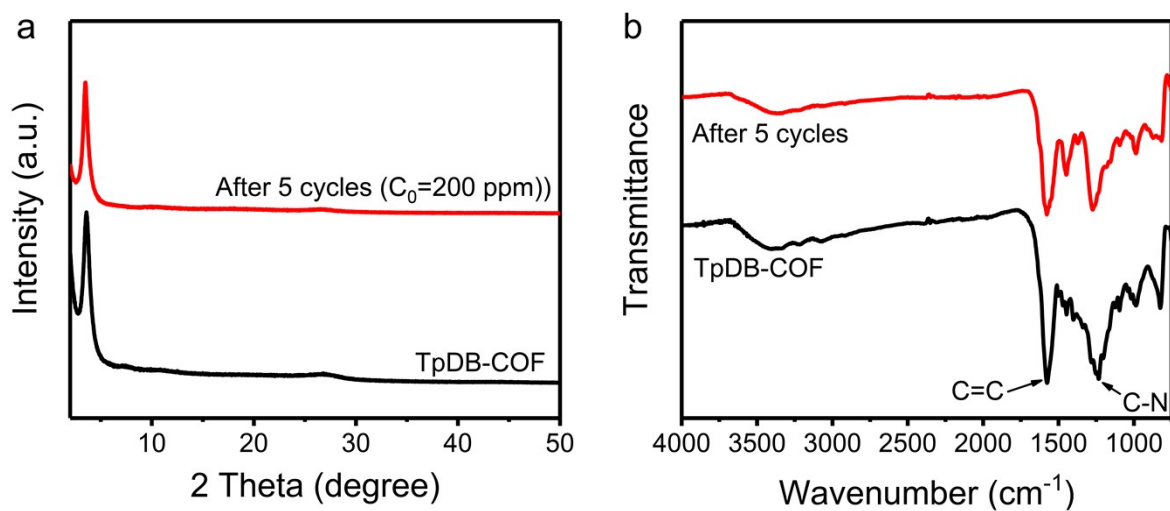


Figure S8. (a) Powder XRD patterns and (b) FT-IR spectra of fresh TpDB-COF and the sample after 5 cycles in 1 M HNO_3 with initial concentration of $\text{ReO}_4^- \sim 200$ ppm (solid/liquid ratio of 20 mg mL^{-1}).

Table S1. Comparison of reaction solvents, reaction time, product per batch, equilibrium time and adsorption capacities of TpDB-COF with other MOF/COF-based adsorbents.

Materials	Reaction solvents	Reaction time	Product per batch (g)	Adsorption equilibration time (min)	Adsorption capacity (mg g ⁻¹)	Refs
SCU-COF-1	1,2-dichlorobenzene	120 °C 6d	<0.025 ^a	1	367.6	1
DhaTGCI	THF/H ₂ O	120 °C 3d	0.072	5	437	2
[C2vimBr] _x %TbDa-COF	1,2-dichlorobenzene/ n-butylalcohol	120 °C 3d	0.099	30	952	3
MOF-SCU-101	DMF, Ethanol, H ₂ O	100 °C 3d	0.491	10	247	4
UiO-66-NH ₂	DMF	120 °C 1d	0.65	~720	159	5
Poly(ionic liquids)@MOF	DMF	200 °C 1d	-	0.5	362	6
MOF-SCU-103	DMF/H ₂ O	140 °C 3d	0.065	5	318	7
Olefin-COF	Mesitylene/1,4-dioxane/ acetonitrile	150 °C 3d	0.032	1	726	8
Vinylene-3D COF	Mesitylene/1,4-dioxane	150 °C 3d	0.025	0.5	542.3	9
PS-COF-1	mesitylene/ ethanol	80 °C 3d	<0.08 ^a	180	1262	10
PIL@MOF@COF	n-butyl alcohol/o-dichlorobenzene	120 °C 3d	<0.245 ^a	2	382	11
SCU-CPN-1	DMF	100 °C 4h (150 psi, 150W)	0.154	0.5	876	12
TpDB-COF	H ₂ O	125 °C 1d	1.12	1	570.4	This work

^a The yield was not given. The calculation is based on the amount of reaction precursors.

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