

Supporting Information

Enhancing the Stability of Poly(ionic liquids)@MOFs@COFs via Core-Shell Protection Strategy for $^{99}\text{TcO}_4^-$ Sequestration

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Material and methods

1.1 Materials and characterization methods

Commercially available reagents were used directly. ^1H NMR spectra were recorded on a Bruker AV 400 spectrometer, and the chemical shifts were reported in ppm with respect to reference standards. FT-IR spectra were taken on a Bruker ALPHA FT-IR spectrometer (KBr pellets) in $4000\text{--}400\text{ cm}^{-1}$. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer (Cu-K α , $\lambda = 1.5406\text{ \AA}$), operating at 40 kV and 100 mA, and the intensity data were obtained by the continuous scans in the $2\theta/\theta$ mode with scan speed of 2 s/step and step size of 0.02° . X-ray photoelectron spectroscopy (XPS) measurements were taken on a Thermo Scientific ESCALAB 250Xi spectrometer. The scanning transmission electron microscope (STEM) and energy-dispersive X-ray spectroscopy (EDS) were taken on a Thermo Fisher Scientific Talos F200X scanning electron microscope, with the electron beam energy of 200 keV. N_2 sorption isotherms at 77 K were obtained on Micromeritics

ASAP 2020 HD88. The ReO_4^- concentrations in solution were determined on a Perkin-Elmer NexION 350D inductively coupled plasma mass spectrometer (ICP-MS) after degradation of the sample in HNO_3 . Thermogravimetric analysis (TGA) plots were recorded on a Rigaku TG-DTA 8122 thermal analyzer in 30–800 °C at a heating rate of 20 °C/min under N_2 atmosphere.

1.2 Synthesis of $\text{NH}_2\text{-UiO-66}$

A mixture of ZrCl_4 (18.11 mg, 0.1 mmol), 2-aminoterephthalic acid ($\text{NH}_2\text{-BDC}$) (23.3 mg, 0.1 mmol), CH_3COOH (1.374 mL), and DMF (10 mL) was treated under sonification for 1 h, and heated at 120 °C for 24 h under hydrothermal conditions. The resulting solids were washed several times with DMF, $\text{C}_2\text{H}_5\text{OH}$, and CH_3OH and dried under vacuum at 120 °C for 24h.

1.3 Synthesis of $\text{bis-PC}_2@\text{NH}_2\text{-UiO-66}$

3,3'-Divinyl-1,1'-(1,2-ethanediyl)diimidazolium dibromide (*bis-C₂*) was prepared according to the literature method [28]. A mixture of $\text{NH}_2\text{-UiO-66}$ (400 mg) and *bis-C₂* (400 mg) was stirred in CH_3OH solution (20 mL) at room temperature under vacuum for 24 h. Then, 2,2'-azobis(isobutyronitrile) (AIBN, 50 mg) in CH_3OH (5 mL) was added and then heated to 65 °C under N_2 atmosphere for 24 h. After that, additional CH_3OH solution (5 mL) of AIBN (50 mg) was added, which was heated at 65 °C under N_2 atmosphere for 48 h. The resulting white solids were washed with CH_3OH for three times, and dried at 120 °C under vacuum for 12 h.

1.4 Synthesis of $\text{bis-PC}_2@\text{NH}_2\text{-UiO-66}@COF$

A mixture of *bis*-PC₂@NH₂-UiO-66 (40 mg), dimethoxyterephthaldehyde (DMTP) (93 mg), CH₃COOH (0.4 mL, 6 M) and *n*-butyl alcohol (2 mL) in a Pyrex tube (10 mL) was degassed through three freeze-pump-thaw cycles. And then, 1,3,5-tri-(4-aminophenyl)benzene (TAPB) (112 mg) and *o*-dichlorobenzene (2 mL) were added to the solution, which was degassed through three freeze-pump-thaw cycles. The tube was flame sealed and heated at 120 °C for three days. After cooling to room temperature, the precipitate was isolated by centrifugation and washed with THF for three times. Then the powder material was immersed in THF solution and dried at 120 °C under vacuum for 12 h to get the as-synthesized *bis*-PC₂@NH₂-UiO-66@COF. In addition, *bis*-PC₂@NH₂-UiO-66@COF was treated by saturated NaCl solution to yield *bis*-PC₂(Cl)@NH₂-UiO-66@COF.

1.5 Sorption experiments

In the batch sorption experiments, the removal percentage (%), the sorption capacity at equilibrium, q_e (mg g⁻¹), and the distribution coefficient, K_d (mL g⁻¹), were calculated by the following equations:

$$\text{Removal percentage (\%)} = \frac{c_0 - c_e}{c_0} \times 100\% \quad (\text{Eq. 1})$$

$$q_e = \frac{c_0 - c_e}{m} \times V \quad (\text{Eq. 2})$$

$$k_d = \frac{c_0 - c_e}{c_e} \times \frac{V}{m} \quad (\text{Eq. 3})$$

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.

ReO₄⁻ sorption data fitting by kinetics models. In the sorption experiment, *bis-PC₂@NH₂-UiO-66@COF* (20 mg) was added to a water solution of ReO₄⁻ (5 mL, 25 ppm). The samples were collected after stirring for 30 s, 45 s, 1 min, 2 min, 5 min, 10 min, 15 min, 20 min, 30 min, 45 min, and 1 h. The concentrations of ReO₄⁻ remaining in the water phase were determined by ICP-MS. The equation of linearized form of pseudo-second-order model is

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (\text{Eq. 4})$$

where the measured q_t is the uptake amount of ReO₄⁻ at t min (mg g⁻¹), q_e is the uptake amount of ReO₄⁻ at equilibrium (mg g⁻¹), and k_2 is the pseudo-second-order rate constant (g mg⁻¹ min⁻¹). The fitting model parameter and correlation coefficient are listed in [Table S1](#).

ReO₄⁻ sorption data fitting by isotherm models. In the sorption experiment, *bis-PC₂@NH₂-UiO-66@COF* or *bis-PC₂(Cl)@NH₂-UiO-66@COF* (5 mg) was added to a water solution (5 mL) of ReO₄⁻ at a given concentration (20–3000 ppm), which was stirred for 12 h to ensure the equilibrium ([Table S2](#)). The concentration of ReO₄⁻ remaining in the water phase was determined by ICP-MS.

The Langmuir and Freundlich sorption models were used to study the removal thermodynamics of ReO₄⁻ by *bis-PC₂@NH₂-UiO-66@COF* and *bis-PC₂(Cl)@NH₂-UiO-66@COF* ([Table S3](#)). In the Langmuir model, the sorption of ReO₄⁻ was assumed on a homogenous surface of sorbent to follow a monolayer sorption process. The equation of the Langmuir model is

$$\frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m} \quad (\text{Eq. 5})$$

in which c_e is the equilibrium concentration of Re in ReO_4^- (mg g^{-1}), q_e and q_m are the equilibrium and maximum Re sorption amounts (mg g^{-1}), and k_L is the constant indirectly related to the sorption amount and sorption energy (L mg^{-1}), characterizing the affinity of ReO_4^- anion with sorbent. The fitting line was obtained by plotting c_e/q_e against c_e , and q_m and k_L can be calculated from the slope and intercept.

Regarding the Freundlich sorption model, it is based on a heterogeneous surface, suggesting different binding energies between ReO_4^- and the surface sites of sorbent. The equation of the Freundlich model is

$$\ln q_e = \ln k_F + \frac{1}{n} \ln c_e \quad (\text{Eq. 6})$$

in which c_e and q_e are the equilibrium concentration of Re in ReO_4^- (mg g^{-1}) and equilibrium Re sorption amount (mg g^{-1}), and k_F and n are the Freundlich constants related to the sorption amount and sorption intensity, characterizing the affinity of ReO_4^- with sorbent.

Stability. Stability was studied by immersing *bis*-PC₂@NH₂-UiO-66@COF into NaOH solution (1 or 2 M), HNO₃ solution (1 or 3 M), as well as different pH values (1–13) for two days at room temperature. The solid was separated for PXRD test and Brunauer-Emmett-Teller (BET) surface area analysis.

Effect of pH. The effect of pH on ReO_4^- sorption was performed in the solutions of pH = 0–14. *bis*-PC₂@NH₂-UiO-66@COF (20 mg) was added into a water solution

of ReO_4^- (1 mL, 50 ppm). The sample was stirred for 2 h to ensure the equilibrium. The concentrations of ReO_4^- remaining in the water phase were determined by ICP-MS.

Anion Competition. The as-synthesized $\text{bis-PC}_2@\text{NH}_2\text{-UiO-66@COF}$ (10 mg) was immersed in an aqueous solution (1 mL) containing KReO_4 (0.5 mmol) and Na_nX (0.5 mmol, $n = 1$ or 2 , $\text{X} = \text{NO}_3^-$, NO_2^- , ClO_4^- , CO_3^{2-} or SO_4^{2-}) at room temperature for 12 h. The concentration of ReO_4^- remaining in the water phase was determined by ICP-MS. To test the anion competition of ReO_4^- to NO_3^- or SO_4^{2-} , the as-synthesized $\text{bis-PC}_2@\text{NH}_2\text{-UiO-66@COF}$ (10 mg) was immersed in an aqueous solution (1 mL) containing KReO_4 (0.1 mmol) and NaNO_3 or Na_2SO_4 (0.1, 0.5, 1, 2, and 10 mmol) at room temperature for 12 h. The concentration of ReO_4^- remaining in the water phase was determined by ICP-MS.

Sorption in low active waste stream. The simulated Hanford low active waste (LAW) stream was prepared (Table S4), in which TcO_4^- was replaced with ReO_4^- . $\text{bis-PC}_2@\text{NH}_2\text{-UiO-66@COF}$ (100 mg) was added to the simulated waste (1 mL), which was stirred for 6 h. The concentration of ReO_4^- remaining in the water phase was determined by ICP-MS.

Sorption in alkaline high-level waste stream. The simulated Savannah River Site (SRS) high level waste (HLW) stream was prepared (Table S5), in which TcO_4^- was replaced with ReO_4^- . In a batch experiment, $\text{bis-PC}_2@\text{NH}_2\text{-UiO-66@COF}$ (100 or 200 mg) was added to the simulated waste (2 mL), which was stirred for 6 h. The concentration of ReO_4^- remaining in the water phase was determined by ICP-MS.

Recyclability. In the first cycle, *bis*-PC₂@NH₂-UiO-66@COF (60 mg) was immersed in an aqueous solution of ReO₄⁻ (15 mL, 50 ppm) for 4 h and the concentration of ReO₄⁻ remaining in the water phase was determined by ICP-MS. After that, the ReO₄⁻ adsorbed material was eluted with 1 mol/L NaCl solution overnight (with several solvent changes) and the solid was collected by centrifugation. Such recovered material was then subject to the next cycling test.

Synthesis of *bis*-C₂: The synthesis of *bis*-C₂ using the same methods as our previous reported. A mixture of 1-vinylimidazole (18.8 g, 0.2 mol), 1,2-dibromoethane (18.7 g, 0.1 mol), and acetonitrile (150 mL) was heated at 60 °C under N₂ atmosphere for 48 h. After naturally cooling to room temperature, the obtained white solid was washed by ethyl ether for several times and dried overnight under vacuum. Yield: 27.75 g (74%). ¹H NMR (400 MHz, DMSO-*d*⁶): δ (ppm) 9.58 (s, 1H), 8.22 (s, 1H), 7.97 (s, 1H), 7.31 (dd, *J* = 16.0, 8.0 Hz, 1H), 5.98 (dd, *J* = 16.0, 4.0 Hz, 1H), 5.42 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.24 (dd, *J* = 12.0, 4.0 Hz, 2H).

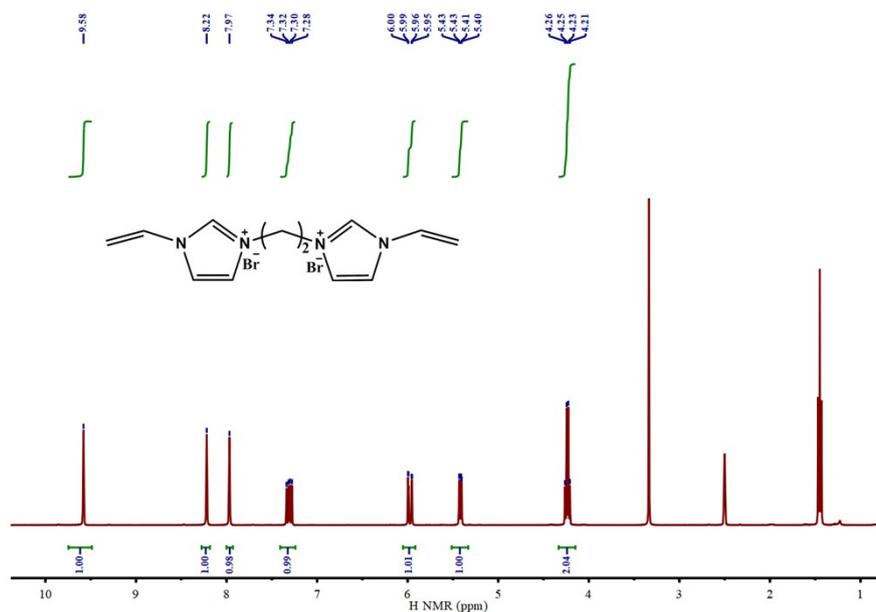


Figure S1. ¹H NMR spectra of *bis*-C₂.

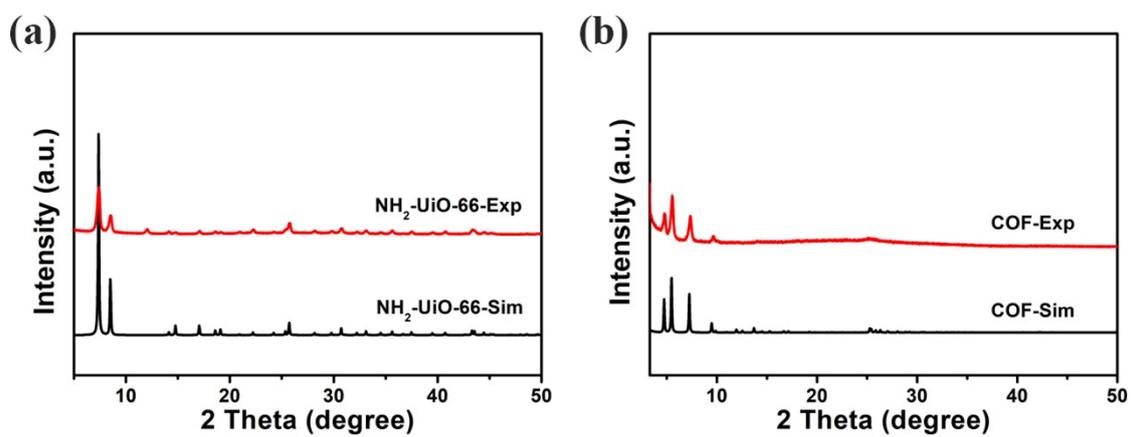


Figure S2. The comparison of experimental PXRD pattern of NH₂-UiO-66 (a) and COF (b) with simulated PXRD patterns.

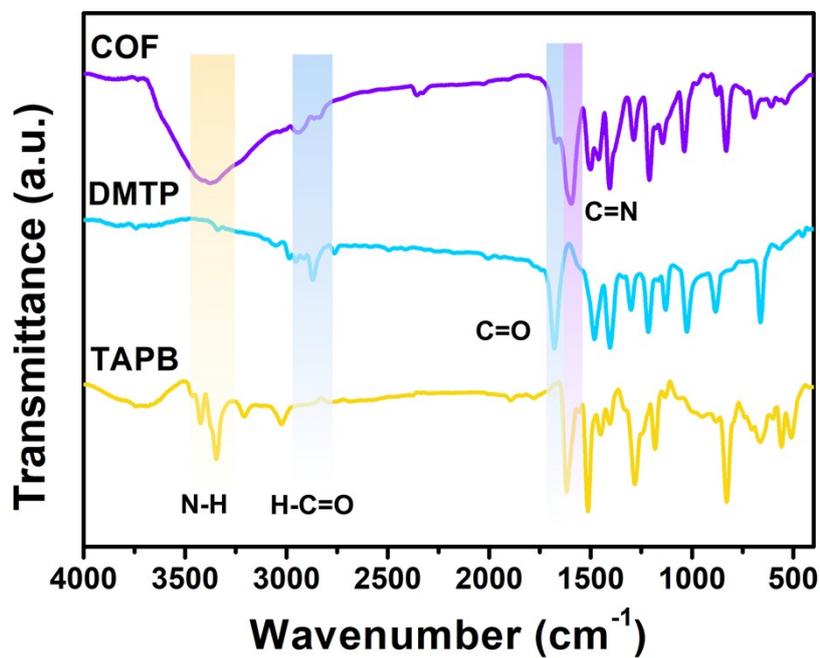


Figure S3. FT-IR spectra of TAPB (yellow), DMTP (blue) and COF (purple).

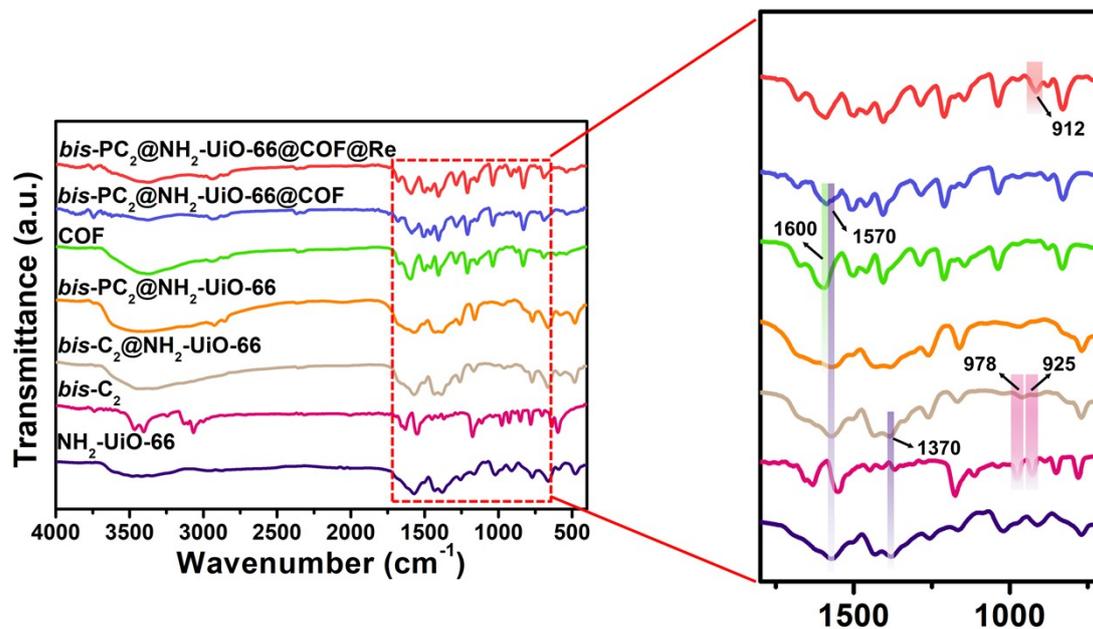


Figure S4. FT-IR spectra of *NH₂-UiO-66*, *bis-C₂*, *bis-C₂@NH₂-UiO-66*, *bis-PC₂@NH₂-UiO-66*, COF, *bis-PC₂@NH₂-UiO-66@COF* and *bis-PC₂@NH₂-UiO-66@COF@Re*.

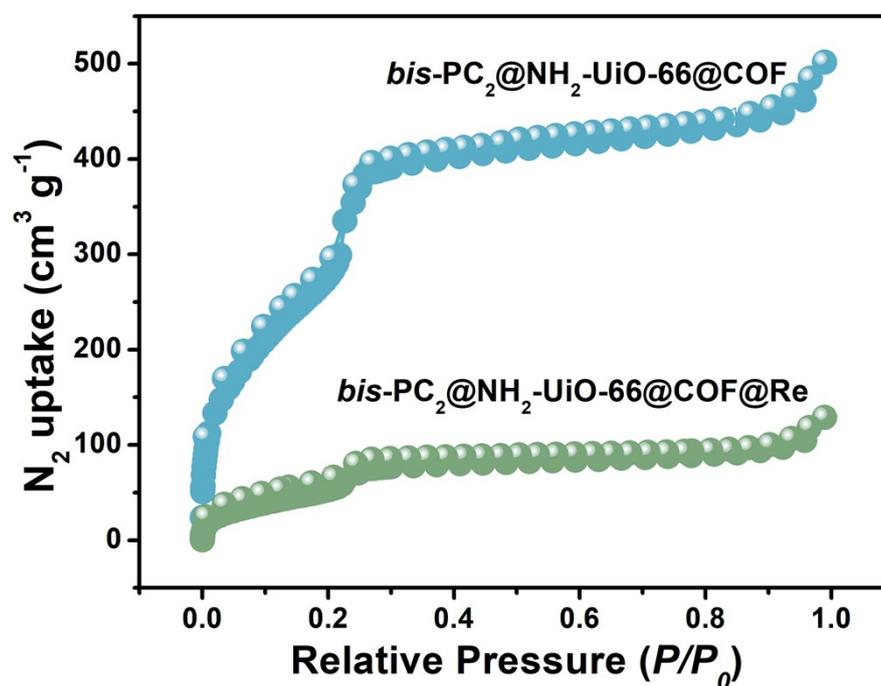


Figure S5. The N₂ sorption isotherms of *bis-PC₂@NH₂-UiO-66@COF* and *bis-PC₂@NH₂-UiO-66@COF@Re*.

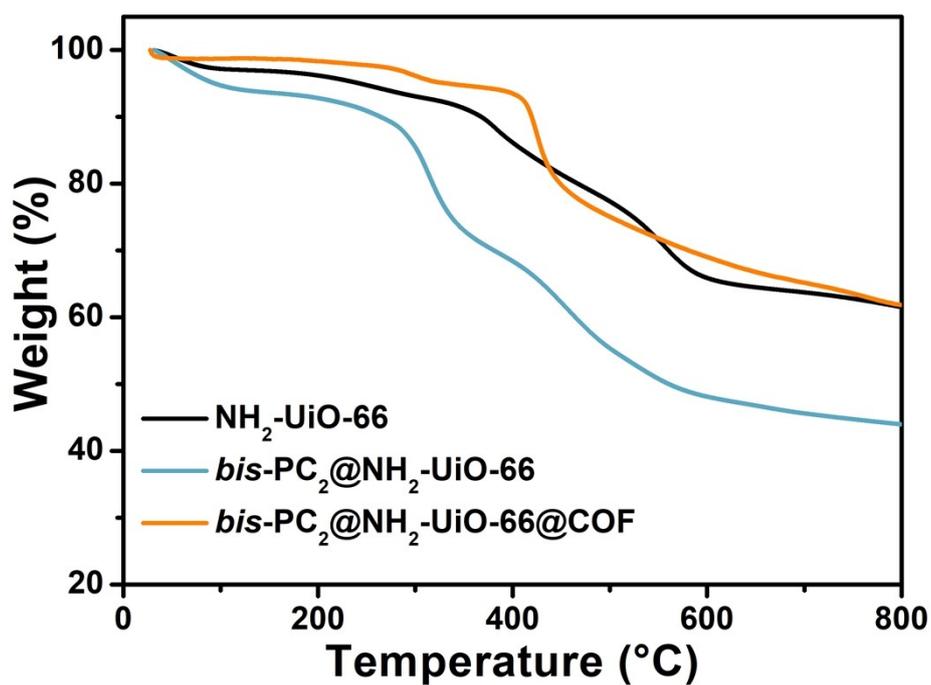


Figure S6. TGA plots of NH₂-UiO-66, bis-PC₂@NH₂-UiO-66 and bis-PC₂@NH₂-UiO-66@COF.

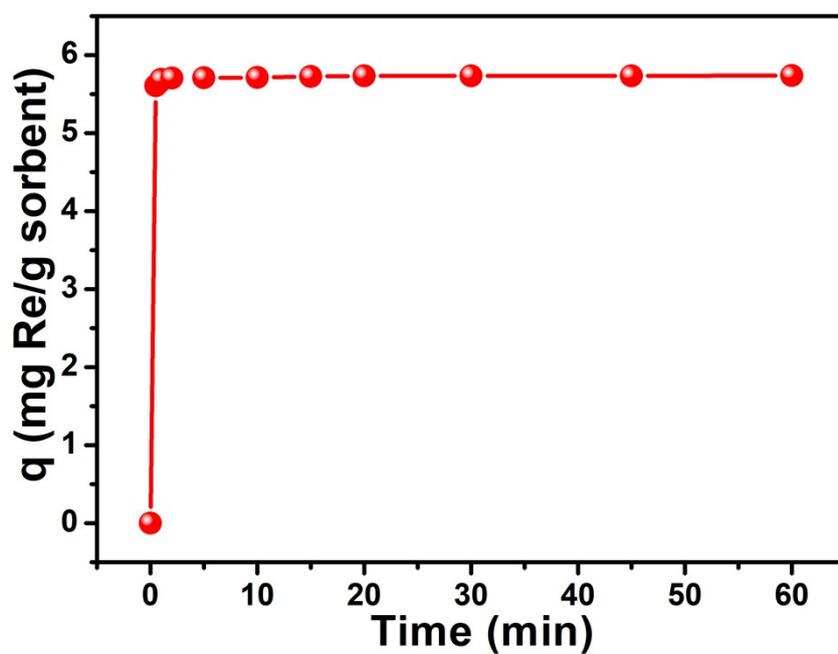
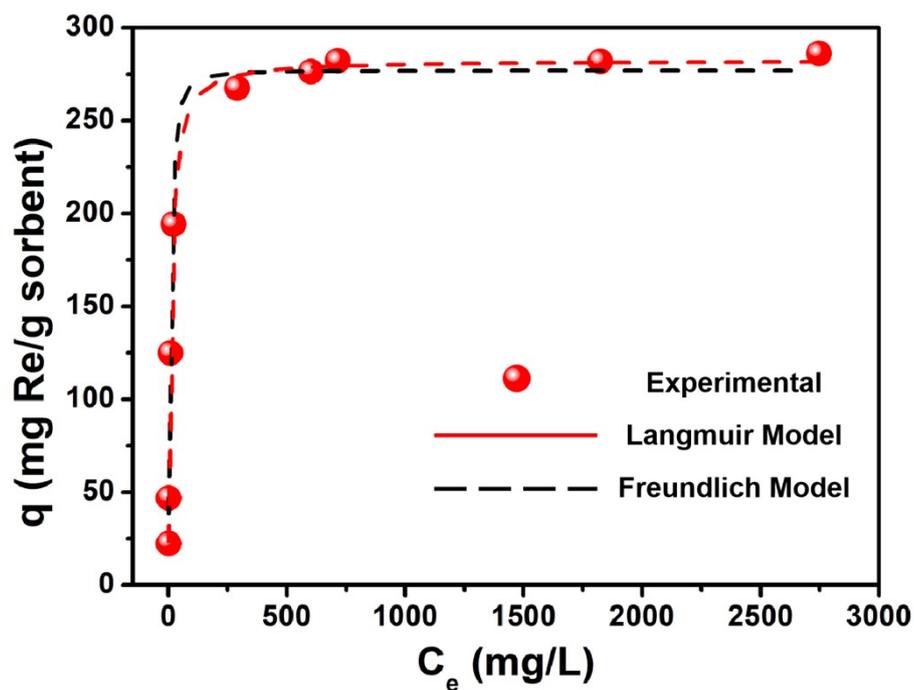
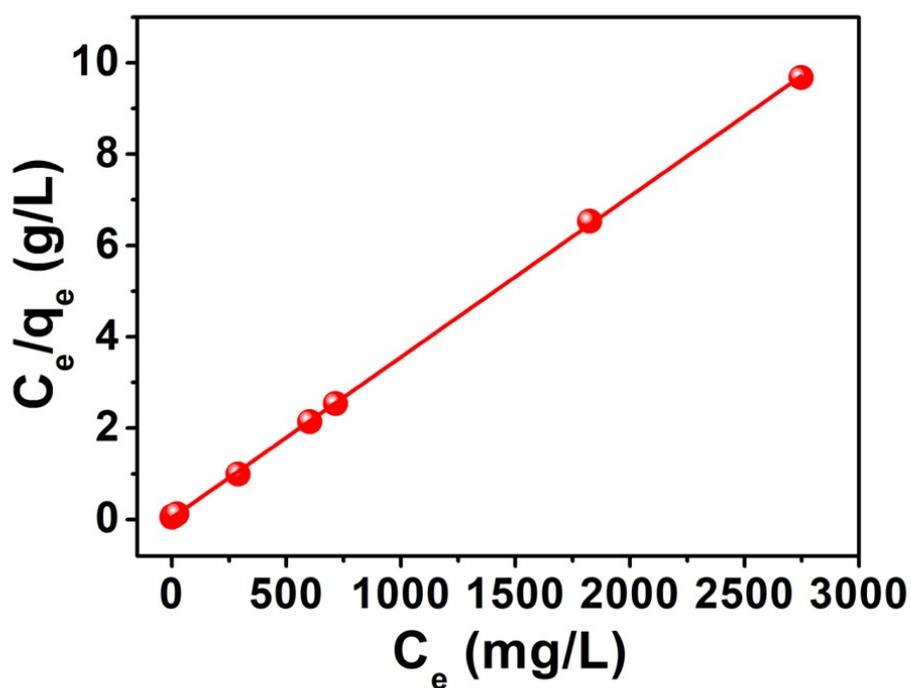


Figure S7 Sorption kinetics of ReO₄⁻ by bis-PC₂@NH₂-UiO-66@COF, with the function of q vs contact time.



(a)



(b)

Figure S8 (a) Sorption isotherm of *bis*-PC₂@NH₂-UiO-66@COF for Re. (b) Linear regression by fitting the equilibrium data using the Langmuir sorption model.

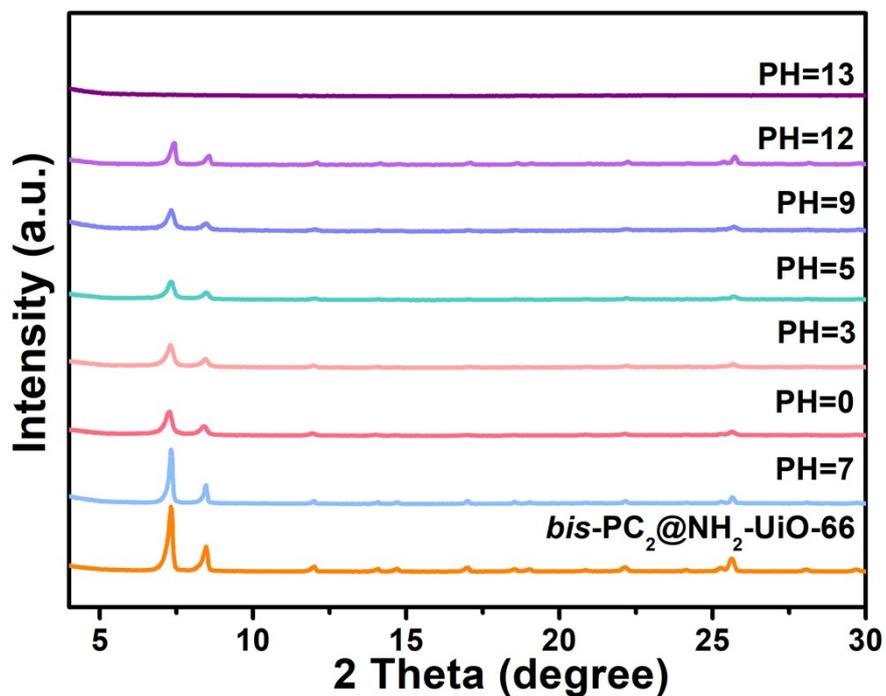


Figure S9. The PXR D patterns of *bis-PC₂@NH₂-UiO-66* under different pH conditions.

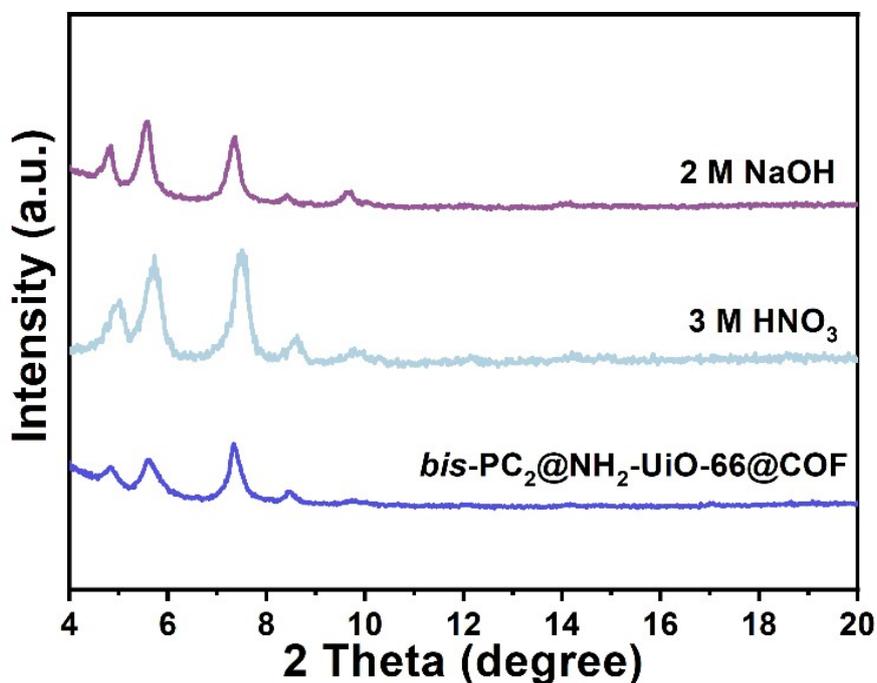


Figure S10. The PXR D patterns of *bis-PC₂@NH₂-UiO-66@COF* as well as in 2 M NaOH and 3 M HNO₃ solutions.

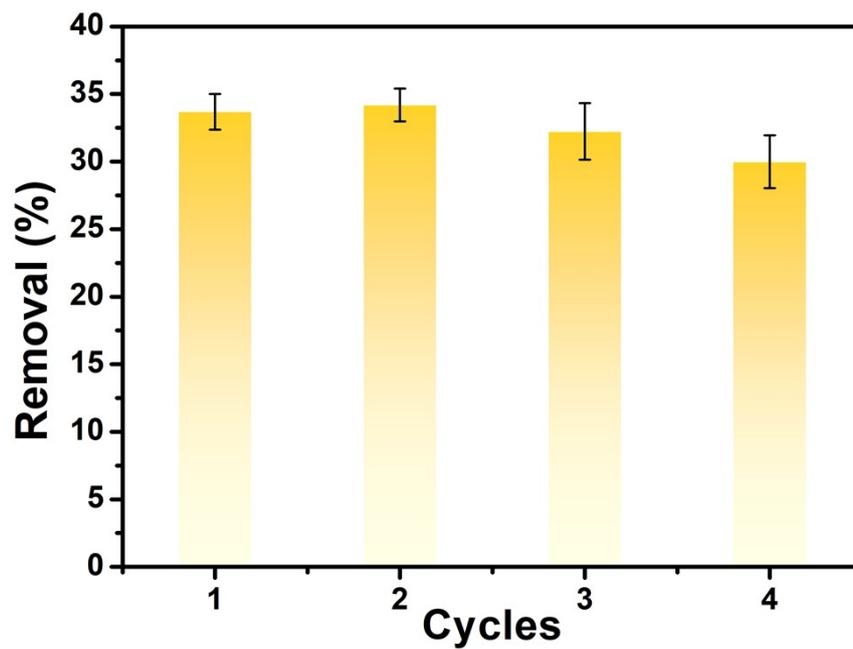


Figure S11. The reversibility of *bis-PC₂@NH₂-UiO-66@COF* under the condition of 2 M NaOH.

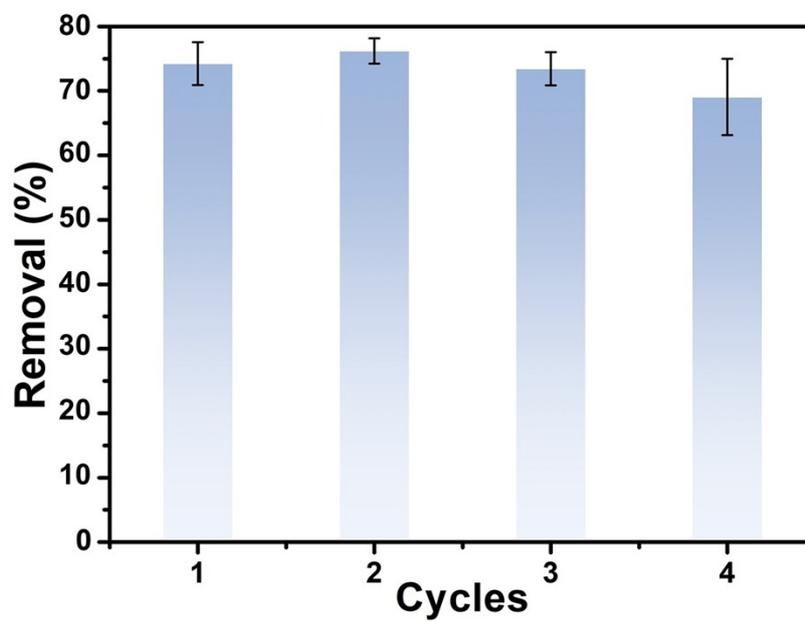


Figure S12. The reversibility of *bis-PC₂@NH₂-UiO-66@COF* under the condition of 3 M HNO₃.

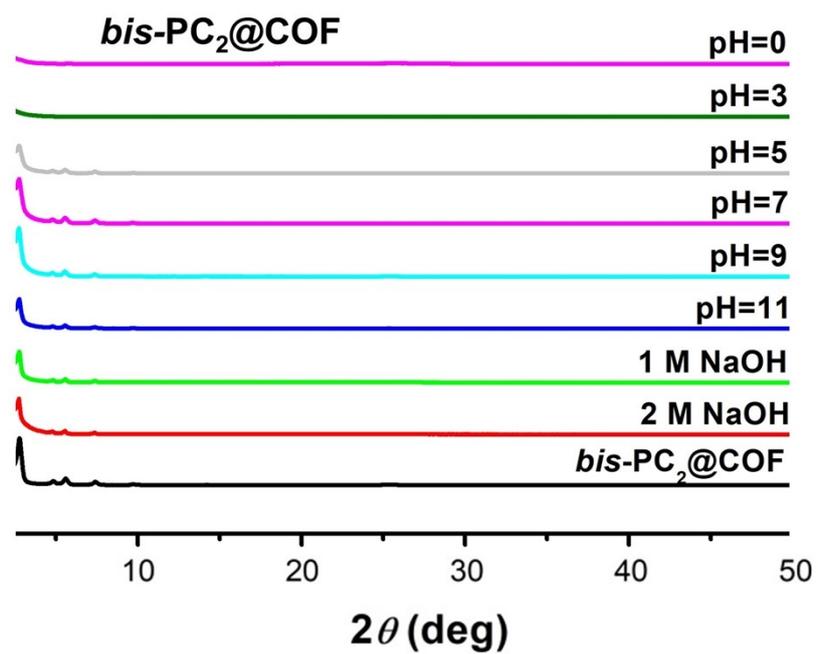
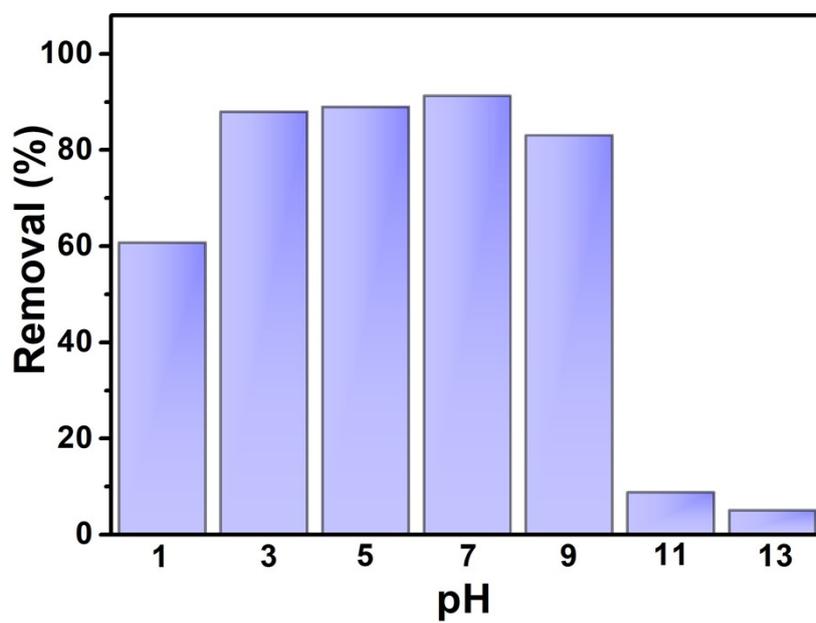
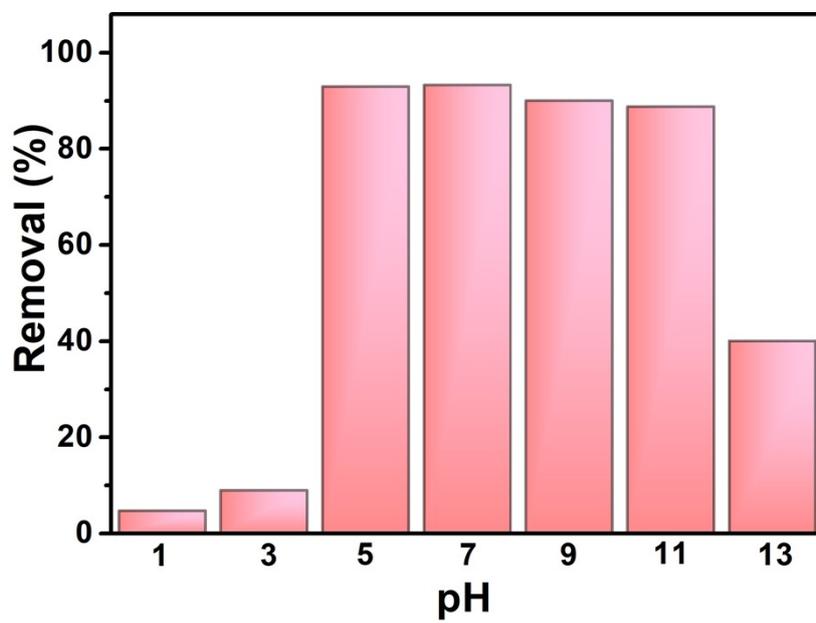


Figure S13. PXRD patterns of *bis-PC₂@COF* under different pH for 2 h.



(a)



(b)

Figure S14. Effect of pH on ReO_4^- uptake by $\text{bis-PC}_2@NH_2\text{-UiO-66}$ and $\text{bis-PC}_2@COF$.

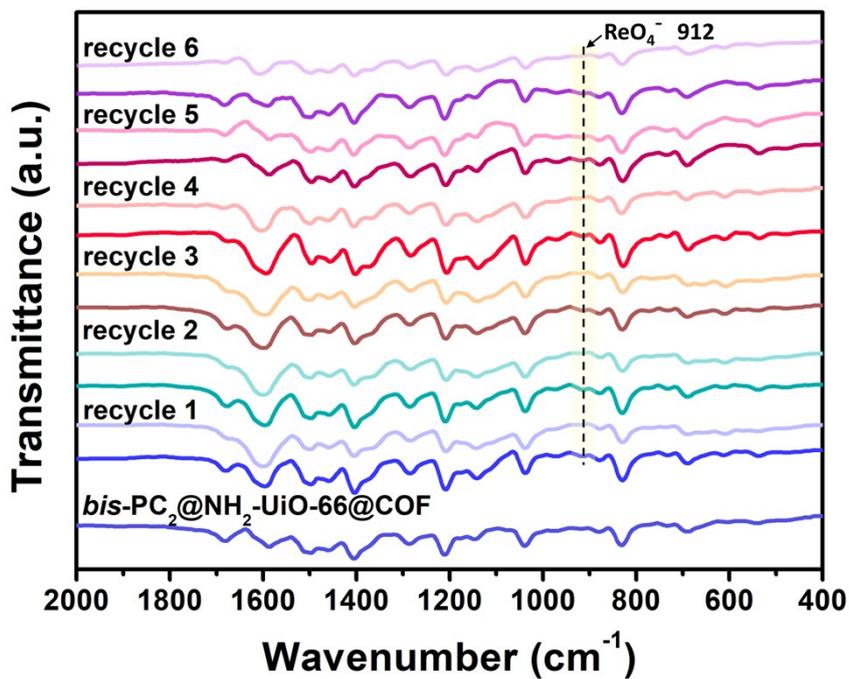


Figure S15. FT-IR spectra of *bis-PC*₂@NH₂-UiO-66@COF after six cycles of ReO₄⁻ sorption.

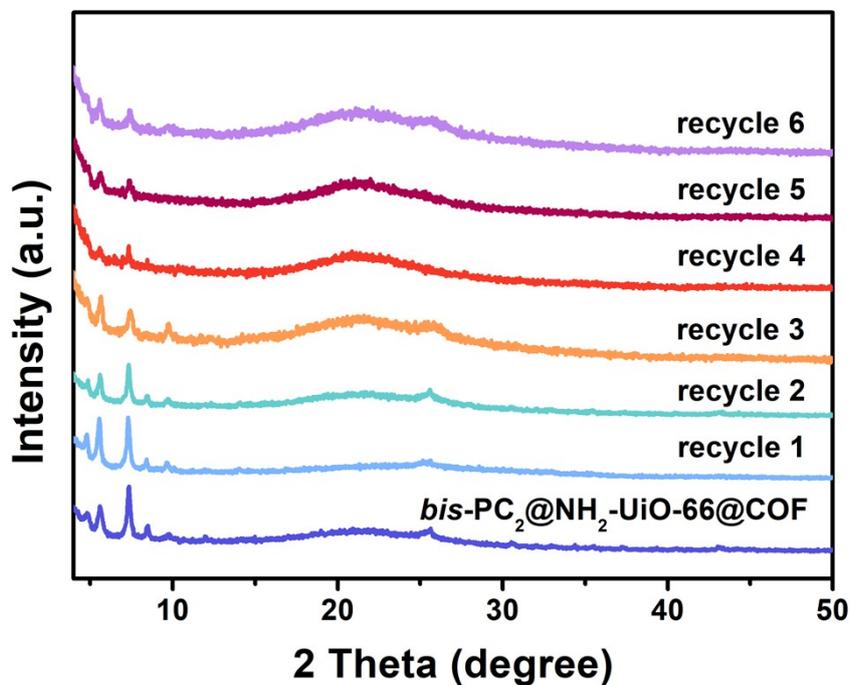


Figure S16. PXRD patterns of *bis-PC*₂@NH₂-UiO-66@COF after six cycles of ReO₄⁻ sorption.

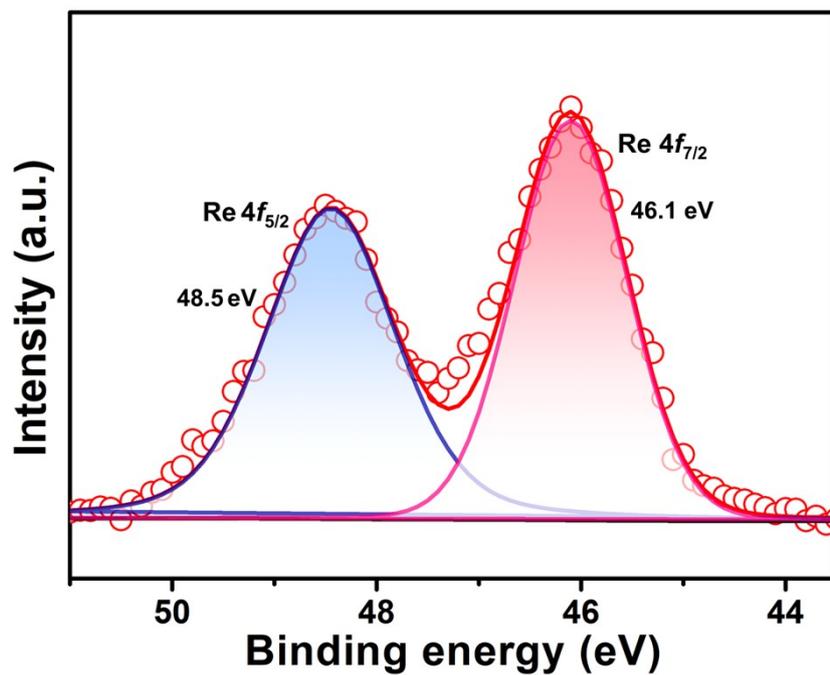


Figure S17. Re 4f XPS spectra of *bis-PC*₂@NH₂-UiO-66@COF@Re.

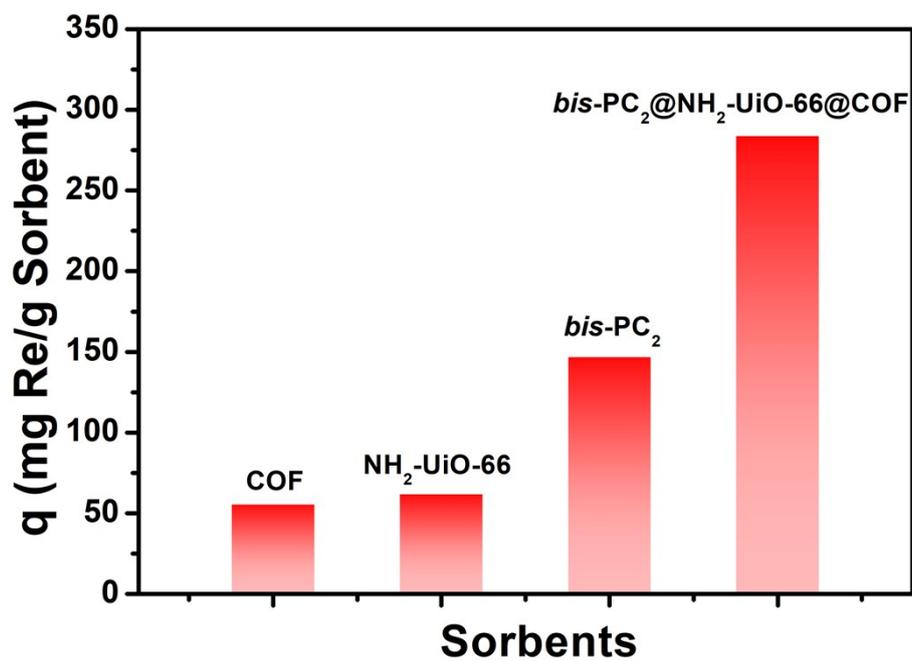


Figure S18. The comparison of ReO₄⁻ sorption amounts between the single component (NH₂-UiO-66, COF, *bis-PC*₂) and *bis-PC*₂@NH₂-UiO-66@COF.

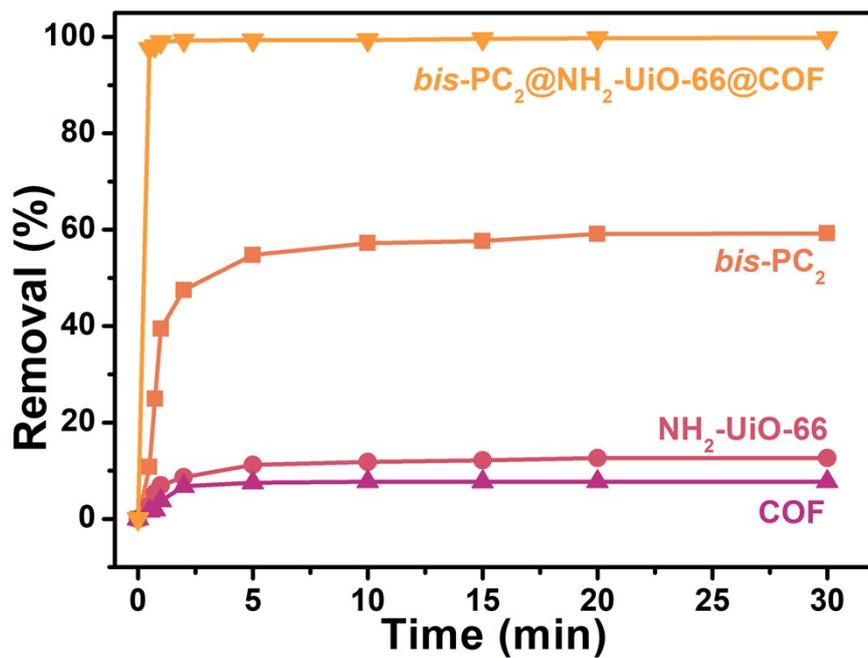


Figure S19. The comparison of ReO_4^- sorption kinetics between the single component ($\text{NH}_2\text{-UiO-66}$, COF, *bis-PC₂*) and *bis-PC₂@NH₂-UiO-66@COF*.

Table S1. Model parameters and correlation coefficient for ReO_4^- sorption kinetics by *bis-PC*₂@NH₂-UiO-66@COF.

Samples	Kinetics			K_d (mL/g)
	k_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2	
<i>bis-PC</i> ₂ @NH ₂ -UiO-66@COF	10.85	5.73	0.9999	1.12×10^5
<i>bis-PC</i> ₂ @COF	3.66	23.27	0.999	1.72×10^4
<i>bis-PC</i> ₂ @NH ₂ -UiO-66	16.76	5.56	0.995	4.03×10^4

Table S2. Removal performances of *bis*-PC₂@NH₂-UiO-66@COF from the ReO₄⁻ solutions at different concentrations (50 to 3000 ppm).

Concentration (ppm)	C ₀ (ppm)	C _e (ppm)	q _e (mg g ⁻¹)
20	23.35	1.15	22.2
50	50.2	3.4	46.8
100	133.7	8.81	124.9
200	218.2	24	194.2
500	533.6	266.1	267.5
800	868.6	592.3	276.3
1000	997.9	715.6	282.3
2000	1824	1542	282
3000	3053	2767	286

Table S3. Fitting results of ReO_4^- sorption by *bis-PC₂@NH₂-UiO-66@COF* based on the Langmuir and Freundlich models.

Samples	Langmuir			Freundlich		
	q_m (mg g ⁻¹)	k_L (L mg ⁻¹)	R^2	k_F (L ⁿ /mol ⁿ⁻¹ g)	n	R^2
<i>bis-PC₂@NH₂-UiO-66@COF</i>	284.09	0.099	>0.9999	277.02	0.055	0.96
<i>bis-PC₂(Cl)@NH₂-UiO-66@COF</i>	357.14	0.029	0.9889	96.65	5.54	0.93

Table S4. Composition of Hanford Low Activity Waste (LAW) Melter Recycle Stream.

Anion	Concentration (mol L ⁻¹)	Anion: TcO ₄ ⁻ (mole ratio)
TcO ₄ ⁻ /ReO ₄ ⁻	1.94×10 ⁻⁴	1.0
NO ₃ ⁻	6.07×10 ⁻²	314
Cl ⁻	6.39×10 ⁻²	330
NO ₂ ⁻	1.69×10 ⁻¹	873
SO ₄ ²⁻	6.64×10 ⁻⁶	0.343
CO ₃ ²⁻	4.30×10 ⁻⁵	0.222

Table S5. Composition of Savannah River Site (SRS) High-Level Waste (HLW)

Stream.		
Anion	Concentration (mol L ⁻¹)	Anion: TcO ₄ ⁻ (mole ratio)
TcO ₄ ⁻ /ReO ₄ ⁻	7.92×10 ⁻⁵	1.0
NO ₃ ⁻	2.6	32819
OH ⁻	1.33	16788
NO ₂ ⁻	1.34×10 ⁻¹	1691
SO ₄ ²⁻	5.21×10 ⁻¹	6576
CO ₃ ²⁻	2.6×10 ⁻²	328