Supplementary Information

Mechanism Unravelling for Ultrafast and Selective $^{99}TcO_4^-$ Uptake by a Radiation-Resistant Cationic Covalent Organic Framework: A Combined Radiological Experiment and Molecular Dynamics Simulation Study

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Sorption data fitting by isotherm models

The Langmuir model supposes that the sorption of metal ions presents on a homogenous surface by monolayer sorption. There is no interaction between adsorbed ions. The binding sites are homogeneous and the metal ions have equivalent sorption energies. The linear equation of the Langmuir isotherm model is described and expressed as followed[24]:

$$\frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m}$$

where q_m is the maximum sorption capacity of the sorbents corresponding to complete monolayer coverage (mg/g) and k_L is a constant indirectly related to sorption capacity and energy of sorption (L/mg), which characterizes the affinity of the adsorbate with the adsorbent. The linearized plot was obtained when we plotted Ce/qe against Ce and qm and k_L could be calculated from the slope and intercept.

The Freundlich equation is an empirical equation based on sorption on a heterogeneous surface. The isotherm assumes that adsorbent surface sites have a spectrum of different binding energies. The linear equation can be described and expressed by:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln c_e$$

where k_F and n are the Freundlich constants related to the sorption capacity and the sorption intensity, respectively.

The distribution coefficient K_d was calculated using the equation of $K_d = [(c_0 - c_e)V/c_e]/m$, where c_0 and c_e are the initial and equilibrium concentration of ReO_4^- (mg/L), V is the volume of the solution (L), m is the mass of SCU-COF-1 sample (mg).

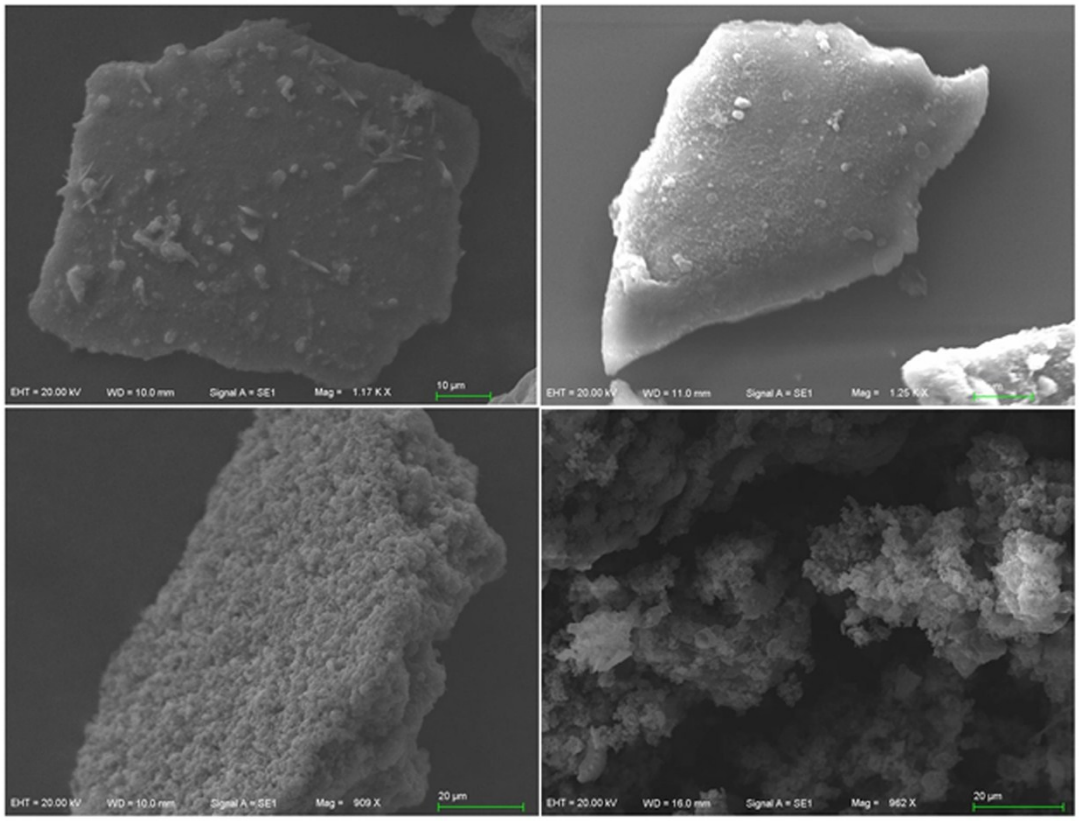


Figure S1. SEM images of SCU-COF-1.

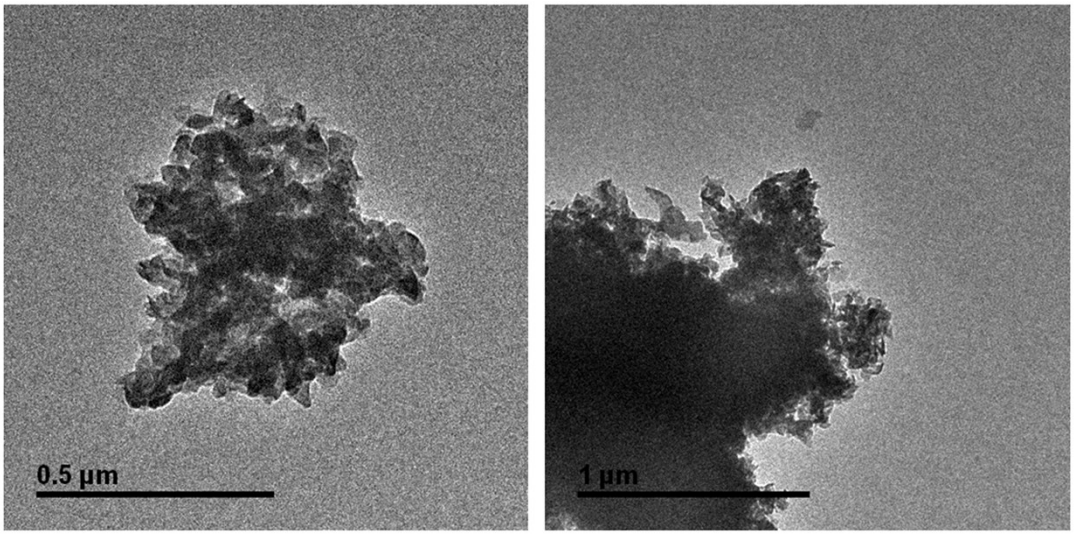


Figure S2. TEM images of SCU-COF-1.

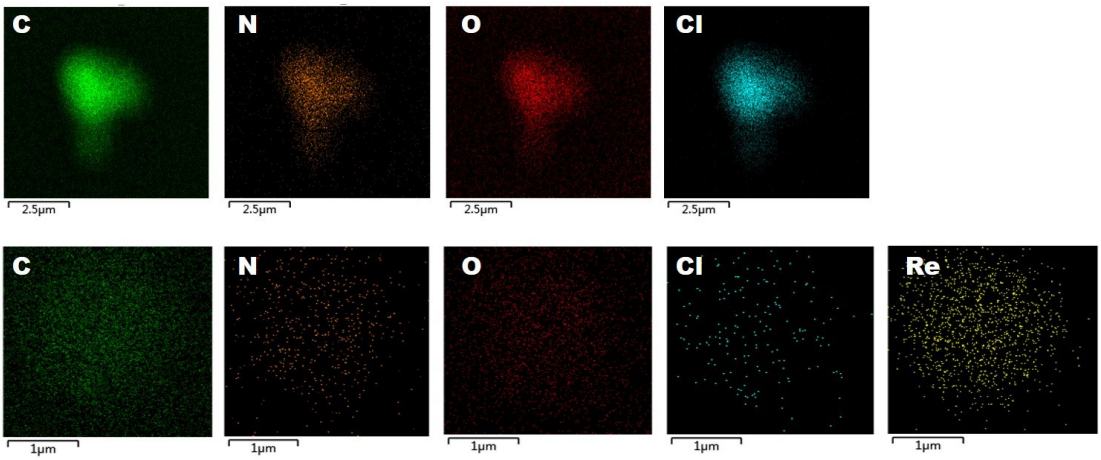


Figure S3. EDS mapping images of SCU-COF-1 before and after sorption with ReO_4^-.

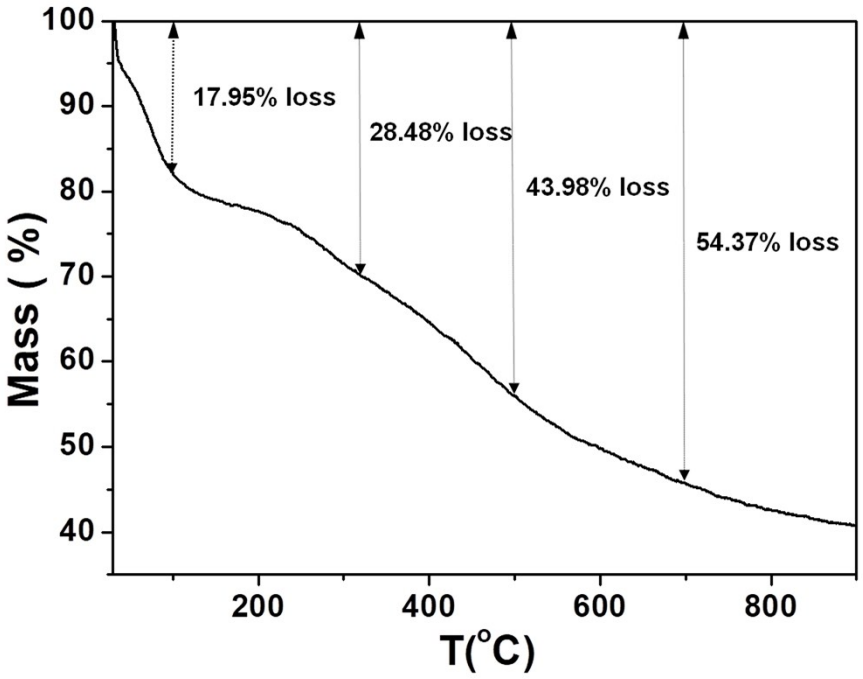


Figure S4. TGA curve of COF SCU-COF-1 under N_2 atmosphere.

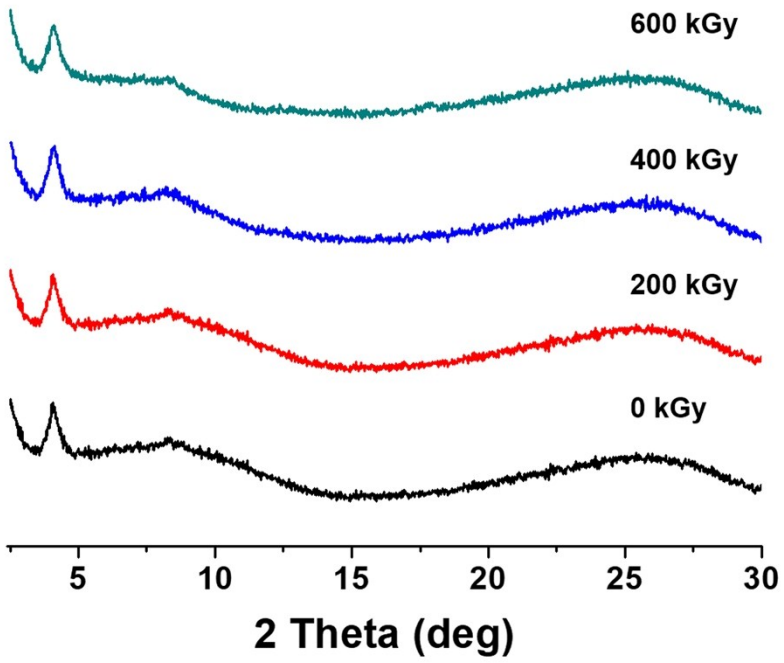


Figure S5. PXRD patterns of SCU-COF-1 after irradiated by various doses of ^{60}Co γ-irradiation.

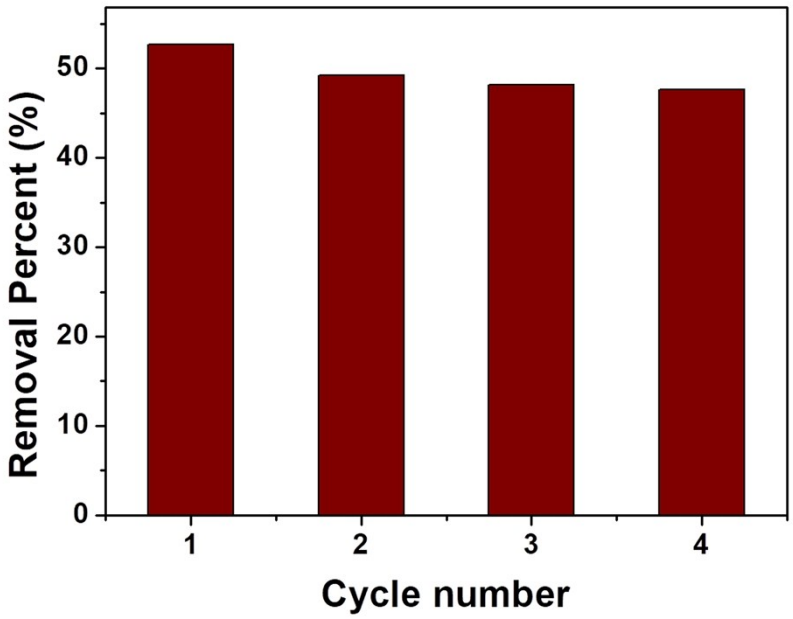
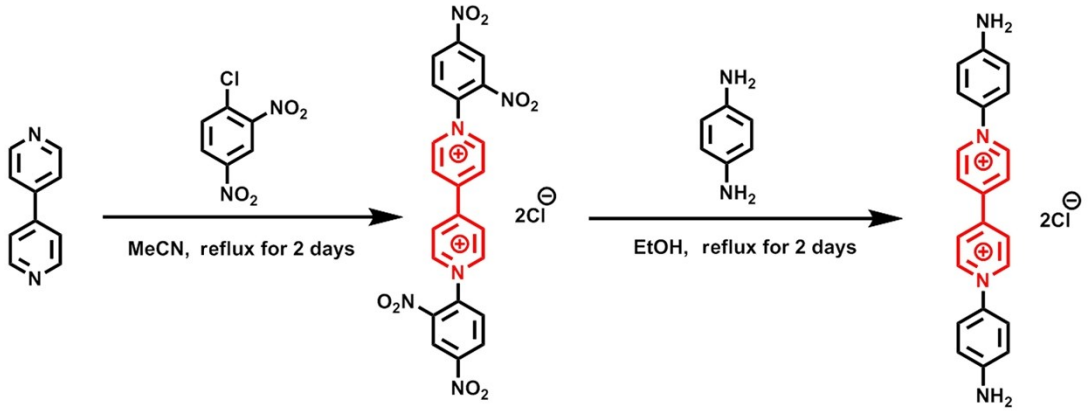


Figure S6. Reversibility of SCU-COF-1 for removing ReO_4^- in 3 M HNO_3 (c_0 = 253 ppm, solid-liquid ratio = 40 : 1).

Scheme S1. Synthetic procedures of Zincke salt [4,4′-bipyridine]-1,1′-diium dichloride (BDB) and aminated viologen (Viologen-NH_2).



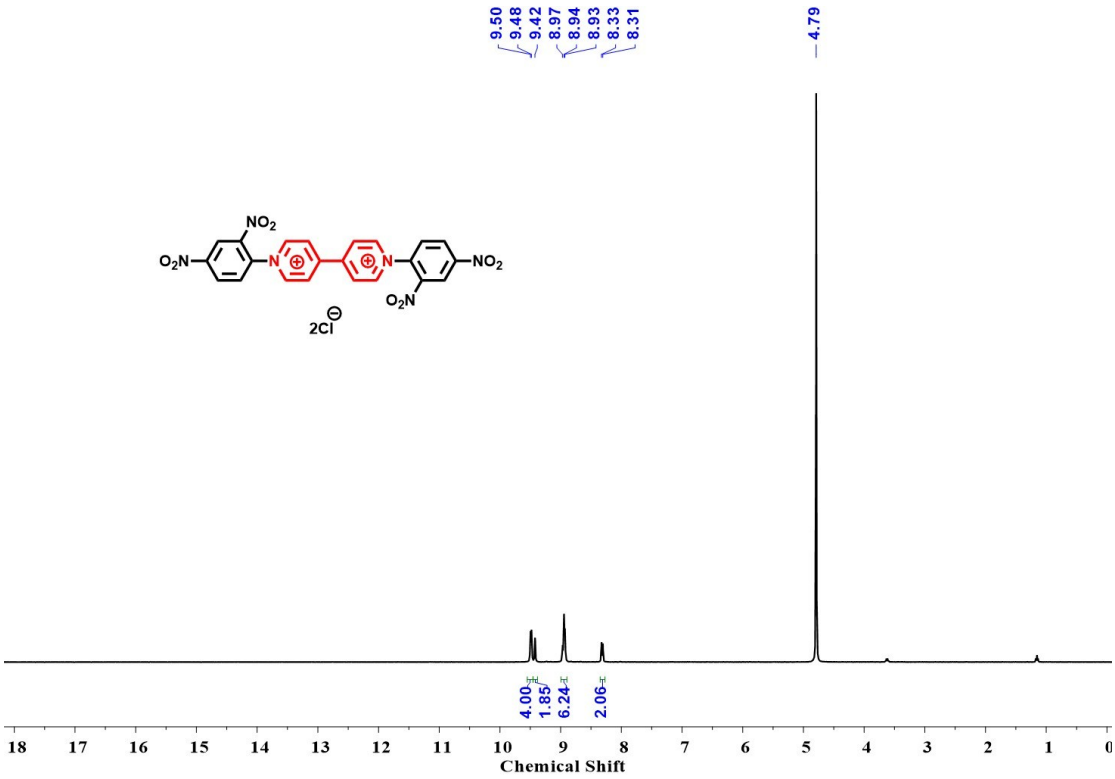


Figure S7. ^{1}H NMR spectrum of ionic compound BDB salt in D_2O.

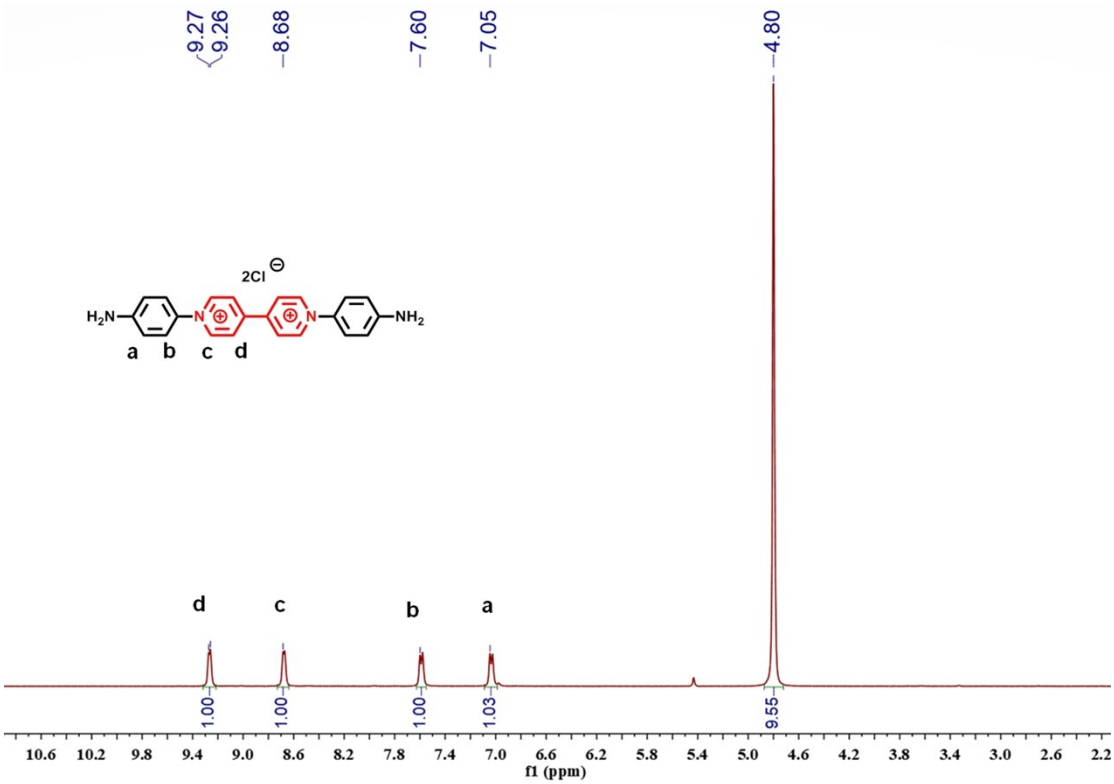


Figure S8. ^{1}H NMR spectrum of ionic compound Viologen-NH_2 in D_2O.

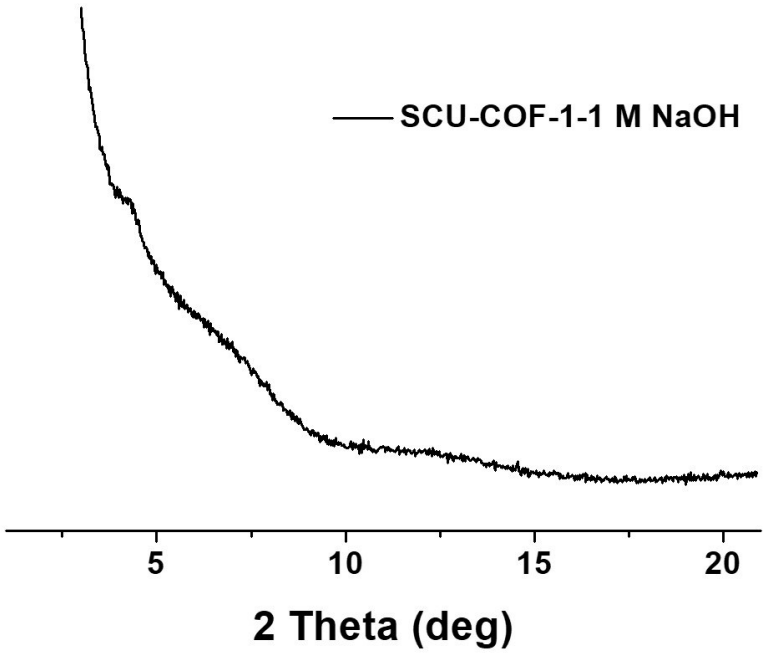


Figure S9. PXRD patterns of SCU-COF-1 after being immersed in 1 M NaOH.

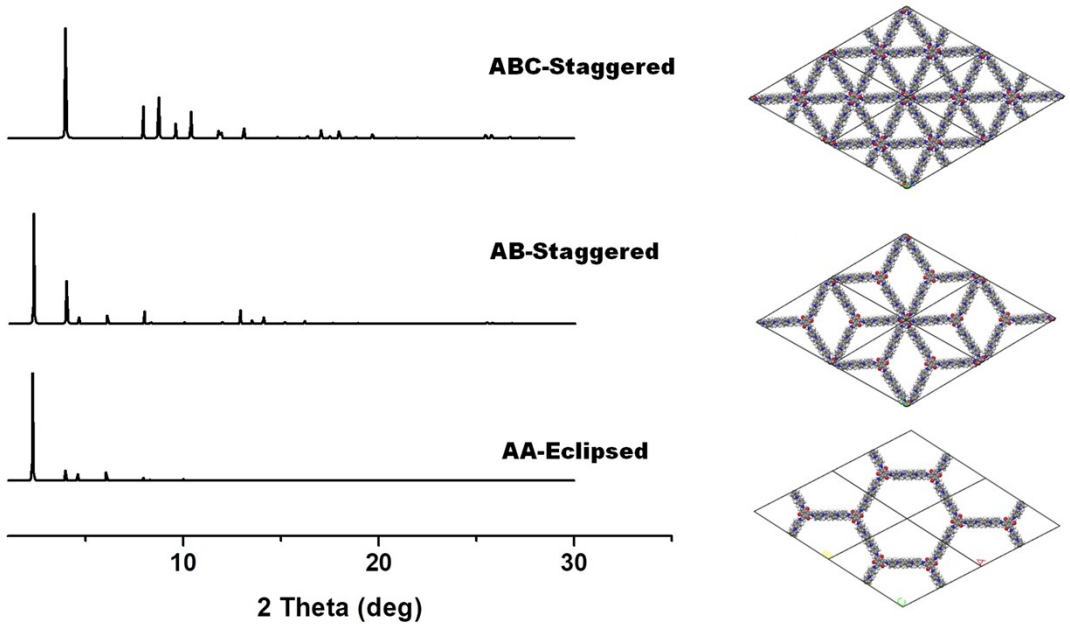


Figure S10. Unit cells for AA-eclipsed, AB-staggered and ABC-staggered stacking model (right) and the corresponding simulated PXRD patterns (left).

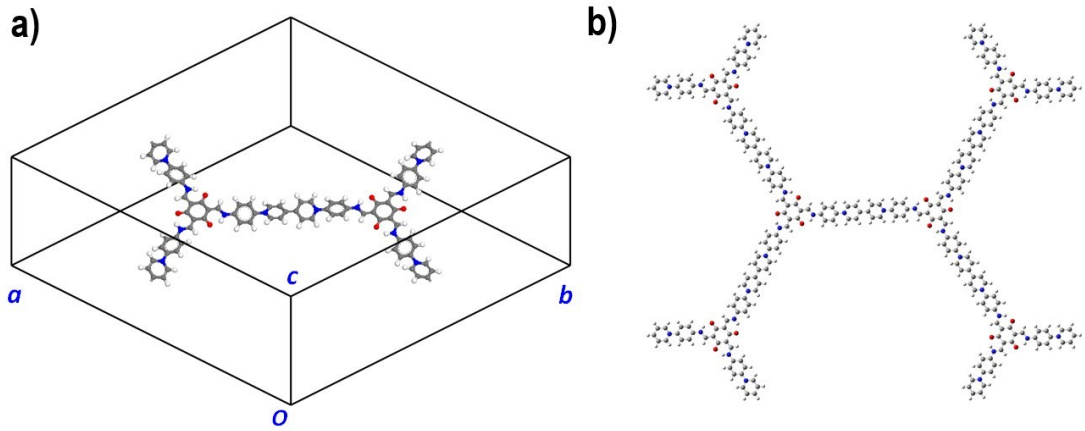


Figure S11. (a) The unit cell of the SCU-COF-1 single layer. (b) The cluster model of the SCU-COF-1 single layer. The dangling carbons in (b) were saturated by H atoms. In both (a) and (b), the grey, red, blue and white balls represent the C, O, N and H atoms.

Geometry and lattice parameters of the unit cell of the SCU-COF-1 single layer, as shown in **Figure S11a**, were optimized at PBE/DNP[1] level using

Dmol3 program.[2] The symmetry was restrained to *P*6 ($a = b$, $\alpha = \beta = 90°$, $\gamma = 120°$) and the c value was fixed to 30 Å during optimizations. A 2 × 2 × 1 k-point set with a global cutoff of 3.7 Å were used. The calculated result showed a balanced lattice parameter of $a = b = 44.5$ Å.

Based on the optimized periodic unit cell, we constructed a large cluster model, as shown in **Figure S11b**, for calculating the atomic charges. Single point energy calculation were performed for this cluster model at HF/6-31G*[3] level using Gaussian 09 program.[4] The atomic charges fit to the electrostatic potential (ESP) according to the MK scheme were then deduced. The ESP charges distributed on the center region were selected for the following classical molecular dynamics simulations.

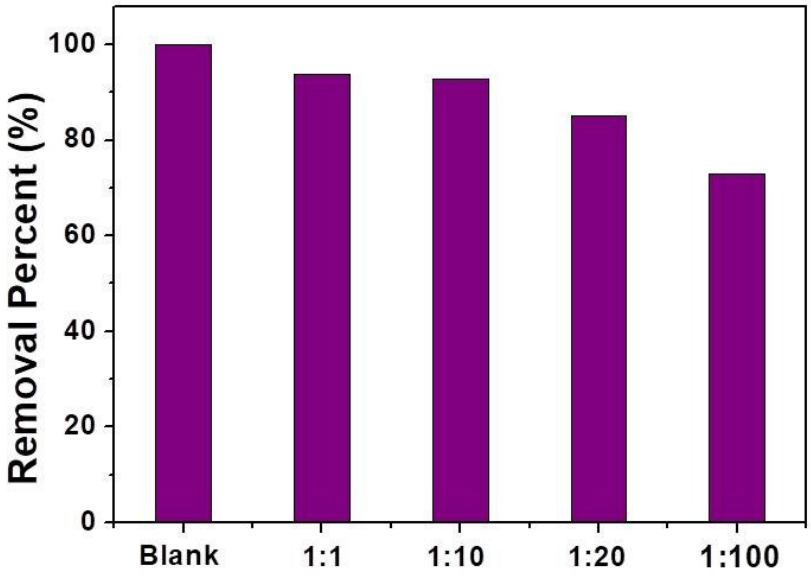


Figure S12. Effect of excessive SO_4^{2-} on the removal percentage of ReO_4^- (molar ratio = 1 : 1, 1 : 10, 1 : 20, 1 : 100, initial concentration of ReO_4^- = 15 ppm).

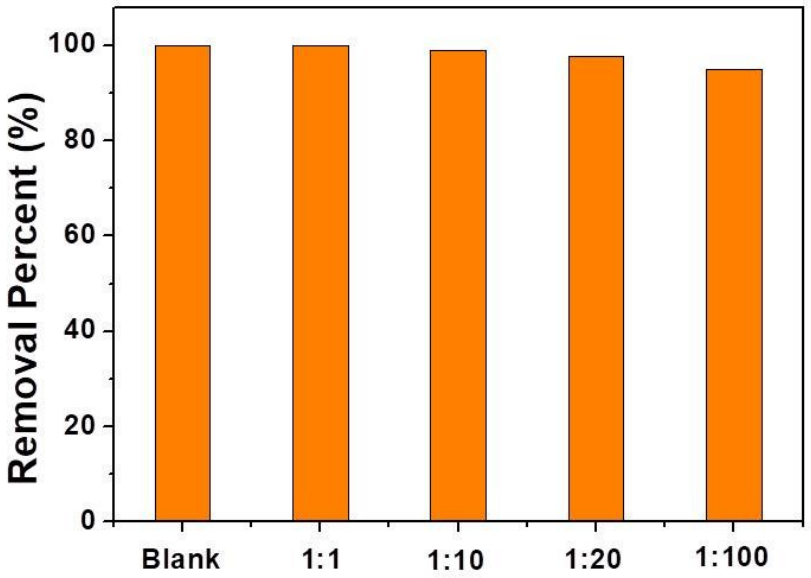


Figure S13. Effect of excessive PO_4^{3-} on the removal percentage of ReO_4^- (molar ratio = 1 : 1, 1 : 10, 1 : 20, 1 : 100, initial concentration of ReO_4^- = 15 ppm).

Table S1. Comparison of equilibrium time of SCU-COF-1 with other reported materials.

Sorbents	Experimental conditions	Equilibrium time	Ref.
SLUG-21	$[Re]_0=1.26\times10^{-3}$ mol/ L; half molar ratio	>24 h	5
Calcined LDH	$[Re]_0=1.26\times10^{-3}$ mol/ L; half molar ratio	>24 h	5
UiO-66-NH_3^+	molar ratio = 1:2 (ReO_4^-:UiO-66-NH_3^+)	>24 h	6
Acidosasa edulis shoot shell bio-char	T = 298 K; pH 1; 3 g/L; $Re(VII)]_0$ = 20 mg/L	350 min	7
4-ATR resi n	Resin = 10.0 mg; $[Re(VII)]_0$= 7.2 mg/50.0 mL; pH = 2.6; 100 rpm.	8 h	8
SCU-100	$[Re(VII)]_0$ = 28 mg/L; pH = 7; 1 g/L; stirring	30 min	9
SCU-101	$[Re(VII)]_0$ = 28 mg/L; pH = 7; 1 g/L; stirring	10 min	19
SBN	$[Re(VII)]_0$ = 28 mg/L; pH = 7; 1 g/L; stirring	10 min	12
Purolite A532E	$[Re(VII)]_0$ = 28 mg/L; pH = 7; 1 g/L; stirring	150 min	10
Purolite A530E	$[Re(VII)]_0$ = 28 mg/L; pH = 7; 1 g/L; stirring	150 min	10
Compound-1	$[Re(VII)]_0$ = 28 mg/L; pH = 7; 1 g/L; shaking	20 min	21
SCU-COF-1	**$[Re(VII)]_0$ = 28 mg/L; pH = 7; 1 g/L; shaking**	**1 min**	**This work**

Table S2. Comparison of distribution coefficient (K_d, mL/g) by cationic materials.

Sorbents	K_d	Ref
Mg-Al-LDH	262	9
NDTB-1	652	9
$Y_2(OH)_5Cl$	112	9
$Yb_3O(OH)_6Cl$	120	9
PAF-1-F	2.55×10^4	20
SCU-6	3.0×10^3	23
SCU-7	63	23
SCU-100	3.3×10^5	10
SCU-101	7.5×10^5	19
SCU-COF-1	**3.89×10^5**	**This work**

Table S3. Fitting results of SCU-COF-1 based on the Langmuir models.

Sample	Langmuir model		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2
SCU-COF-1	367.65	0.14	0.98

Table S4. Composition of Hanford LAW melter off-gas scrubber solution.

Anion	Concentration, mol/L	Anion : TcO_4^- molar ratio
TcO_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}	0.0343
CO_3^{2-}	4.30×10^{-5}	0.222

Table S5. Results of ReO_4^- and TcO_4^- sorption by SCU-COF-1 from simulated Hanford waste.

Simulated wastes	Anions	Solid-to-liquid ratio ($g\ L^{-1}$)	Anion removal percentage (%)
Hanford waste	ReO_4^-	1:1	17.8
	ReO_4^-	5:1	56.3
	TcO_4^-	1:1	20.9
	TcO_4^-	5:1	62.8

Table S6. Results of ReO_4^- desorption from sorbed SCU-COF-1 at 300 K.

Dsorption temperature	Concentrations of desorption solution (NaCl, mol/L)	Desorption percentage (%)
25 ℃	1	79.24
	2	87.65
	3	95.03

Table S7. Comparison of the maximum ReO_4^- sorption capacities.

Materials	Sorbents	Experimental conditions	Capacity (mg/g)	Ref.
Inorganic Materials	Biochar	T = 298 K; 12 h; 3 g/L	46.5	11
	$Yb_3O(OH)_6Cl$	Ambient temperature; pH = 7.0 ± 0.1; 0.5 g/L	48.6	10
	NDTB-1	Ambient temperature; pH = 7.0 ± 0.1; 0.5 g/L	49.4	10
	LDHs	Ambient temperature; pH = 7.0 ± 0.1; 0.5 g/L	**130.2**	10
Composites	ZrO_2@rGO	T = 303 K; 24 h	43.55	13
	NZVI/rGOs	0.1 g/L; pH 5	85.77	14
	GO-DEA-DIBA	303 K; 2 g/L; 48 h	**140.82**	15
	PS-g-4VP-IE	Ambient temperature; 2 h	252	16
	D318 resin	T = 298 K; pH 5.2; 1 g/L	351	17
	4-ATR resin	T = 298 K; 8 h; pH 2.6; 10 h	354	8
	R_2SO_4 resin	Ambient temperature; 1.3 g/L; pH 6.25; 4 h	462	18
	Purolite A532E	Ambient temperature; pH = 7.0 ± 0.1; 0.5 g/L	446	12
	Purolite A530E	Ambient temperature; pH = 7.0±0.1; 0.5 g/L	**706**	9
MOFs	UiO-66-NH_3^+	24 h	159	6
	SCU-101	Ambient temperature; pH = 7.0 ± 0.1; 1 g/L	217	19
	SCU-100	Ambient temperature; pH = 7.0 ± 0.1; 1 g/L	541	9
	SLUG-21	Ambient temperature; 48 h; 1.6 g/L	602	5
	SBN	Ambient temperature; pH = 7.0 ± 0.1; 0.5 g/L	**786**	10

	PAF-1-F	Molar ratio, ReO_4^-: PAF-1-F =1:2; 24 h	420	20
POPs	Compuond-1	Ambient temperature; 24 h; 2 g/L	517	21
	SCU-CPN-1	Ambient temperature; 12 h; 1 g/L	999	22
COFs	**SCU-COF-1**	**Ambient temperature; 12 h; 1 g/L**	**367**	**This work**
		373 K; 14 h; 1g/L	**702.4**	

Table S8. Fractional atomic coordinates for the unit cell of SCU-COF-1 (AA-Eclipsed).

SCU-COF-1 (AA-Eclipsed)			
*P*6			
N1	0.45929	0.90830	0.47138
C2	0.44126	0.92434	0.36033
C3	0.45647	0.95995	0.36335
C4	0.49161	0.98099	0.46680
C5	0.50983	0.96386	0.56987
C6	0.49333	0.92812	0.57730
C7	0.44252	0.87109	0.47796
C8	0.40772	0.85165	0.59424
C9	0.39126	0.81575	0.59879
C10	0.40936	0.79870	0.48691
C11	0.44450	0.81855	0.37717
C12	0.46098	0.85445	0.37154
N13	0.39405	0.76282	0.48242
C14	0.35997	0.73917	0.49587
C15	0.34758	0.70395	0.49755
C16	0.37136	0.69024	0.49402
O17	0.30640	0.59625	0.48390
H18	0.34120	0.74833	0.49702
H19	0.40903	0.75059	0.46715
H20	0.45848	0.80533	0.28498
H21	0.48759	0.86917	0.26748
H22	0.39386	0.86440	0.69962
H23	0.36474	0.80116	0.70456
H24	0.50595	0.91414	0.68007
H25	0.53669	0.97820	0.66596
H26	0.44098	0.97120	0.26595
H27	0.41493	0.90745	0.25993

Table S9. Fractional atomic coordinates for the unit cell of SCU-COF-1 (AB-Staggered).

SCU-COF-1 (AB-Staggered)			
*P*6			
N1	-0.20737	0.57497	0.23569
C2	-0.22541	0.59100	0.18017
C3	-0.21020	0.62662	0.18167
C4	-0.17506	0.64766	0.23340
C5	-0.15683	0.63052	0.28493
C6	-0.17334	0.59479	0.28865
C7	-0.22415	0.53775	0.23898
C8	-0.25895	0.51832	0.29712
C9	-0.27540	0.48241	0.29940
C10	-0.25731	0.46536	0.24345
C11	-0.22216	0.48521	0.18859
C12	-0.20569	0.52111	0.18577
N13	-0.27262	0.42949	0.24121
C14	-0.30670	0.40604	0.24794
C15	-0.31909	0.37061	0.24877
C16	-0.29530	0.35690	0.24701
O17	-0.36027	0.26291	0.24195
H18	-0.32547	0.41499	0.24851
H19	-0.25764	0.41726	0.23358
H20	-0.20818	0.47219	0.14249
H21	-0.17908	0.53583	0.13374
H22	-0.27281	0.53107	0.34981
H23	-0.30192	0.46783	0.35228
H24	-0.16072	0.58081	0.34004
H25	-0.12998	0.64487	0.33298
H26	-0.22569	0.63786	0.13298
H27	-0.25174	0.57412	0.12997
N28	-0.12596	-0.24163	0.23569

C29	-0.10793	-0.25767	0.18017
C30	-0.12313	-0.29328	0.18167
C31	-0.15827	-0.31432	0.23340
C32	-0.17650	-0.29719	0.28493
C33	-0.16000	-0.26146	0.28865
C34	-0.10919	-0.20442	0.23898
C35	-0.07439	-0.18498	0.29712
C36	-0.05793	-0.14908	0.29940
C37	-0.07603	-0.13203	0.24345
C38	-0.11117	-0.15188	0.18859
C39	-0.12765	-0.18778	0.18577
N40	-0.06072	-0.09616	0.24121
C41	-0.02663	-0.07271	0.24794
C42	-0.01424	-0.03728	0.24877
C43	-0.03803	-0.02357	0.24701
O44	0.02694	-0.07042	0.24195
H45	-0.00787	-0.08166	0.24851
H46	-0.07570	-0.08392	0.23358
H47	-0.12515	-0.13886	0.14249
H48	-0.15426	-0.0250	0.13374
H49	-0.06053	-0.19774	0.34981
H50	-0.03141	-0.13449	0.35228
H51	-0.17262	-0.24747	0.34004
H52	-0.20336	-0.31153	0.33298
H53	-0.10765	-0.30453	0.13298
H54	-0.08159	-0.24079	0.12997

Table S10. Fractional atomic coordinates for the unit cell of SCU-COF-1 (ABC-Staggered).

SCU-COF-1 (ABC-Staggered)			
*R*3			
N1	0.45929	0.90830	-0.00417
C2	0.44126	0.92434	-0.04119
C3	0.45647	0.95995	-0.04018
C4	0.49161	0.98099	-0.00570
C5	0.50983	0.96386	0.02866
C6	0.49333	0.92812	0.03113
C7	0.44252	0.87109	-0.00198
C8	0.40772	0.85165	0.03678
C9	0.39126	0.81575	0.03830
C10	0.40936	0.79870	0.00100
C11	0.44450	0.81855	-0.03557
C12	0.46098	0.85445	-0.03745
N13	0.39405	0.76282	-0.00049
C14	0.35997	0.73917	0.00399
C15	0.34758	0.70395	0.00455
C16	0.39136	0.69024	0.00337
O17	0.30640	0.59625	0.00000
H18	0.34120	0.74833	0.00437
H19	0.40903	0.75059	-0.00558
H20	0.45848	0.80533	-0.06631
H21	0.48759	0.86917	-0.07214
H22	0.39386	0.86440	0.07191
H23	0.36474	0.80116	0.07355
H24	0.50595	0.91414	0.06539
H25	0.53669	0.97820	0.06069
H26	0.44098	0.97120	-0.07265
H27	0.41493	0.90745	-0.07465
N28	0.54071	0.09170	-0.00417

C29	0.55874	0.07566	-0.04119
C30	0.54353	0.04005	-0.04018
C31	0.50839	0.01901	-0.00570
C32	0.49017	0.03614	0.02866
C33	0.50667	0.07188	0.03113
C34	0.55748	0.12891	-0.00198
C35	0.59228	0.14835	0.03678
C36	0.60874	0.18425	0.03830
C37	0.59064	0.20130	0.00100
C38	0.55550	0.18145	-0.03557
C39	0.53902	0.14555	-0.03745
N40	0.60595	0.23718	-0.00049
C41	0.64003	0.26063	0.00399
C42	0.65242	0.29605	0.00455
C43	0.62864	0.30976	0.00337
O44	0.69360	0.40375	0.00000
H45	0.65880	0.25167	0.00437
H46	0.59097	0.24941	-0.00558
H47	0.54152	0.19447	-0.06631
H48	0.51241	0.13083	-0.07214
H49	0.60614	0.13560	0.07191
H50	0.63526	0.19884	0.07355
H51	0.49405	0.08586	0.06539
H52	0.46331	0.02180	0.06069
H53	0.55902	0.02880	-0.07265
H54	0.58507	0.09255	-0.07465

References

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