Pore-Size Engineering of Imine-Linked Covalent Organic Frameworks for Decoupling Th(IV) Adsorption Capacity and Kinetics

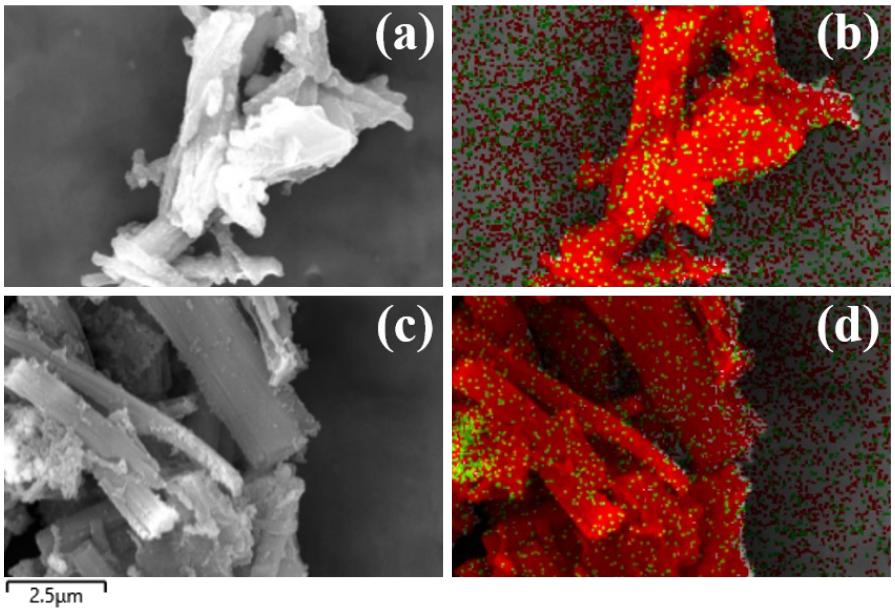
S1 Synthesis of COF-1:

TFPPy (62.1 mg) and PyTTA (56.7 mg) were added to 10 mL Pyrex tubes, followed by 1 mL of mesitylene, 1 mL of dioxane, 0.7 mL of N, N-dimethylacetamide and 0.2 mL of acetic acid (3 mol/L). Ultrasound for 3 minutes. Subsequently, the tubes were subjected to flash freezing with liquid nitrogen at 77K and degassed three times through a freeze-pump-thawing cycle. After that, heat the tube at 140℃ for 72 hours. When the reaction is completed, cool the tube to room temperature, clean it with N, N-dimethylacetamide, and purify the resulting yellow precipitate with anhydrous tetrahydrofuran using the Soxhlet extraction method for 24 hours. Finally, the material was vacuum-dried at 120℃ to obtain the earth-yellow solid powder COF-1, with a yield of 90.2mg and a yield rate of 76%.

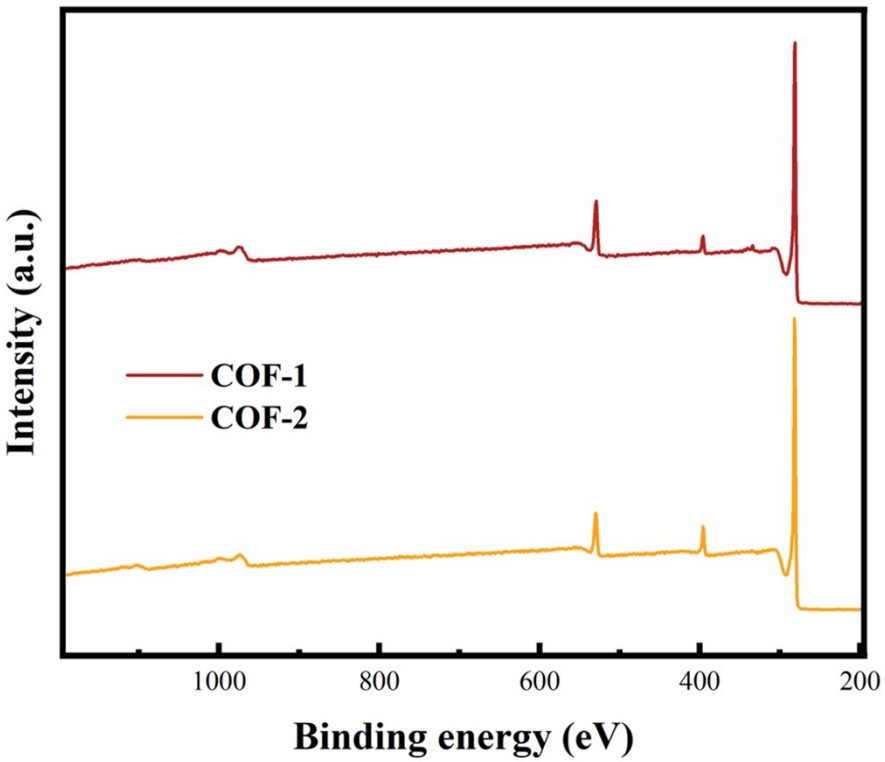
S2 Synthesis of COF-2:

TFPPy (15.0 mg) and PDA (5.22 mg) were added to 10 mL Pyrex tubes, o-dichlorobenzene/n-butanol mixed solvent (1 mL, volume ratio 1:1) and acetic acid (6 M, 0.1 mL) were added successively. The mixture was ultrasonically treated for 10 minutes, then degassed through three cycles of freezing - degassing - thawing, and sealed under vacuum. The mixture was heated and reacted at 120 ° C for 96 hours. After the reaction was completed, the precipitate was collected, washed with tetrahydrofuran, and then vacuum-dried overnight at 120 ° C. Eventually, yellow powder-like COF-2 was obtained.

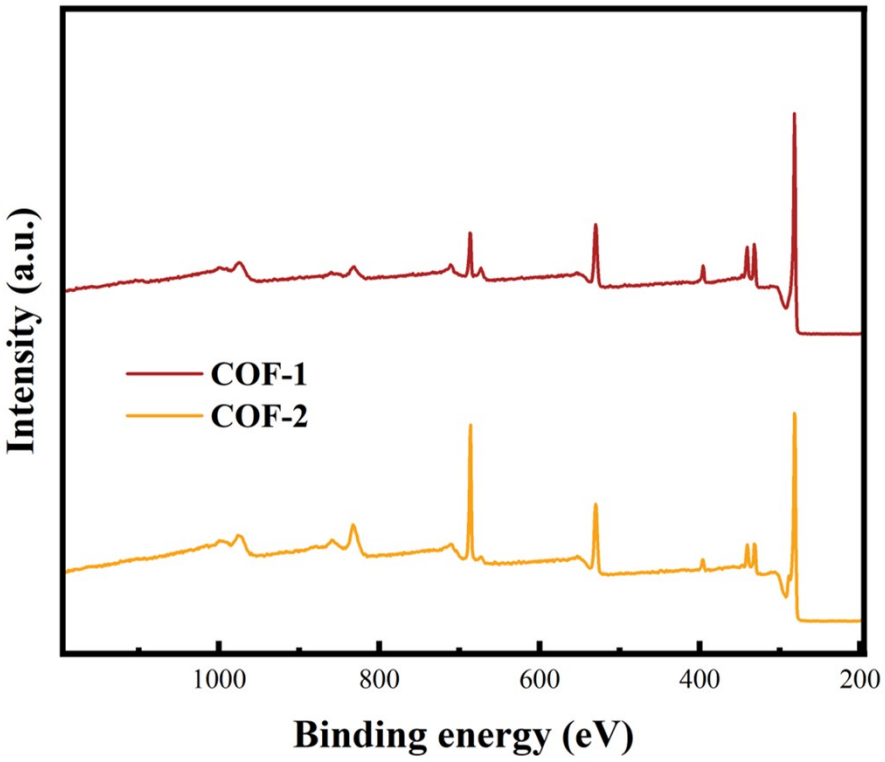
S3 SEM (a) and EDS (b) images of COF-1 after Th(IV) adsorption, as well as SEM (c) and EDS (d) images of COF-2 after adsorption



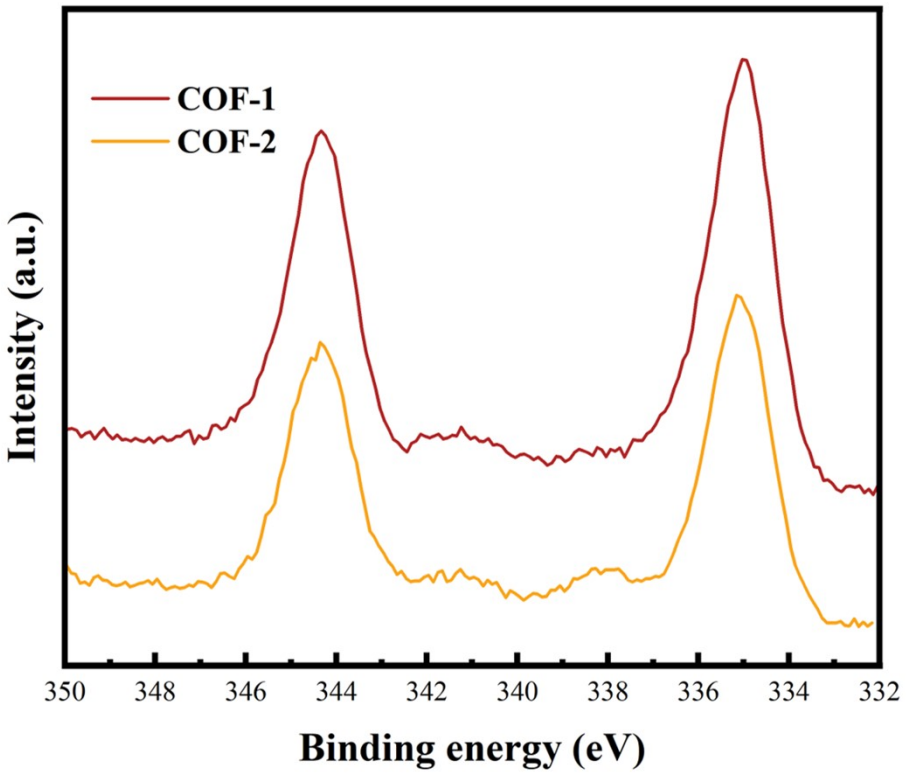
S4. XPS spectra of COF-1 and COF-2 before Th(IV) adsorption



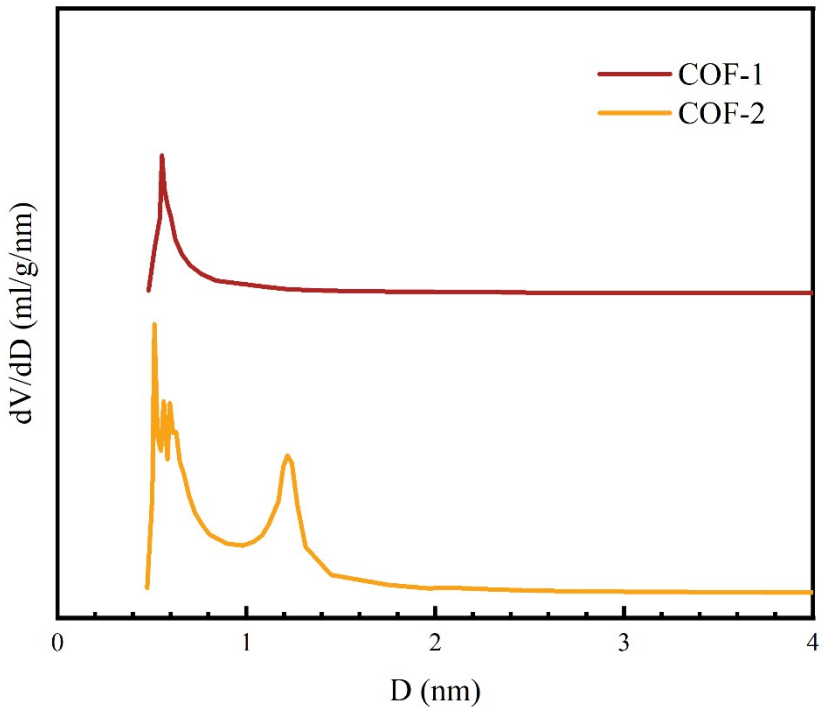
S5. XPS spectra of COF-1 and COF-2 after Th(IV) adsorption



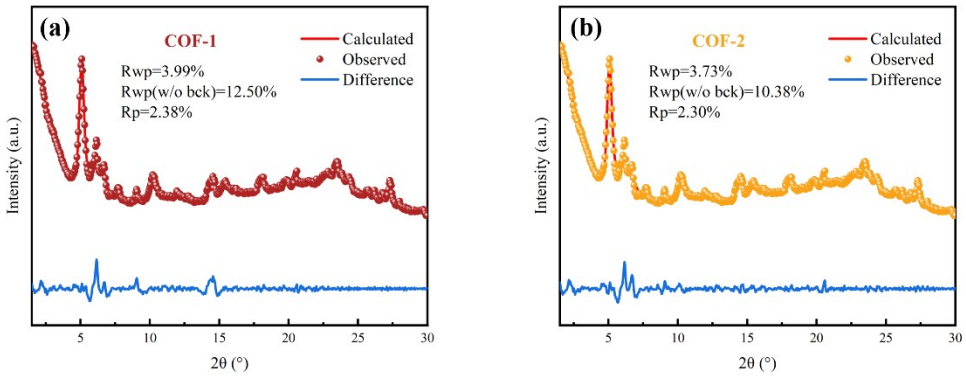
S6. Th 4f high-resolution XPS spectra of COF-1 and COF-2 after Th(IV) adsorption



S7. Pore size distributions of COF-1 and COF-2 determined by non-local density functional theory (NLDFT) analysis.



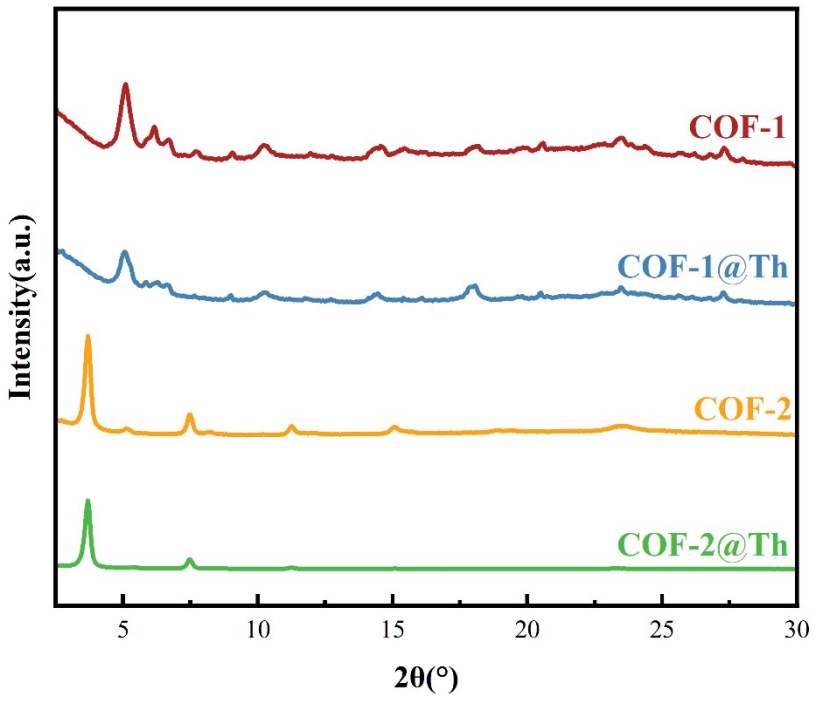
S8. Pawley refinement profiles of simulated and experimental PXRD patterns for COF-1 and COF-2, with Rwp values indicating goodness of fit.



S9. Elemental composition (EDS) and normalized adsorption capacity of COF-1 and COF-2.

Sample	N content (wt%)	Active site density* (mmol/g)	Q_e (mg/g)	Q_{mmol} (mmol/g)	Ratio (Q_{mmol} /site)
COF-1	29.30	20.93	200	0.862	0.0412
COF-2	26.14	18.67	178	0.767	0.0411

S10. Powder X-ray diffraction (PXRD) patterns of COF-1 and COF-2 after five consecutive adsorption-desorption cycles.



S11. Performance comparison of recently reported adsorbents for Th(IV) adsorption

Material	Type	Q_m ($mg \cdot g^{-1}$)	Equilibrium time	Key design strategy
SiO_2@Al-MOF	MOF-based composite	1707.0	~300 min	Silica reinforcement; O-donor sites
TAPT-DHTA COF	COF (N,O-functionalized)	1394.0	~60 min	Bidentate N,O-chelating ligands
Al-MOF	MOF	1324.6	~180 min	High-density carboxylate sites
Py-TFlm-25 COF	COF (imidazole)	808.0	~1 min	Imidazole N-sites (Im vs. C=N)
Oxygen-rich microporous carbon	Carbon	625.0	—	Oxygen functional groups + micropore sieving
ABI-COF	COF (imidazole)	617.0	~3 min	High imidazole content N-sites
3D-Por-COF-A	COF (porphyrin)	575.2	~20 min (90%)	Porphyrin + imine dual N-sites
Hb-TMT COF	COF (sp^2c)	543.5	~5 min	Hydroxyl-functionalized N,O synergy
DhaTph COF	COF (Lewis base)	525.0	~90 min	Lewis base C=N and –OH sites
MNPs-SA@Cu MOF	MOF composite	434.8	~10 min	Magnetic alginate-Cu MOF beads
DFB-TMT COF	COF (sp^2c)	377.4	~3 min	sp^2c-conjugated triazine N-sites
UiO-66-PO_3	MOF (phosphonic acid)	320.0	~180 min	Phosphonic acid functionalization
g-C_3N_4/AX electrode	Carbon nitride composite	275.7	~30 min	Amidoxime-modified electrode
COF-1 (this work)	COF (imine)	199.8	~40 min	Dense linker → high N-density, capacity-optimized
COF-2 (this	COF (imine)	177.9	~40 min	Open linker → fast

Material	Type	Q_m ($mg \cdot g^{-1}$)	Equilibrium time	Key design strategy
work)				mass transfer, kinetics-optimized