Supporting information for

Thiol functionalized covalent organic frameworks for highly selective enrichment and detection of mercury by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry

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Materials and reagents. 1,3,5-tris(4-aminophenyl) benzene (Tab) and 2,5-bis(2-propyn-1-yloxy)-1,4-benzenedicarboxaldehyde (BPTP) were purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co. Ltd. (Jilin, China). Pentaerythritol tetra (3-mercaptopropionate) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). 4-mercaptobenzoic acid was obtained from Tokyo Chemical Industry. (Tokyo, Japan). All metal solutions and solvents were of analytical grade.

Characterization. The structure and composition of the alkynyl-terminated COFs and COFs-SH materials were characterized by scanning electron microscopy (SEM; Nova NanoSEM 230, FEI Czech Republic S.R.O, Czech Republic), transmission electron microscopy (TEM; TECNAI G2 F20, FEI, USA), powder X-ray diffraction (PXRD; DY5261/Xpert3, CEM, USA), N_2 adsorption and desorption (ASAP 2020, Micromeritics, USA), X-ray photoelectron spectroscopy (XPS; ESCALAB 250, VG, USA), nuclear magnetic resonance spectrometer (NMR; AVANCE Ⅲ 500, Bruker, Switzerland), Fourier transform infrared (FT-IR) spectra (AVATAR360, Thermo, USA), element analysis (Vario EL Cube, elementar, Germany).

Adsorption kinetic models

The pseudo-first order and pseudo-second order kinetics models were expressed as follow:

pseudo-first-order kinetics: $\log (Qe-Qt) = \log Qe - K_1t/2.303$

pseudo-second-order kinetics: $t/Qt = t/Qe + 1/K_2Qe^2$

where Qt (mg/g) is the amount of Hg^{2+} adsorbed at time t (min), Qe (mg/g) is the amount of Hg^{2+} adsorbed at equilibrium, K_1 (min^{-1}) and K_2 (g $mg^{-1}min^{-1}$) is represented as the rate constant for pseudo-first-order kinetics pseudo-second-order kinetics.

Adsorption isothermal models

To further evaluate the maximum adsorption capacity of COFs-SH, other adsorption isothermal models, including the Freundlich, and the Temkin models, were employed. The expressions were given as follow:

Freundlich model: $InQe = InK_F + InCe/n$

Temkin: $Qe = BIna_T + BInCe$

where the Freundlich constant and 1/n is the intensity of adsorption, a_T is the equilibrium gas constant, B is the correlation constant of Temkin model.

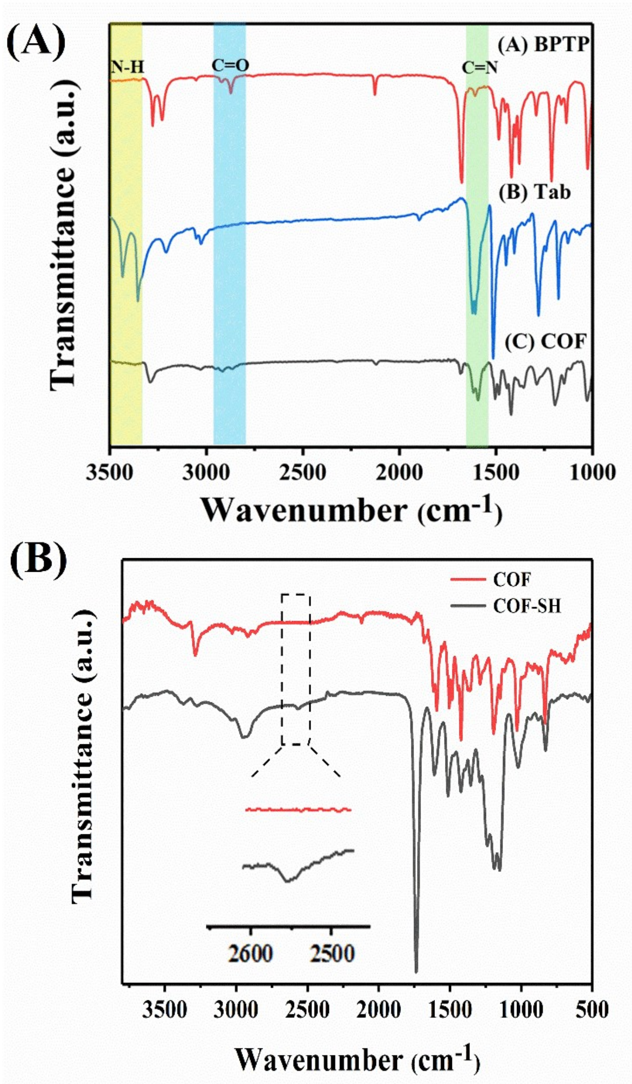

Fig. S1. (A) FT-IR spectra of alkynyl-terminated COFs and corresponding monomers; (B) FT-IR spectra of alkynyl-terminated COFs and COFs-SH;

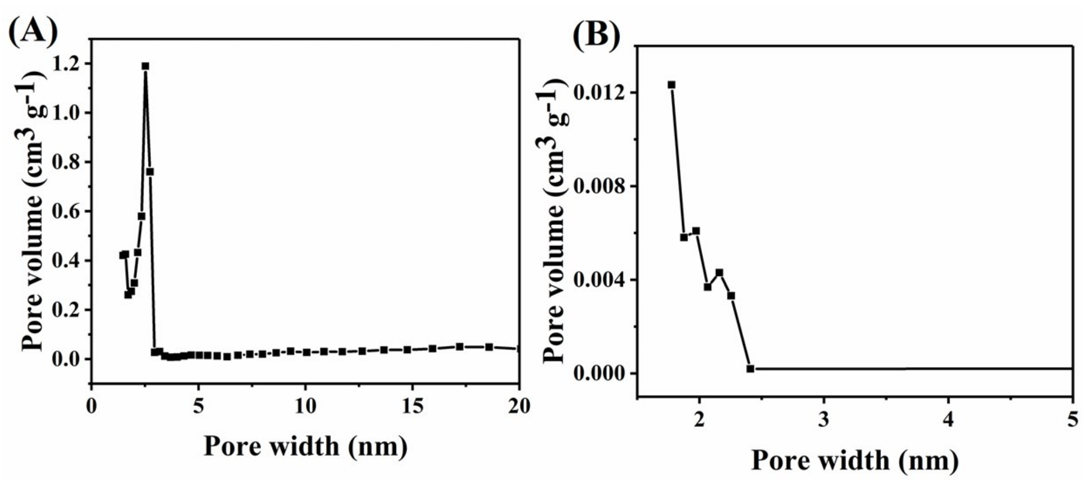

Figure S2. Pore size distribution of (A) alkynyl-terminated COFs and (B) COFs-SH.

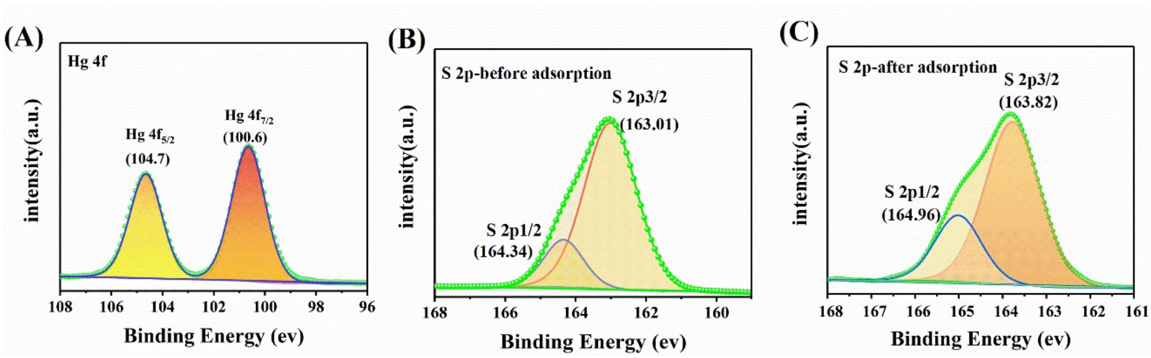

Figure S3. The XPS spectra of (A) Hg 4f; (B) S 2p (before adsorption with COFs-SH); (C) S 2p (after adsorption with COFs-SH).

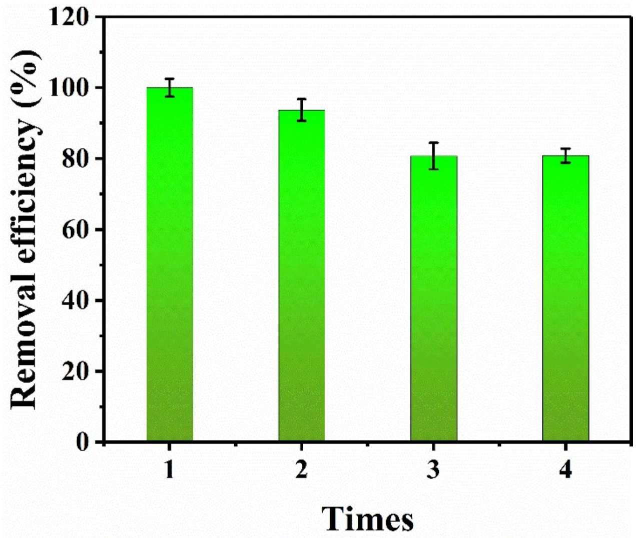

Fig. S4. Reusability of COFs-SH for the adsorption of Hg^{2+}.

Table S1. The elemental analysis of N, C, H, S of COFs-SH.

Sample	N（%）	C（%）	H（%）	S（%）
□	3.00	57.07	4.69	11.36

Table S2. Kinetic parameters for Hg^{2+} adsorption.

Model	Qm (mg/g), cal	K	Qm (mg/g), exp	R^2
Pseudo-first-order	70.87	0.044	572.43	0.9164
Pseudo-second-order	574.71	0.002	572.43	0.9998

Table S3. Adsorption isotherms parameters for Hg^{2+} adsorption.

Adsorption isothermal models	parameters	Hg^{2+}
Freundlich model	K_F	16.86
	n	14.54
	R^2	0.962
Temkin model	a_T	35.17
	B	37.93
	R^2	0.970

Table S4. The reproducibility of the analysis of $Hg^{2+}$with the developed method.

Analytes	shot-to-shot RSD (n=3)[a]	sample-to-sample RSD (n=3)[b]	LOD (pg/mL)
Hg^{2+}	4.5%	4.7%	80

[a] The shot-to-shot RSDs were measured based on 3 shots at different locations on the matrix.

[b] The sample-to-sample RSDs were measured based on 3 samples in different batches.

Table S5. Comparison of the current work with the other references.

Analysis technology	Materials	LODs	References
fluorometric detection	BODIPY	0.37 μM	[45]
electrochemical detection	pS-rGO	0.5 nM	[46]
fluorescence detection	CQDs	12.43 nM	[47]
ICP-OES	MGO	0.05 μg/L	[48]
electrochemical sensor	Zr-DMBD MOFs/3D-KSC	0.05 μM	[49]
MALDI-TOF-MS	Thymine chitosan nanomagnets	0.05 nM	[50]
MALDI-TOF-MS	COFs-SH	80 pg/mL (equal to 396 amoL/μL)	This work