Supporting Information

Construction of cationic covalent organic framework for efficient gold extraction

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EXPERMENTS

1. Materials and general methods

All the organic monomers and ligand were purchased from Jilin Chinese Academy of Sciences -Yanshen Technology Co., Ltd. Others were purchased from Adamas Reagent, Ltd. and used as received without further purification. X-ray powder diffraction was collected by a Bruker AXSD8 Discover powder diffractometer at 40 kV, 40 mA for Cu Kλ (λ= 1.5406 Å). The simulated powder patterns were calculated by Mercury 1.4. Infrared Spectra (IR) were measured by a Bruker VERTEX70 spectrometer in the 500-4000 cm^{-1} region. The gas adsorption isotherms were collected on a Belsorp-max. Ultrahigh-purity-grade (>99.999%) N_2 gases were used during the adsorption measurement. SEM and EDS measurements were carried out using a Hitachi S-4800 microscope. The analyses of concentrations of metal ions in the solution was carried out by ThermoFisher iCap7600 ICP-OES instruments. X-ray photoelectron spectra (XPS) were collected by Thermo Scientific ESCALAB 250 Xi spectrometer. Solid-state NMR experiments were performed on Varian Infinityplus 300 solid-state NMR spectrometer (300MHz).

2. Synthesis of ECUT-iCOF-5

2-Chloro-1,3-dimethylimidazolinium Tetrafluoroborate (CIB) (0.3 mmol, 33.06 mg), 1,3,5-Tris(p-formylphenyl)benzene (0.2 mmol, 39.04 mg), benzoic anhydride (2.2 mmol, 500 mg) and zinc acetate (0.8 mmol, 150 mg) were weighed into a Pyrex tube. Then the tube was placed in a 190 °C for 3 days. fter cooling to room temperature, the precipitated was washed with a large number of DMF and then methanol. The resulting powder was collected by filtration and dried at 80°C under vacuum overnight to afford reddish brown crystallites in 80% yield for ECUT-iCOF-5.

3. Structural simulation

The theoretical framework of ECUT-iCOF-5 is created by repeating the unit of the monomer molecules. The geometrical structure is optimized by using the Forcite Plus module and the Universal force field in Material Studio 5.5 from Accelrys. Subsequently, Pawley refinement on the experimental PXRD data is carried out to obtain the exact structure of ECUT-iCOF-5.

4. Photocatalytic reduction of gold (Au^{3+})

Au^{3+} solution was prepared by dissolving $NaAuCl_4 \cdot 2H_2O$ in deionized water. Adsorption temperature is 298 K. Visible light was perpendicularly irradiated on the reaction vessel from a 350W Xe lamp with λ>400 nm.

In kinetics experiments, the Au solution with initial concentration of 100 ppm was used. The dose of adsorbent is 5 mg, while the Au solution is 50 mL. In addition, add 5 mL methanol solution and the contact time is 1.5 h.

In selective adsorption experiments, a 6 cation ions mixed solution contains both Au and other

5 metal ions with respectively initial concentration of 10mg/L were used. In the same condition, we just changed the cation ions into anion ions, and the anions were separated for experiments. The dose of adsorbent is 5 mg, while the solution is 50 mL. In addition, add 5 mL methanol solution and the contact time is 1.5 h.

The adsorption amount, Q_e (mg/g), was calculated by the difference of Au equilibrium concentration before and after adsorption (see equation 1):

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \qquad S1$$

Where C_0 (mg/L) and C_e (mg/L) are the initial concentration and equilibrium concentration of uranium in the solutions, respectively; V (mL) is the volume of testing solution and m (mg) is the amount of sorbent.

5. Adsorption kinetics modeling and analysis

The fitting formula of quasi-first-order kinetic model:

$$\ln (q_e - q_t) = \ln q_e - \frac{k_1 t}{2.303} \qquad S2$$

Where t (min) means reaction time; q_e ($mg \cdot g^{-1}$) means adsorption capacity of uranium at adsorption equilibrium; q_t ($mg \cdot g^{-1}$) means adsorption capacity of uranium at time t; k_1 (min^{-1}) means adsorption rate constant of quasi-first-order kinetic mode.

The fitting formula of quasi-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad S3$$

where t (min) means reaction time; q_e ($mg \cdot g^{-1}$) means the adsorption capacity of uranium at adsorption equilibrium; q_t ($mg \cdot g^{-1}$) means the adsorption capacity of uranium at time t; k_2 (min^{-1}) means the adsorption rate constant in the quasi-second-order kinetic model.

Langmuir isotherm model:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad S4$$

where C_e ($mg \cdot L^{-1}$) means the mass concentration of uranium in solution at equilibrium; q_e ($mg \cdot g^{-1}$) means the adsorption capacity of uranium at adsorption equilibrium; q_m ($mg \cdot g^{-1}$) means the maximum adsorption capacity of uranium; K_L ($L \cdot mg^{-1}$)means the constant related to adsorption, the greater the value, the greater the adsorption affinity.

Freundlich isotherm model:

$$\ln q_e = \ln K_F - \frac{1}{n}\ln C_e \qquad S5$$

where C_e (mg·L^{-1}) means mass concentration of uranium in solution at equilibrium; q_e (mg·g^{-1}) means adsorption capacity of uranium at adsorption equilibrium; K_F (mg·g^{-1}) means constant related to adsorption; n means parameter related to adsorption strength.

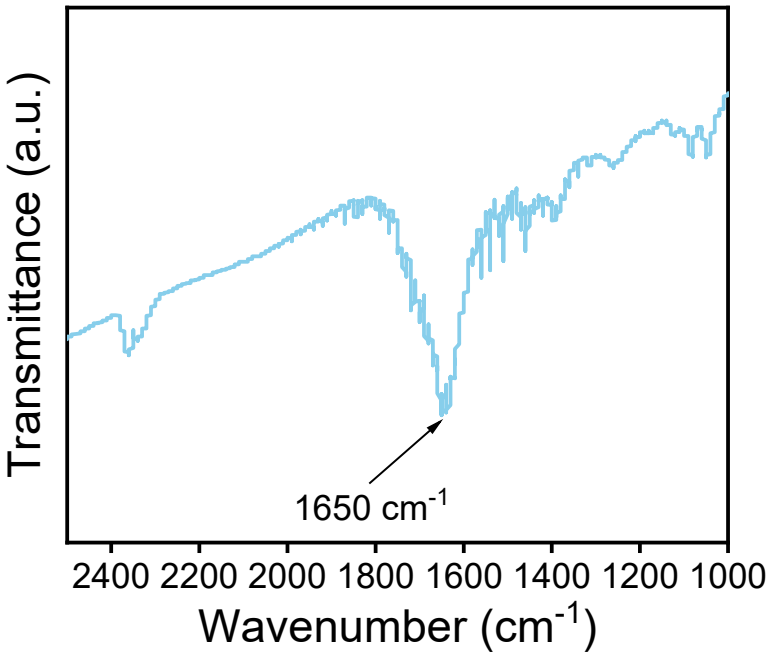

Fig. S1 FT-IR spectra of ECUT-iCOF-5.

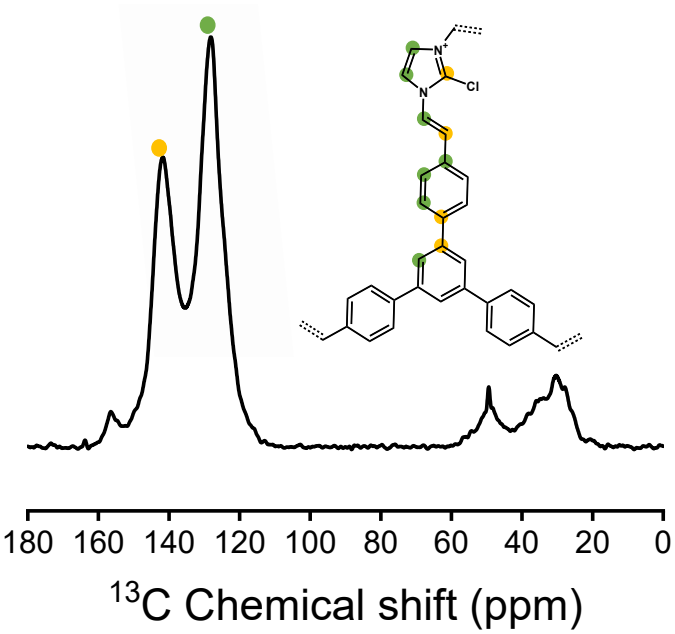

Fig. S2 Solid-state ^{13}C NMR of ECUT-iCOF-5 with the assignment.

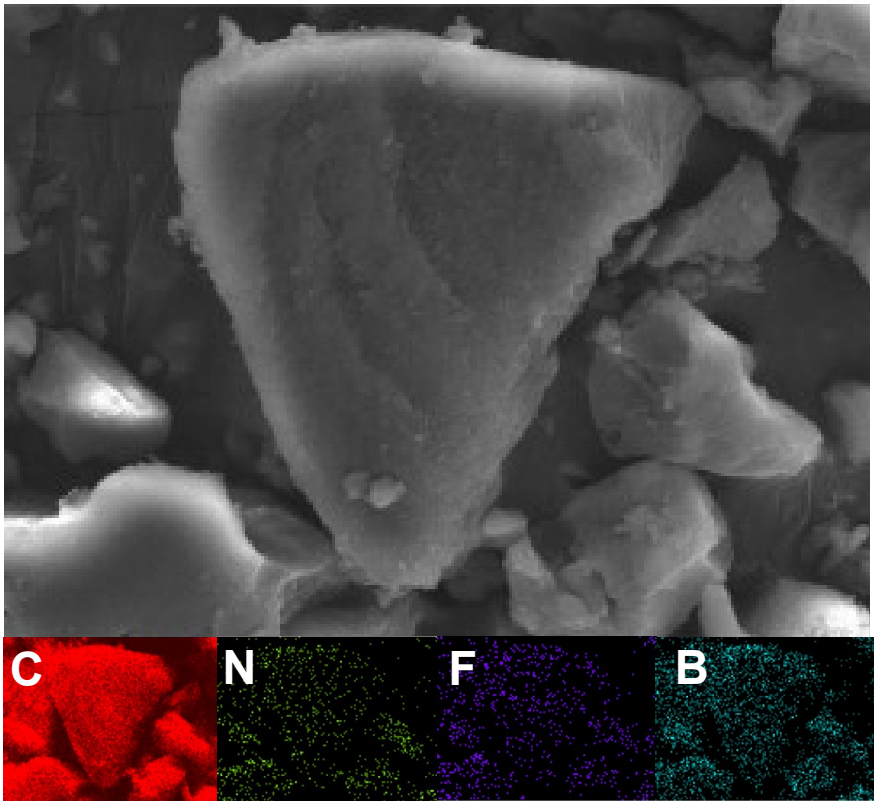

Fig. S3 The SEM-EDS image of C, N, F, B element in ECUT-iCOF-5.

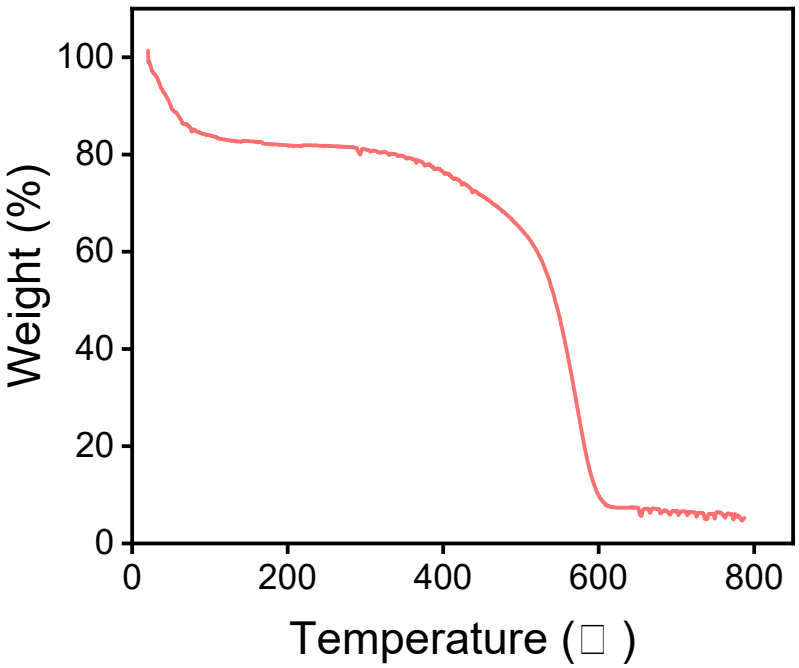

Fig. S4 TG curve of ECUT-iCOF-5.

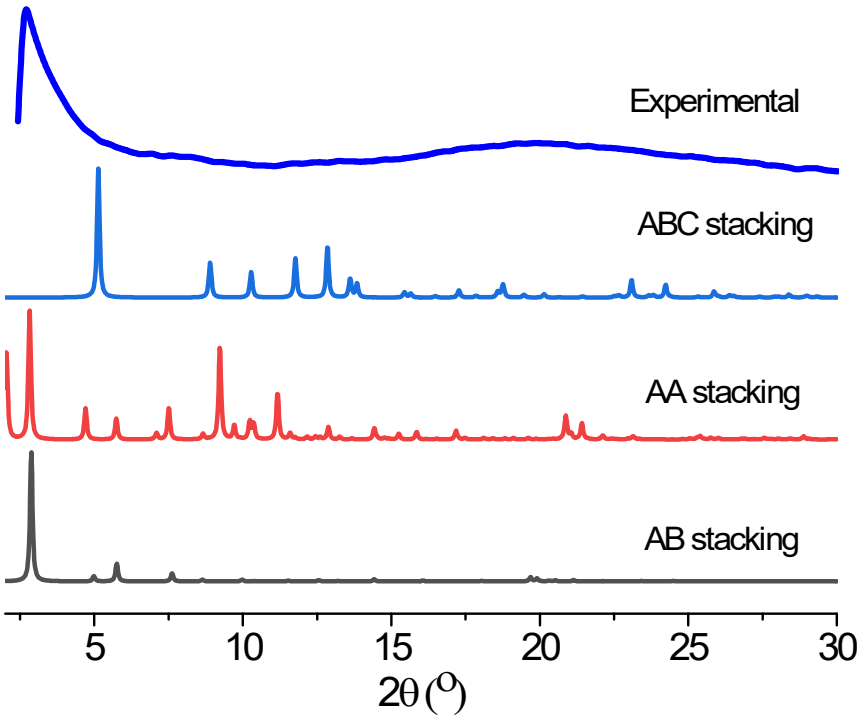

Fig. S5 A comparison of PXRD patterns among the experimental value and the calculated values of AA, AB, and ABC stacking.

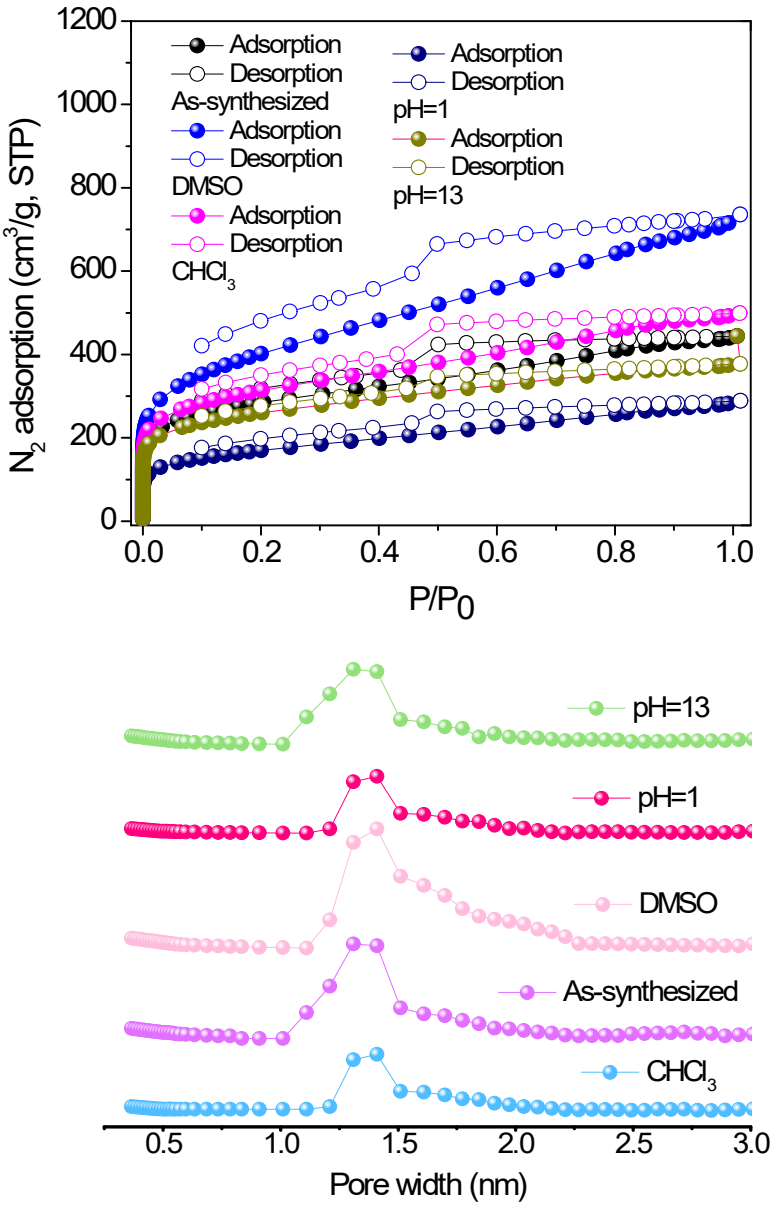

Fig. S6 A comparison in N_2 adsorption at 77 K and its aperture distribution among these samples in water at pH=1 (BET=600 m^2/g) and 13 (BET=936 m^2/g) or in organic solvents such as DMSO (BET=1411 m^2/g) and trichloromethane (BET=1117 m^2/g) for 24 hours.

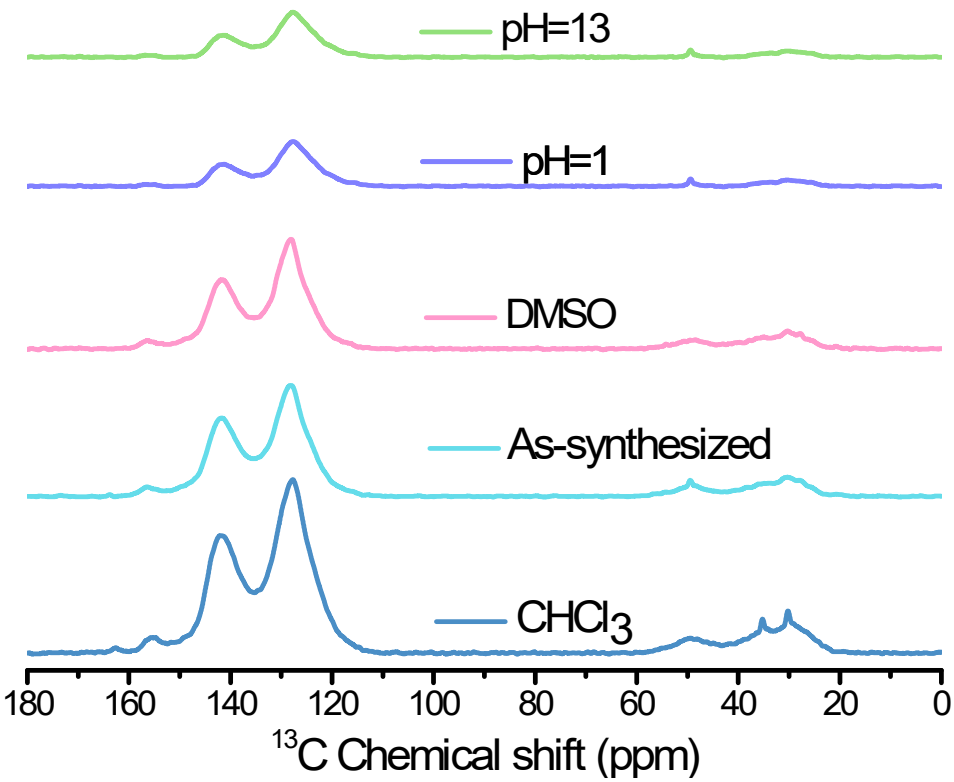

Fig. S7 A comparison of solid-state ^{13}C NMR spectrum among the samples soaking in water at pH=1 and 13 or in organic solvents such as DMSO and trichloromethane for 24 hours.

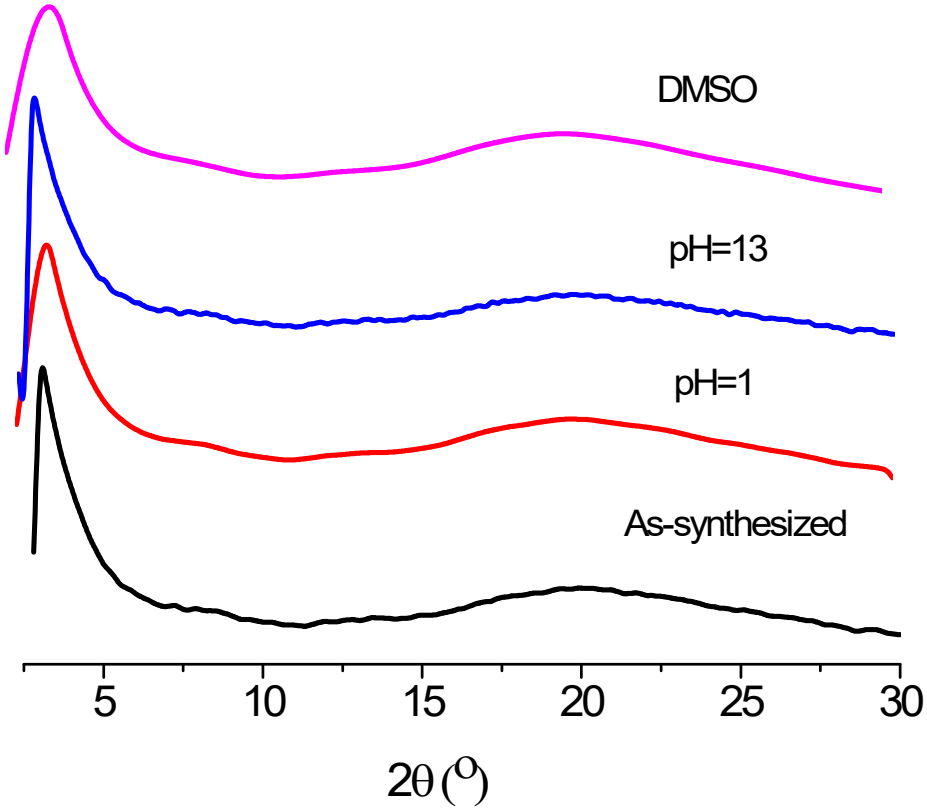

Fig. S8 A comparison of PXRD among the samples soaking in water at pH=1 and 13 or in DMSO for 24 hours.

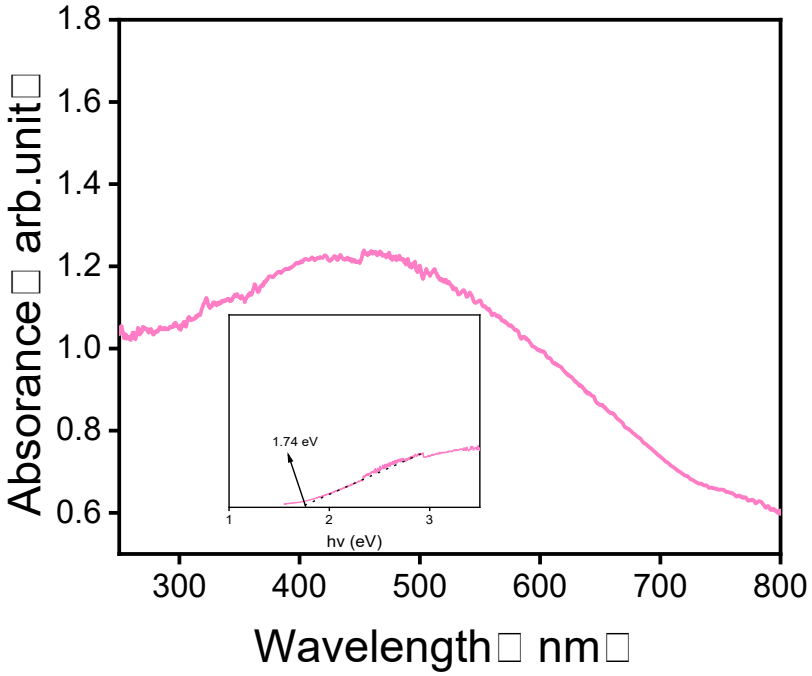

Fig. S9 UV-vis diffuse reflection spectrum of ECUT-iCOF-5.

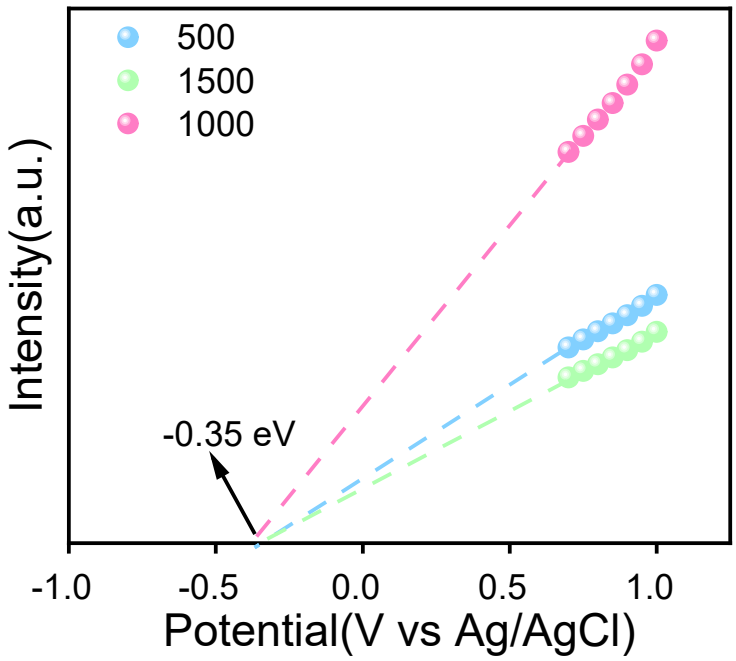

Fig. S10 Mott−Schottky plots of ECUT-iCOF-5.

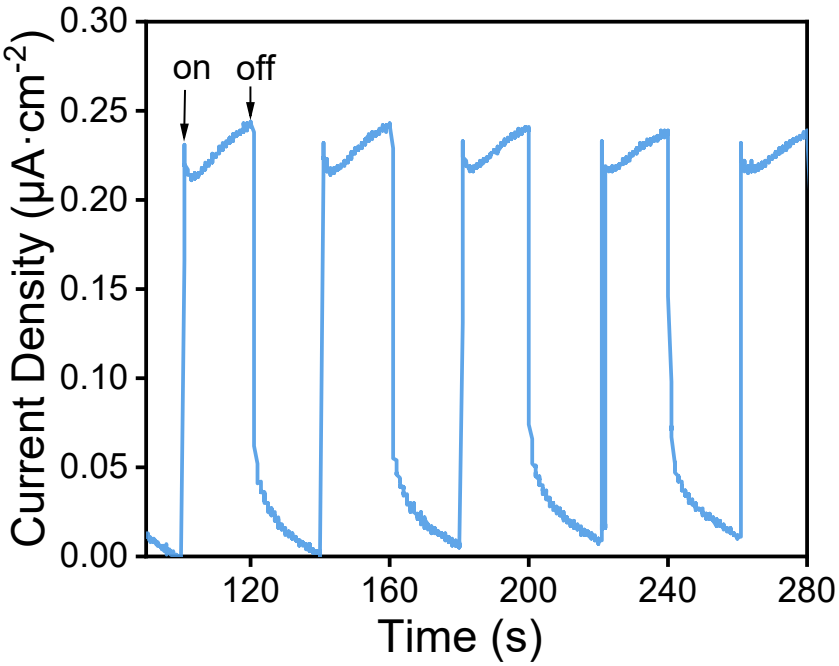

Fig. S11 Transient photocurrent response.

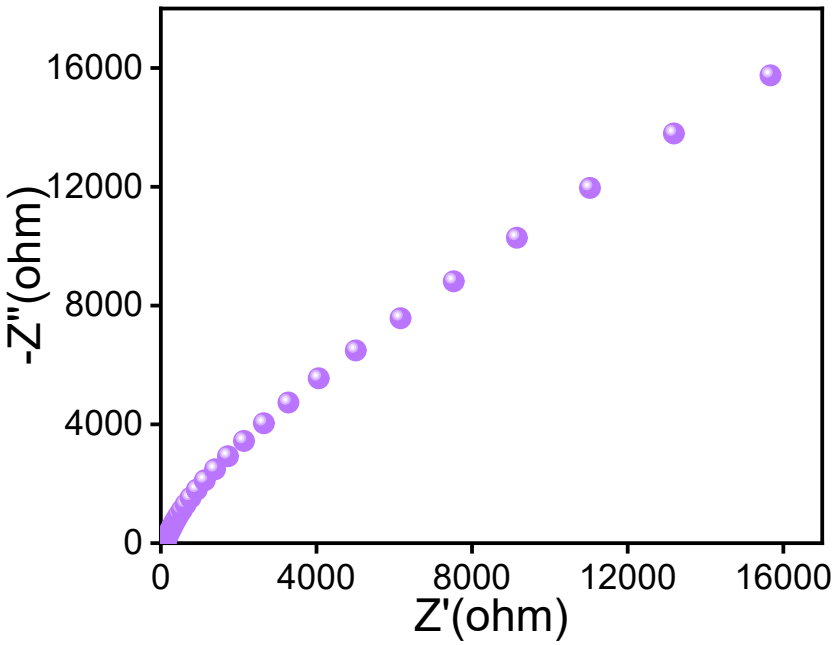

Fig. S12 EIS Nyquist plots of ECUT-iCOF-5.

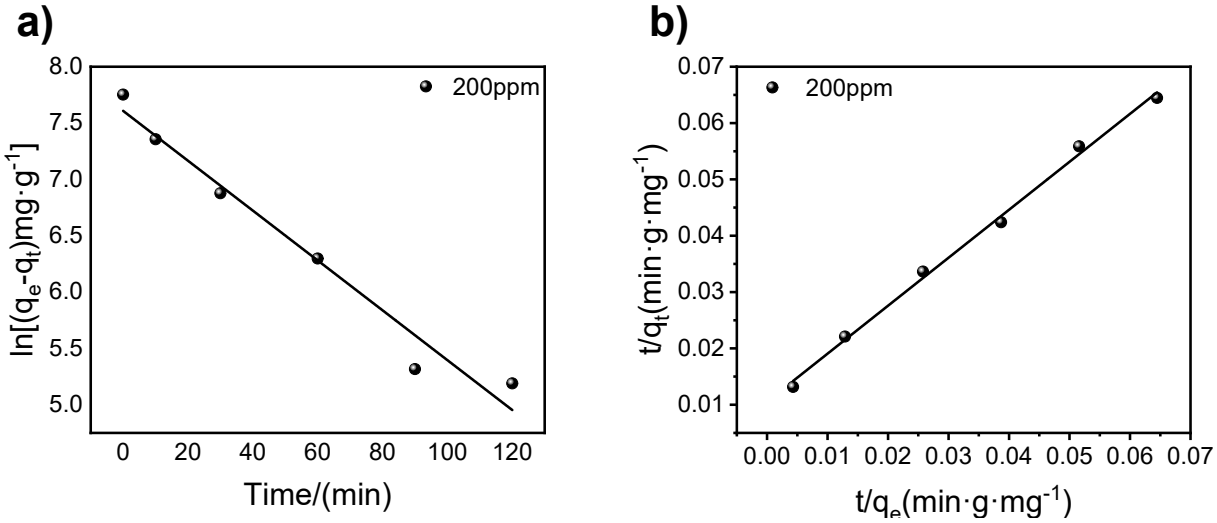

Fig. S13 The a) pseudo-first-order and b) pseudo-second-order models for Au^{3+} adsorption of ECUT-iCOF-5.

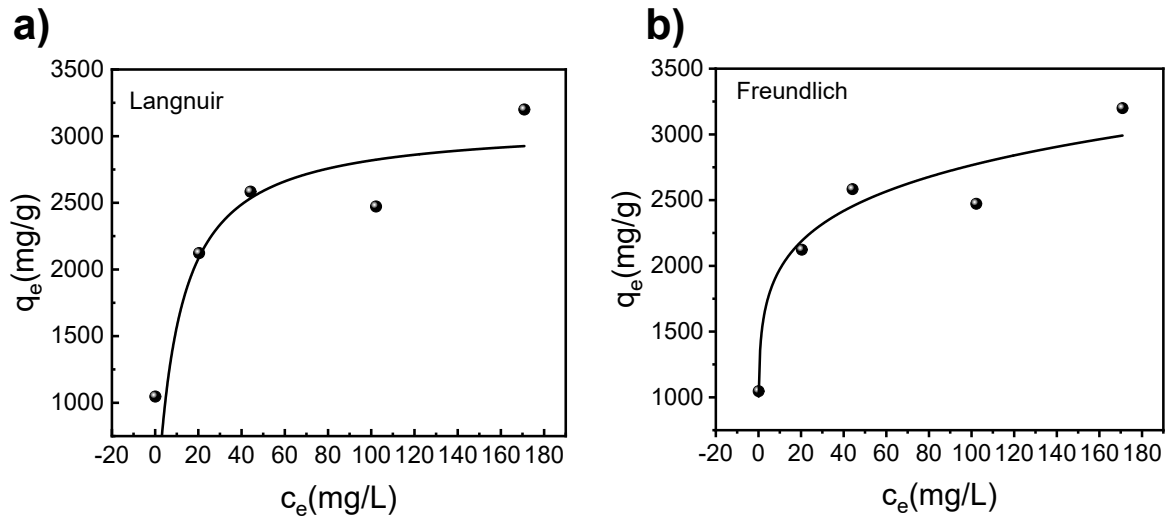

Fig. S14 a) Langmuir adsorption isotherm model and b) Freundlich adsorption isotherm model for Au^{3+} adsorption of ECUT-iCOF-5.

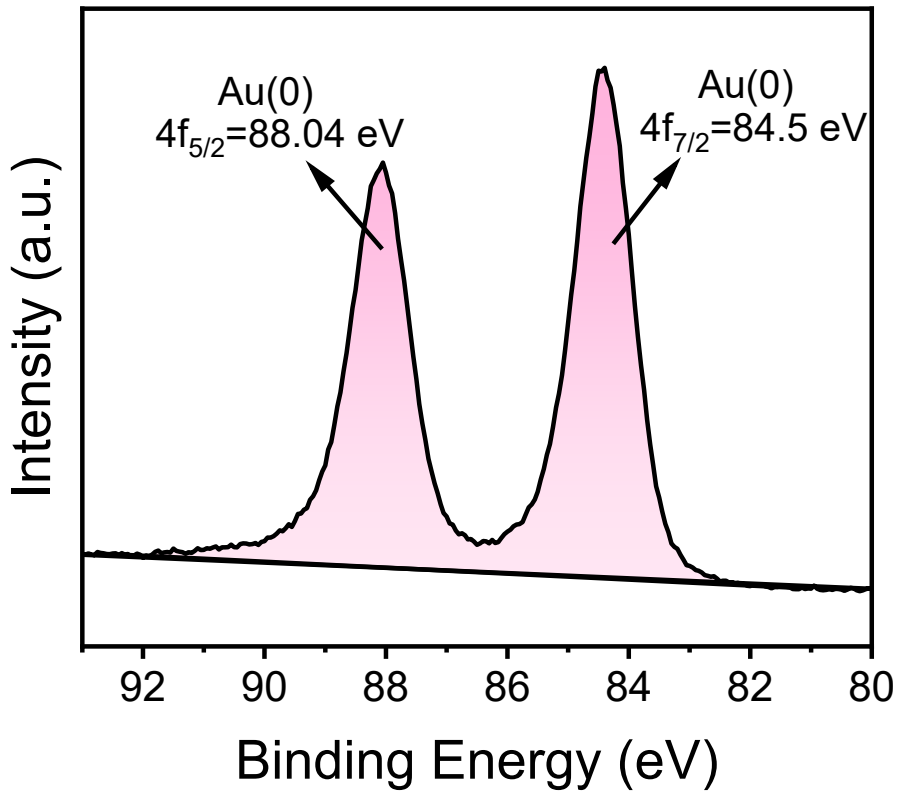

Fig. S15 XPS spectra of Au element after photocatalysis.

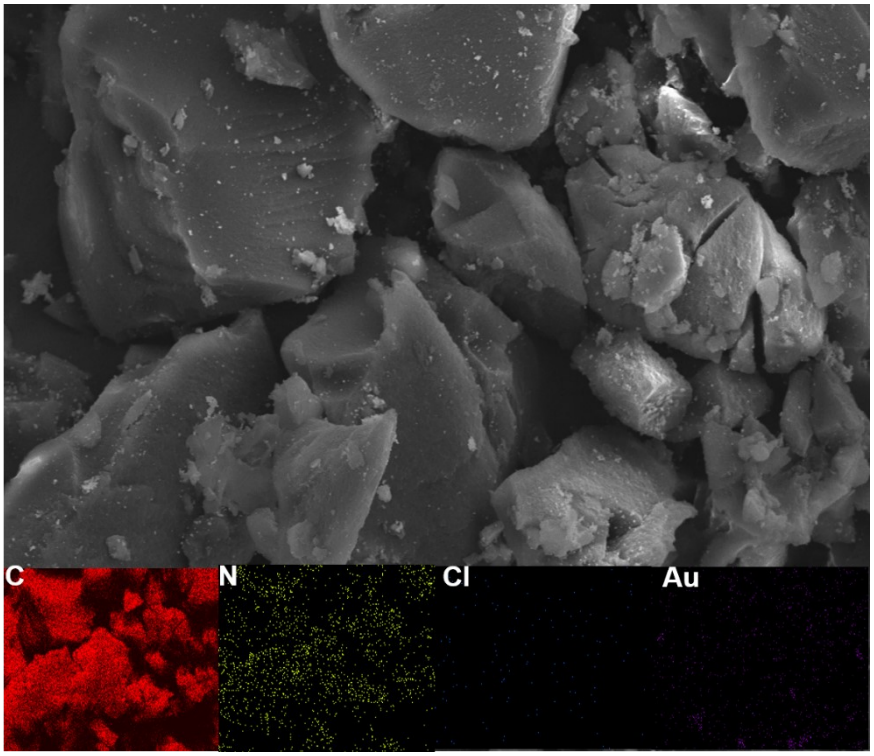

Fig. S16 The SEM image and EDS of C, N, Cl, Au element in ECUT-iCOF-5 after gold extraction.

Table S1. Calculated drystallography data of CUT-iCOF-5.

data_ECUT-iCOF-5=1

_audit_creation_date 2024-05-07

_audit_creation_method 'Materials Studio'

_symmetry_space_group_name_H-M 'P-6'

_symmetry_Int_Tables_number 174

_symmetry_cell_setting hexagonal

loop_

_symmetry_equiv_pos_as_xyz

x,y,z

-y,x-y,z

-x+y,-x,z

x,y,-z

-y,x-y,-z

-x+y,-x,-z

_cell_length_a 35.0212

_cell_length_b 35.0212

_cell_length_c 7.4477

_cell_angle_alpha 90.0000

_cell_angle_beta 90.0000

_cell_angle_gamma 120.0000

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_adp_type

				_atom_site_occupancy			
B1	B	0.40644	0.44625	0.20526	0.00000	Uiso	1.00
F2	F	0.40642	0.44477	0.36158	0.00000	Uiso	1.00
F3	F	0.43297	0.42993	0.14981	0.00000	Uiso	1.00
F4	F	0.42322	0.48998	0.15847	0.00000	Uiso	1.00
F5	F	0.36315	0.42022	0.15288	0.00000	Uiso	1.00
F6	F	0.38125	0.54782	0.37111	0.00000	Uiso	1.00
C7	C	0.95140	0.96428	0.50000	0.00000	Uiso	1.00
C8	C	0.96475	0.01273	0.50000	0.00000	Uiso	1.00
C9	C	0.86947	0.93931	0.50000	0.00000	Uiso	1.00
C10	C	0.90287	0.92860	0.50000	0.00000	Uiso	1.00
C11	C	0.88971	0.88376	0.50000	0.00000	Uiso	1.00
C12	C	0.84570	0.85154	0.50000	0.00000	Uiso	1.00
C13	C	0.81294	0.86284	0.50000	0.00000	Uiso	1.00
C14	C	0.82560	0.90712	0.50000	0.00000	Uiso	1.00
C15	C	0.76544	0.83055	0.50000	0.00000	Uiso	1.00
N16	N	0.62815	0.71935	0.50000	0.00000	Uiso	1.00
N17	N	0.70170	0.75548	0.50000	0.00000	Uiso	1.00
C18	C	0.66510	0.75920	0.50000	0.00000	Uiso	1.00
C19	C	0.74797	0.78703	0.50000	0.00000	Uiso	1.00
C20	C	0.58199	0.70463	0.50000	0.00000	Uiso	1.00
C21	C	0.36674	0.71125	0.50000	0.00000	Uiso	1.00
C22	C	0.37968	0.67968	0.50000	0.00000	Uiso	1.00
C23	C	0.42751	0.69229	0.50000	0.00000	Uiso	1.00
C24	C	0.46127	0.73638	0.50000	0.00000	Uiso	1.00
C25	C	0.50503	0.74777	0.50000	0.00000	Uiso	1.00
C26	C	0.51740	0.71596	0.50000	0.00000	Uiso	1.00
C27	C	0.48451	0.67202	0.50000	0.00000	Uiso	1.00
C28	C	0.44060	0.66051	0.50000	0.00000	Uiso	1.00

C29	C	0.56478	0.73086	0.50000	0.00000	Uiso	1.00
C30	C	0.04560	0.35573	0.50000	0.00000	Uiso	1.00
C31	C	0.02509	0.31283	0.50000	0.00000	Uiso	1.00
Cl32	Cl	0.19372	0.85911	0.50000	0.00000	Uiso	1.00
H33	H	0.93961	0.02192	0.50000	0.00000	Uiso	1.00
H34	H	0.87587	0.97229	0.50000	0.00000	Uiso	1.00
H35	H	0.91257	0.87224	0.50000	0.00000	Uiso	1.00
H36	H	0.83813	0.81803	0.50000	0.00000	Uiso	1.00
H37	H	0.80129	0.91713	0.50000	0.00000	Uiso	1.00
H38	H	0.74506	0.84473	0.50000	0.00000	Uiso	1.00
H39	H	0.76954	0.77379	0.50000	0.00000	Uiso	1.00
H40	H	0.56049	0.66981	0.50000	0.00000	Uiso	1.00
H41	H	0.39099	0.74467	0.50000	0.00000	Uiso	1.00
H42	H	0.45543	0.76331	0.50000	0.00000	Uiso	1.00
H43	H	0.52950	0.78204	0.50000	0.00000	Uiso	1.00
H44	H	0.49188	0.64594	0.50000	0.00000	Uiso	1.00
H45	H	0.41789	0.62621	0.50000	0.00000	Uiso	1.00
H46	H	0.58543	0.76542	0.50000	0.00000	Uiso	1.00
H47	H	0.03029	0.37560	0.50000	0.00000	Uiso	1.00
H48	H	0.99191	0.29314	0.50000	0.00000	Uiso	1.00
B49	B	-0.61320	0.52804	0.50000	0.00000	Uiso	1.00
F50	F	0.36043	0.48254	0.50000	0.00000	Uiso	1.00
F51	F	0.42930	0.53351	0.50000	0.00000	Uiso	1.00
C52	C	0.28677	0.63384	0.00000	0.00000	Uiso	1.00
C53	C	0.30041	0.67853	0.00000	0.00000	Uiso	1.00
C54	C	0.20537	0.61013	0.00000	0.00000	Uiso	1.00
C55	C	0.23870	0.59914	0.00000	0.00000	Uiso	1.00
C56	C	0.22493	0.55409	0.00000	0.00000	Uiso	1.00
C57	C	0.18081	0.52220	0.00000	0.00000	Uiso	1.00

C58	C	0.14832	0.53385	0.00000	0.00000	Uiso	1.00
C59	C	0.16139	0.57820	0.00000	0.00000	Uiso	1.00
C60	C	0.10070	0.50174	0.00000	0.00000	Uiso	1.00
N61	N	0.96320	0.38943	0.00000	0.00000	Uiso	1.00
N62	N	0.03706	0.42682	0.00000	0.00000	Uiso	1.00
C63	C	0.00002	0.42970	0.00000	0.00000	Uiso	1.00
C64	C	0.08321	0.45826	0.00000	0.00000	Uiso	1.00
C65	C	0.91699	0.37498	0.00000	0.00000	Uiso	1.00
C66	C	0.69961	0.37814	0.00000	0.00000	Uiso	1.00
C67	C	0.71327	0.34708	0.00000	0.00000	Uiso	1.00
C68	C	0.76140	0.36048	0.00000	0.00000	Uiso	1.00
C69	C	0.79478	0.40481	0.00000	0.00000	Uiso	1.00
C70	C	0.83879	0.41684	0.00000	0.00000	Uiso	1.00
C71	C	0.85185	0.38553	0.00000	0.00000	Uiso	1.00
C72	C	0.81930	0.34140	0.00000	0.00000	Uiso	1.00
C73	C	0.77517	0.32920	0.00000	0.00000	Uiso	1.00
C74	C	0.89951	0.40101	0.00000	0.00000	Uiso	1.00
C75	C	0.38319	0.02301	0.00000	0.00000	Uiso	1.00
C76	C	0.35984	0.97849	0.00000	0.00000	Uiso	1.00
Cl77	Cl	0.52072	0.52060	0.00000	0.00000	Uiso	1.00
H78	H	0.27653	0.68822	0.00000	0.00000	Uiso	1.00
H79	H	0.21174	0.64313	0.00000	0.00000	Uiso	1.00
H80	H	0.24725	0.54192	0.00000	0.00000	Uiso	1.00
H81	H	0.17299	0.48862	0.00000	0.00000	Uiso	1.00
H82	H	0.13734	0.58852	0.00000	0.00000	Uiso	1.00
H83	H	0.08016	0.51578	0.00000	0.00000	Uiso	1.00
H84	H	0.10458	0.44481	0.00000	0.00000	Uiso	1.00
H85	H	0.89537	0.34019	0.00000	0.00000	Uiso	1.00
H86	H	0.72351	0.41172	0.00000	0.00000	Uiso	1.00

H87	H	0.78839	0.43142	0.00000	0.00000	Uiso	1.00
H88	H	0.86293	0.45122	0.00000	0.00000	Uiso	1.00
H89	H	0.82706	0.31560	0.00000	0.00000	Uiso	1.00
H90	H	0.75281	0.29471	0.00000	0.00000	Uiso	1.00
H91	H	0.91995	0.43558	0.00000	0.00000	Uiso	1.00
H92	H	0.36933	0.04417	0.00000	0.00000	Uiso	1.00
H93	H	0.32470	0.95840	0.00000	0.00000	Uiso	1.00

Table S2. Kinetic parameters of pseudo-first-order and pseudo-second-order models for Au^{3+} adsorption of ECUT-iCOF-5.

Adsorbent	$q_{e,\,exp}$ (mg·g^{-1})	pseudo-first-order			pseudo-second-order		
		$q_{e,cal}$ (mg·g^{-1})	k_1 (min^{-1})	R^2	$q_{e,\,cal}$ (mg·g^{-1})	k_2 (g·mg^{-1}·min^{-1})	R^2
ECUT-iCOF-5	2326.666667	2184.6563	0.0508963	0.9652	2201.360344	0.00188	0.9964

Table S3. A comparison in Au^{3+} Adsorption/Extraction rate among reported materials and our case.

Materials	Extraction capacity mg/g	References
ECUT-iCOF-5	3260	This work
ECUT-COF-29	3714	Chem. Commun., 2024, 60, 4950-4953
PEIIAC	3078	Sci. Rep. 2021, 11, 17836 .
MoS-TpTa-1.5	2564.8	Sep. Purif. Technol., 2024, 338,126599
Ptriaz-CN-A	2090	Nat. Commun. 2023, 14, 263
rGo	1860	Nat. Commun. 2023, 13, 4472
PYTA-PATA-COF	1834	Angew. Chem. Int. Ed. 2024, e202317015
COF-HNU25	1725	Angew. Chem. Int. Ed. 2023, e202300459
COP-224	1354	Chem. Mater., 2020 32, 12, 5343–5349
COP-TPC6	1157	Chem. Eng. J. 2023, 464, 142459
Fe_3O@SiO@COF-DMSA	1116	Sep. Purif. Technol. 2025, 353, 128582
JNM-100	954	Nat. Commun. 2022, 13, 7771
Tp-BTD-AA	946	ACS Sustainable Chem. Eng. 2022, 10, 30, 9719–9731
COF-V-S-β-CD	820.8	Sep. Purif. Technol. 2024, 239, 125218

Table S4. Isotherm parameters of Langmuir and Freundlich models for Au^{3+} adsorption of ECUT-iCOF-5.

Adsorbent	Langmuir model				Freundlich model		
	$q_{e,\,exp}$ ($mg \cdot g^{-1}$)	K_L ($L \cdot mg^{-1}$)	q_m ($mg \cdot g^{-1}$)	R^2	K_F ($mg^{1-1/n} \cdot g^{-1} \cdot L^{-1/n}$)	$1/n$	R^2
ECUT-iCOF-5	3200	0.06527	3260	0.9651	1.403×10^3	-6.8493	0.9728