Supporting Information

Towards the Fastest Kinetics and Highest Uptake of Post-Functionalized UiO-66 for Hg^{2+} Removal from Water

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Chemicals

Zirconium(IV) chloride (Sigma-Aldrich, ACS reagent, 99.5%), 2-aminoterephthalic acid (Energy Chemical, ACS reagent, 98%), N,N-dimethylformamide (RCI Labscan, AR., 99.9%), dichloromethane (Scharlau, ACS reagent, 99.9%) formic acid (Scharlau, ACS reagent, 98%–100%), nitric acid (Fisher, ACS reagent, 68–70%), 3,3'-disulfanediyldipropanoic acid (Macklin, ACS reagent, 99%), N,N′-Diisopropylcarbodiimide (Energy Chemical, ACS reagent, 98%), Dithiothreitol (Aladdin, ACS reagent, 97%), caesium fluoride (3A, ACS reagent, 99.5%), mercury(II) sulfate (Riedel-de Haën, ACS reagent, 98%), cadmium nitrate tetrahydrate (Sigma-Aldrich, ACS reagent, 98%), cobalt(II) nitrate hexahydrate (Acros Organics, ACS reagent, 98%),

copper(II) nitrate hemi(pentahydrate) (Sigma-Aldrich, ACS reagent, 98%), zinc nitrate hexahydrate (Sigma-Aldrich, reagent grade, 98%), nickel(II) nitrate hexahydrate (Sigma-Aldrich, ACS reagent, 98.5%) lead(II) nitrate (Sigma-Aldrich, ACS reagent, 99.0%), chromium(III) nitrate nonahydrate (Sigma-Aldrich, ACS reagent, 100%), iron(III) nitrate nonahydrate (Sigma-Aldrich, ACS reagent, 98%) were used without further purification. 1,000 ppm arsenic stock solution was purchased from High-Purity Standards. Deionized water (18.2 M Ω cm) was used. The concentration of HNO_3 in all the heavy metal ion stock solutions is 5%.

General testing and characterization methods

The morphologies of the as-synthesized materials were performed on an SEM (JSM-7800). The samples were gold coated before SEM measurement. The crystal structure was examined on an analytical X-ray diffractometer (Cu Kα radiation λ = 1.54056 Å). Nitrogen adsorption/desorption isotherms were recorded with a Micromeritics 3Flex apparatus at 77 K to determine the Brunauer-Emmet-Teller (BET) surface area. Prior to measuring nitrogen isotherms, the samples were activated by heating to 120°C for 3 hours under vacuum at a pressure of 100 mtorr. The Fourier transform infrared (FTIR) spectra were recorded by a Thermo Fisher Nicolet IS50. The X-ray photoelectron spectroscopy (XPS) was measured by a Kratos Axis Ultra DLD multi-technique surface analysis system. TGA was measured from 25°C to 700°C with a heating rate of 5°C min^{-1}. The chemical bonds of the MOFs were measured using Bruker 400 MHz 1H NMR. Contact angle meter Biolin was used for contact angle measurement.

Synthetic Procedures

1. Synthesis of UiO-66-NH_2 MOFs

UiO-66-NH_2 MOFs were prepared by solvothermal strategy.[1] Zirconium(IV) chloride (1.280 g, 5.4926 mmol) and 2-aminoterephthalic acid (0.995 g, 5.4926 mmol) were added in 200 mL of DMF in a 350-mL screw-capped glass jar, sonicated until fully dissolved. Formic acid (50 mL) was added to the solution, then the glass jar was heated in an oven at 100°C for 24 h for a solvothermal reaction. After cooling, the precipitate was washed by centrifugation with DMF and acetone, each for 3 days, and three times per day. The MOFs were dried overnight in the oven at 100°C before characterization.

2. Post-functionalization of UiO-66-NH_2

UiO-66-A.T. were synthesized with some modifications.[2] 3,3'-Disulfanediyldipropanoic acid (210.3 mg, 1.00 mmol), and diisopropylcarbodiimide (162 μL, 1.03 mmol), UiO-66-NH_2 (10.99 mg, contains approximately 0.2 mmol NH_2 functional groups) were added after added to 40 mL of chloroform, heated in reflux for 7 hours. The sample was filtered and washed with acetone. 10.5 mg of the product and 1 g of dithiothreitol were added into 27 mL of ethanol and stirred at room temperature for 1 day. The sample was filtered and washed with ethanol. The powder was dried overnight in the oven at 100°C before characterization. NMR analysis was performed on digested samples. UiO-66-A.T. was acid digested in a mixture of 0.4 mL DMSO-d_6 and 0.2 mL of CsF in D_2O.

A thiol-disulfide exchange reaction took place to form a stable six-membered ring with an internal disulfide bond. The crosslinking reaction was carried out at five different reaction

conditions (Table S3),[2] chloroform in reflux for 7 hours demonstrated the optimized sulfur mass percentage of 9.56%.

NMR Spectra

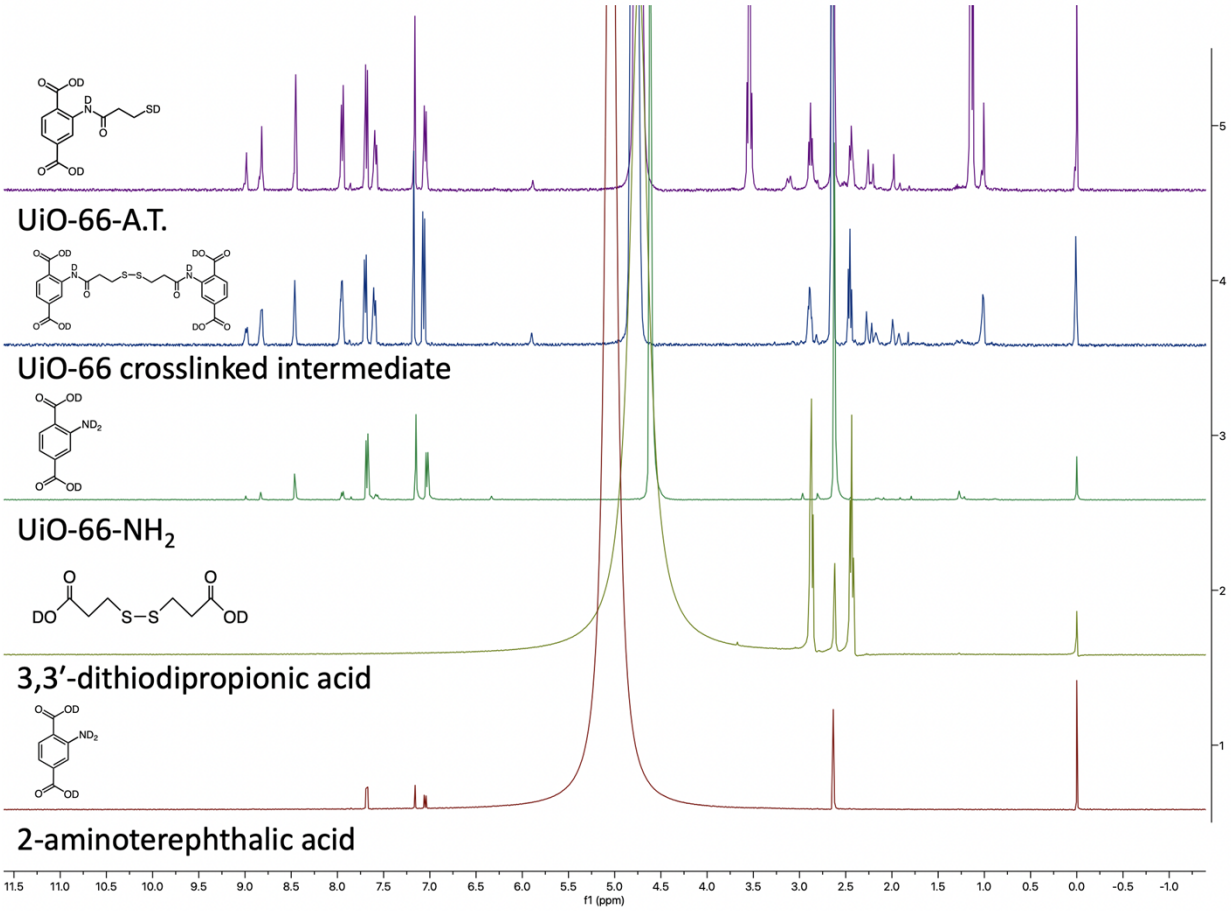

Figure S1a. Stacked ^{1}H NMR spectra of the digested UiO-66-A.T.

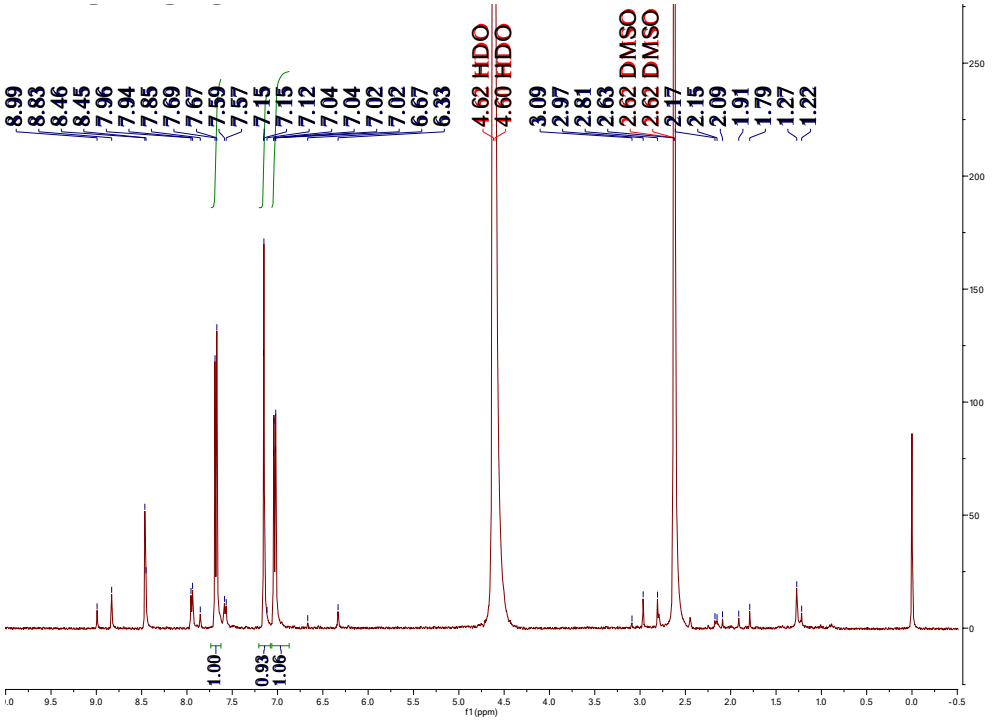

Figure S1b. ^{1}H NMR spectra of the digested UiO-66-NH_2

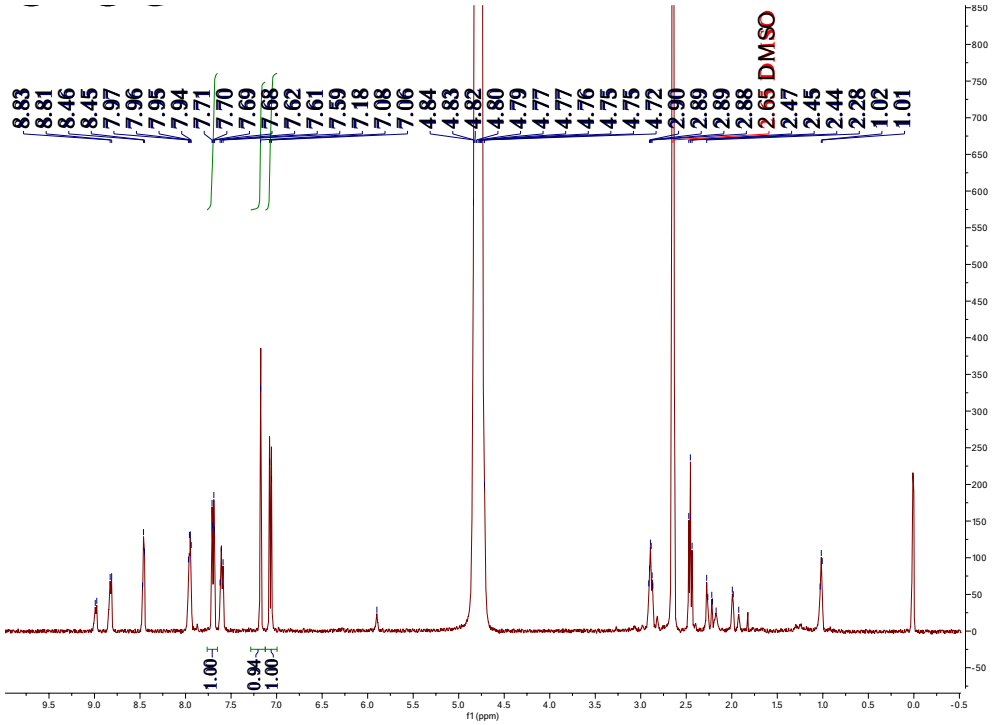

Figure S1c. ^{1}H NMR spectra of the digested UiO-66 crosslinked intermediate before S-S cleavage.

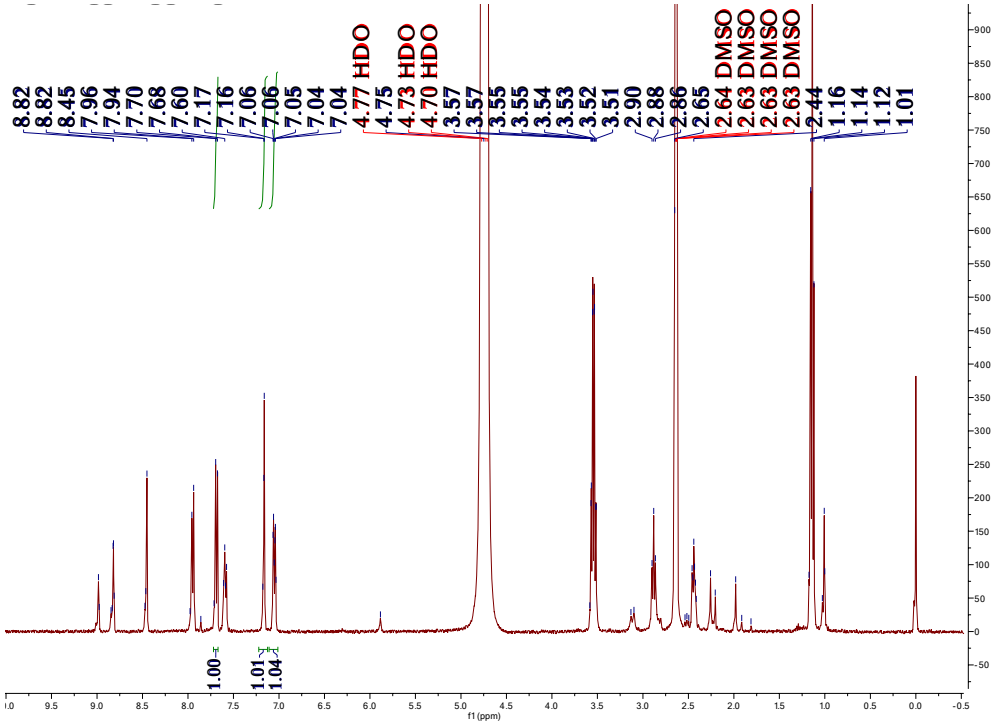

Figure S1d. ^{1}H NMR spectra of the digested UiO-66-A.T.

Figure S1. Digested NMR of the MOFs.

Other data

The adsorption capacity of heavy metal ions was calculated according to Equation S1:

$$q_e = (C_0 - C_e)\frac{V}{m} \ (Eq. S1)$$

where q_e (in mg g^{-1}) is the amount of heavy metal ion adsorbed at equilibrium, C_0 and C_e (in mg L^{-1}) are the initial and equilibrium metal ion concentration, respectively. V (in L) is the volume of the metal solution, and m (in g) is the mass of the adsorbent used.

Freundlich isotherm model (Equation S2) and Langmuir isotherm model (Equation S3) are used to analyze the adsorption kinetics of Hg^{2+} (Fig. S9c, 3f inset).

$$\ln q_e = lnK_f + \frac{1}{n} ln\, C_e \ (Eq. S2)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} b} \ (Eq. S3)$$

where q_{max} is the maximum adsorption capacity, K_f and b are bare Freundlich constant and Langmuir constant, respectively, and n is the dimensionless exponent of Freundlich equation.

Table S1. Mass percentage before and after deprotection obtained by XPS.

Elements	mass %	
	Before deprotection	After deprotection
C	35.65	38.03
N	3.22	3.64
S	11.22	6.24
O	27.25	27.16
Zr	22.67	24.93

Table S2. Hg^{2+} adsorption performance of different adsorbents and post-functionalized UiO-66-NH_2

Adsorbent	Adsorption Capacity (mg g^{-1})	Rate Constant (g mg^{-1} min^{-1})	References
Activated Carbon	2	0.0129	[3]
Zeolite	8	0.0008	[4]
Biomass	20	0.0280	[5]
PTMS-functionalized Silica Gel	132	0.0001	[6]
Thiol functionalized silica nano hollow sphere	210	0.0002	[7]
UiO-66	59	–	[8]
UiO-66-NH_2	103	–	[9]

UiO-66-NH_2	113	–	[10]
UiO-66-NH_2	145	–	[8]
UiO-66-NH_2	208	0.0051	This work
UiO-66-SH	110	0.0114	[11]
Zr-DMBD	172	0.0050	[12]
Zr-L1	193	–	[13]
Zr-L3	245	–	
NSU66	265	–	[14]
Zr-L2	275	–	[13]
Zr-L4	322	–	
UiO-66-AHMT	328 (600 ppm stock solution)	0.0005	[9]
PCN-224-ALA(O)	344	–	[15]
Cys-UiO-66	350	0.0001	[10]
UiO-66-EDTA	372	0.0025	[16]
ZrOMTP	403	–	[17]
PCN-222-MAA(O)	509	–	[15]
UiO-66-QU	556 (600 ppm stock solution)	0.0050	[18]
UiO-66-IT	580 (1500 ppm stock solution)	0.0032	[19]
Zr-MOF-NAC	594 (800 ppm stock solution)	0.0070	[20]

UiO-66-DMTD	671 (700 ppm stock solution)	0.0012	[8]
UiO-66-A.T.	691	0.2823	This work

Table S3. Sulfur mass percentage according to different reaction conditions

Conditions	Attempt	Sulfur mass %	Average sulfur mass %
DMF, rt, 2 days	1	3.88	3.86
	2	3.83	
DMF, 50°C, 7 hours	1	3.01	3.32
	2	3.63	
DCM, rt, 2 days	1	6.24	5.36
	2	4.47	
DCM, reflux, 7h	1	5.03	4.85
	2	4.66	
Chloroform, reflux, 7h	1	7.89	**9.56**
	2	11.22	

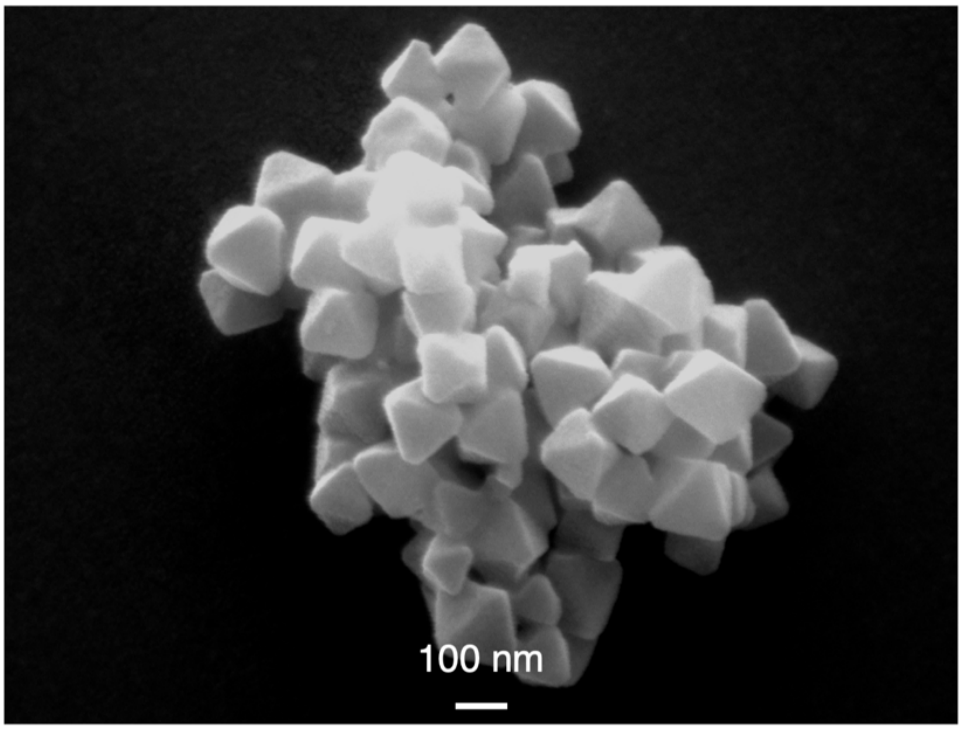

Figure S2. Scanning electron microscopy image of UiO-66-A.T.

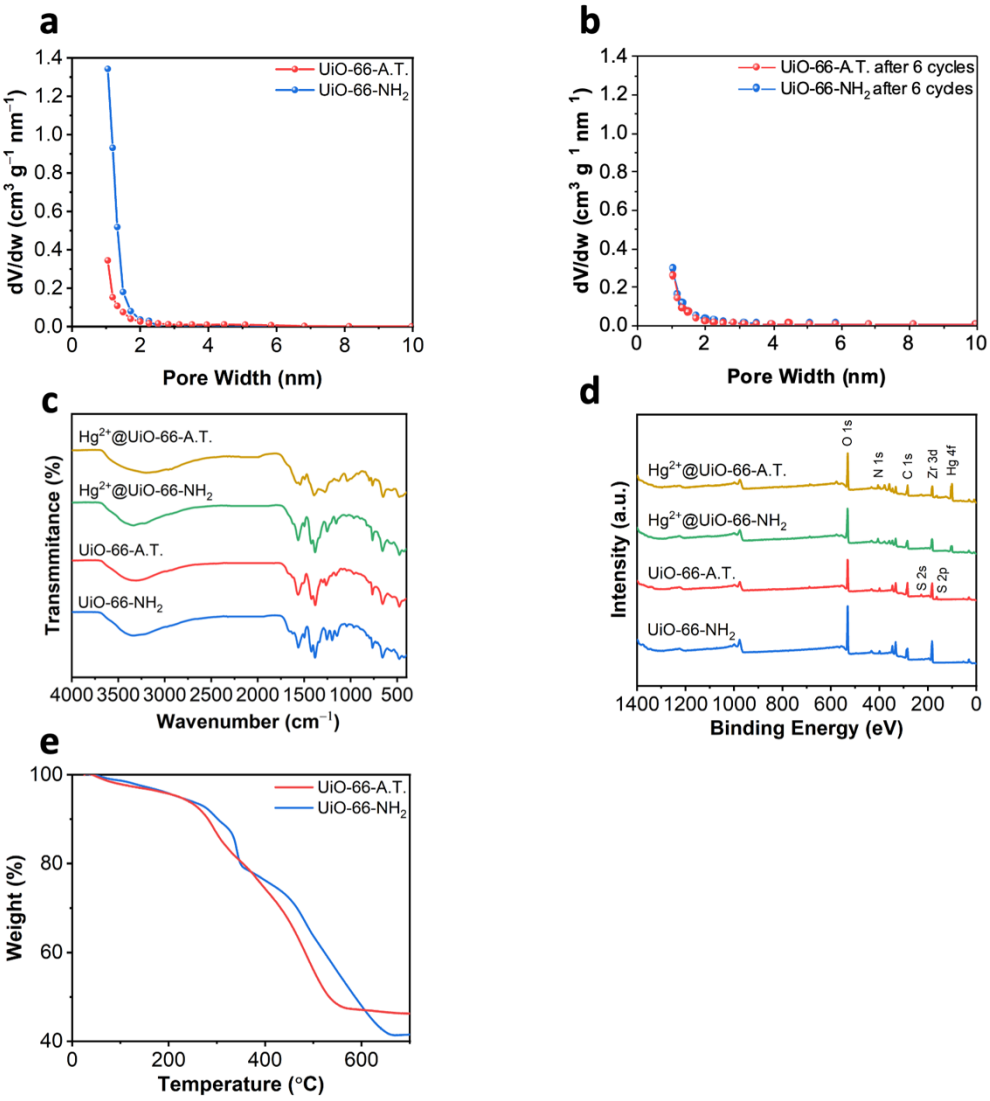

Figure S3. Characterization of UiO-66-MOFs. a, Barrett-Joyner-Halenda (BJH) pore size distributions of UiO-66-A.T. and UiO-66-NH_2. **b,** BJH pore size distributions of UiO-66-A.T. and UiO-66-NH_2 after 6 cycles. **c,** FTIR spectra of UiO-66-A.T., UiO-66-NH_2, Hg^{2+} adsorbed UiO-66-A.T., Hg^{2+} adsorbed UiO-66-NH_2. **d,** XPS spectra of UiO-66-A.T., UiO-66-NH_2, Hg^{2+} adsorbed UiO-66-A.T., Hg^{2+} adsorbed UiO-66-NH_2. **e,** TGA of UiO-66-A.T. and UiO-66-NH_2.

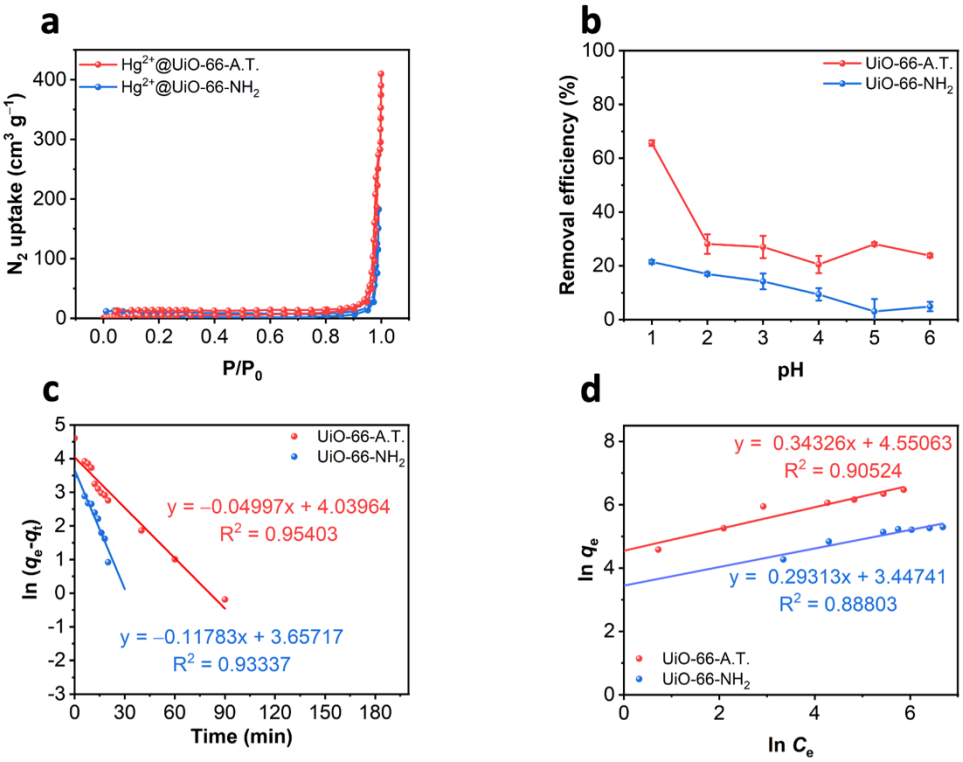

Figure S4. Adsorption performance of UiO-66-MOFs. a, Nitrogen adsorption isotherms of UiO-66-A.T. and UiO-66-NH_2 after Hg^{2+} adsorption. **b,** Removal efficiency at different pH conditions. **c,** Pseudo-first-order fitting. **d,** Linear regression by fitting the equilibrium adsorption data with Freundlich model.

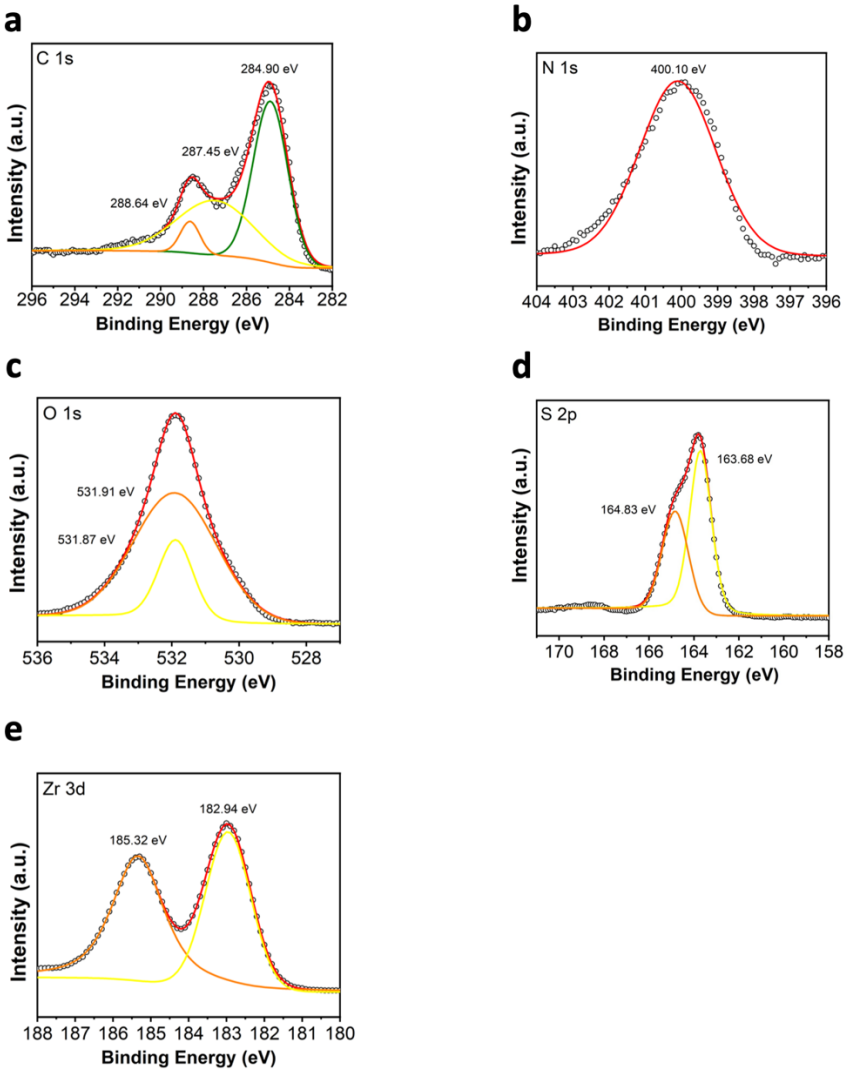

Figure S5. XPS spectra of UiO-66-A.T. a, C 1s spectra. **b,** N 1s spectra. **c,** O 1s spectra. **d,** S 2p spectra. **e,** Zr 3d spectra.

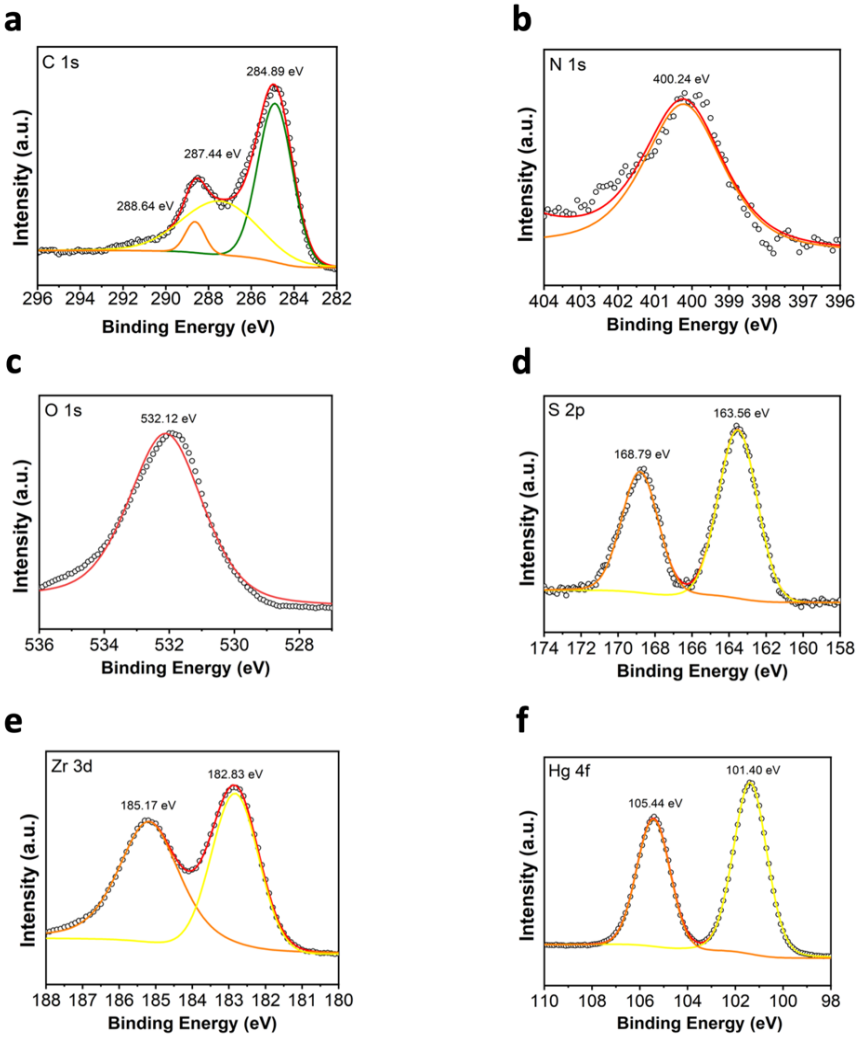

Figure S6. XPS spectra of Hg^{2+}@UiO-66-A.T. a, C 1s spectra. **b,** N 1s spectra. **c,** O 1s spectra. **d,** S 2p spectra. **e,** Zr 3d spectra. **f,** Hg 4f spectra.

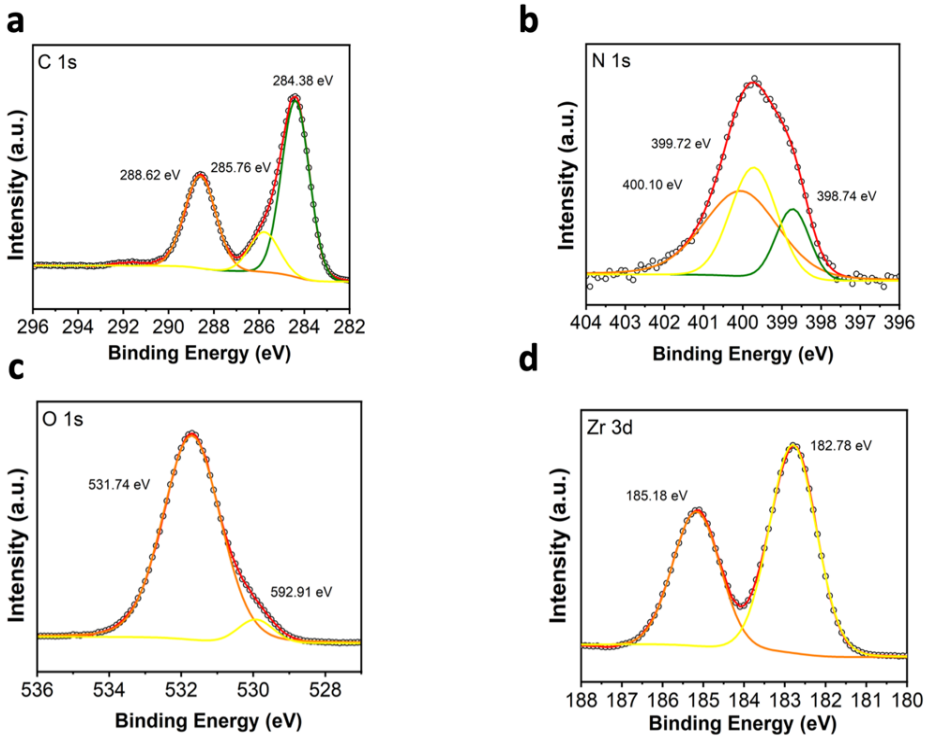

Figure S7. XPS spectra of UiO-66-NH_2. a, C 1s spectra. **b,** N 1s spectra. **c,** O 1s spectra. **d,** Zr 3d spectra.

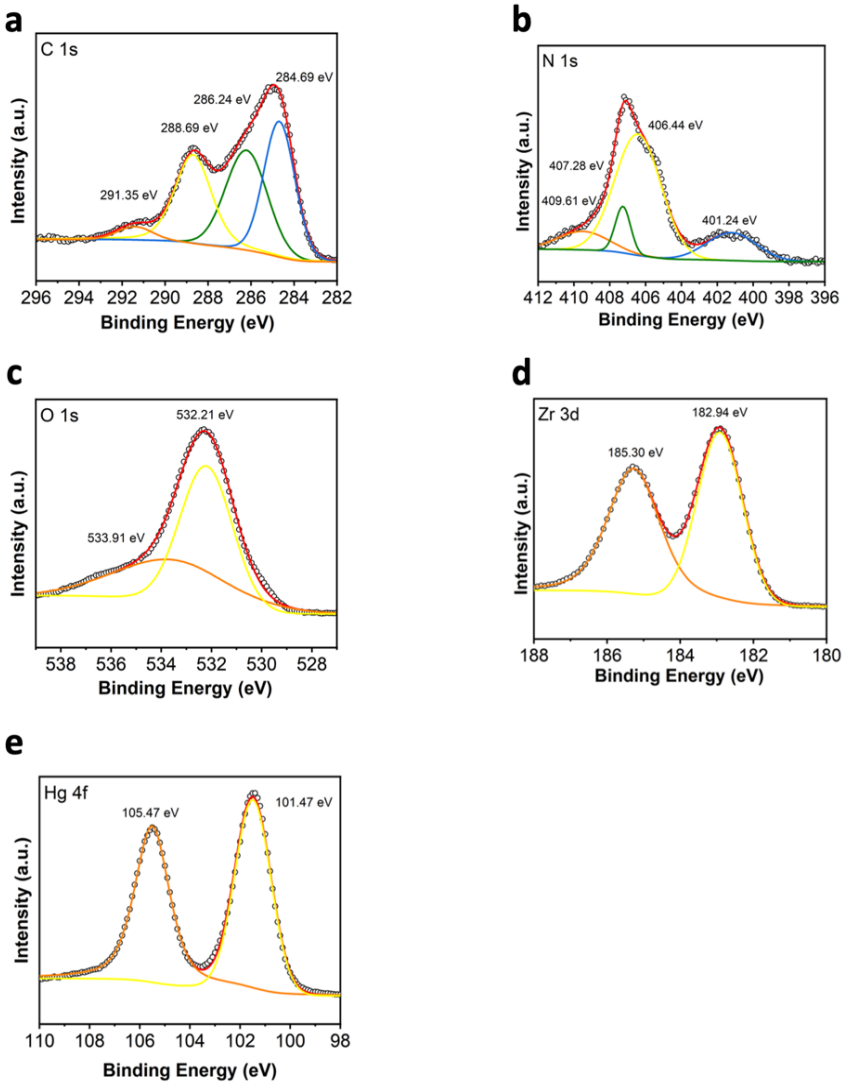

Figure S8. XPS spectra of Hg^{2+}@UiO-66-NH_2. a, C 1s spectra. **b,** N 1s spectra. **c,** O 1s spectra. **d,** Zr 3d spectra. **e,** Hg 4f spectra.

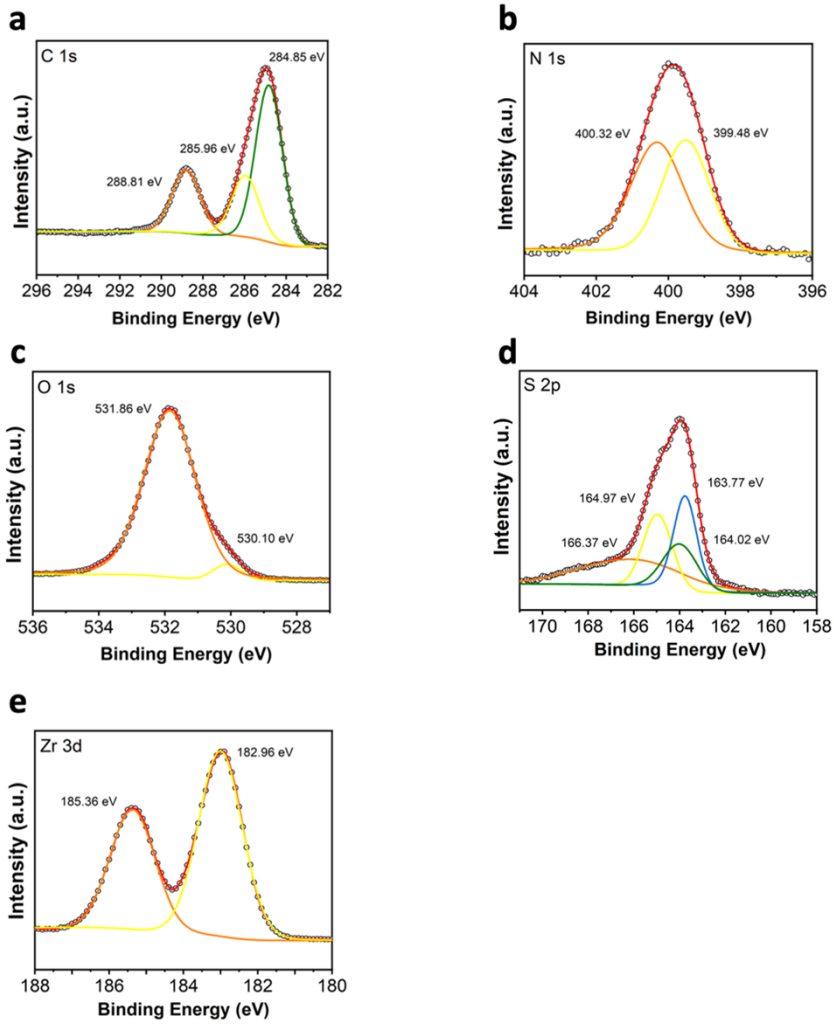

Figure S9. XPS spectra of UiO-66 crosslinked intermediate. a, C 1s spectra. **b,** N 1s spectra. **c,** O 1s spectra. **d,** S 2p spectra. **e,** Zr 3d spectra.

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