

Supporting Information

Thiol-Grafted Covalent Organic Framework Electrochemical Platforms for Sensitive Detection of Hg(II) Ions

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Table of Contents

Section 1. Experimental section.....	2
Section 2. NMR spectra of monomers.....	5
Section 3. Characterizations	6
Section 4. Tables showing the elemental analysis data and porosity parameters of COFs	8
Section 5. Performance comparison for determination of Hg ²⁺	9
Section 6. Table showing the anti-interference experimental data of COF.....	10
Section 7. Table showing determination of Hg ²⁺ in real water samples.....	11
Section 8. References.....	12

Section 1. Experimental section

1.1 Materials

p-Aminobenzonitrile, trifluoromethanesulfonic acid, 2,5-dibromo-*p*-xylene, CrO₃, potassium vinyltrifluoroborate, Pd(PPh₃)₄, K₂CO₃ were purchased from Energy Chemical (Shanghai, China). Azobisisobutyronitrile (AIBN) purchased from Aladdin Industrial Corporation has been purified prior to the polymerization process. All other solvents and reagents were provided by commonly commercial suppliers and used without further purification unless stated otherwise.

1.2 Synthetic procedure for monomers

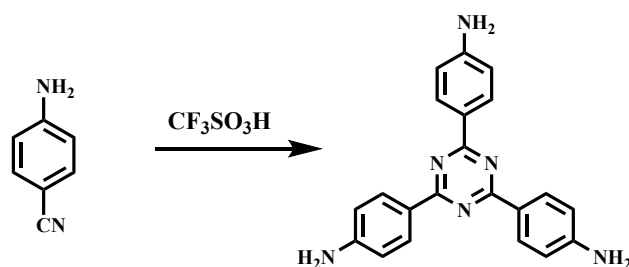
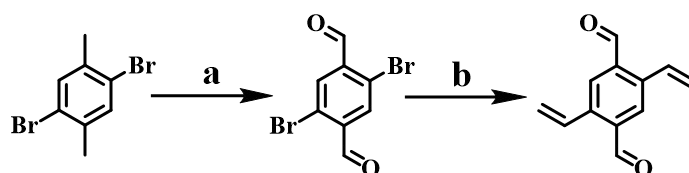


Fig. S1. Synthesis of TAPT.

Synthesis of monomer 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPT)

p-aminobenzonitrile (26 mmol, 3.008 g) was placed in a 50 mL two-necked round-bottomed flask, and 10 mL of chloroform was added, fully stirred in an ice-water bath at 0 °C for 20 min, and then 10 mL of trifluoromethanesulfonic acid was slowly added dropwise to the flask, and then continued to be stirred in an ice-water bath for 30 min, and then stirred at room temperature for 24 h. After the reaction was completed, 50 mL distilled water was added to the solution to dilute, and then 2M NaOH was slowly added to adjust the pH of the solution to weakly alkaline. The solution became turbid and the light yellow solid was precipitated. The solid was collected by filtration and washed with a large amount of distilled water. The obtained product was freeze-dried for 12 h to obtain about 2.4 g of 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (yield 78%).

Synthesis of monomer 2,5-divinyl-terephthalaldehyde (Dva)



Regent: (a) CH₃COOH, (CH₃CO)₂O, H₂SO₄, CrO₃
(b) Pd(PPh₃)₄, potassium vinyltrifluoroborate

Figure S2. Synthesis of Dva.

(1) 2,5-dibromobenzene-1,4-dicarbaldehyde: 2,5-dibromo-p-xylene (0.03 mol, 8 g), acetic acid (40 mL) and acetic anhydride (80 mL) were added into a 250 mL round-bottomed flask, fully stirred, and then concentrated sulfuric acid (28 mL) was slowly added under 0 °C. CrO₃ (12 g) was added to the flask in batches, and the resulting mixture was kept at 0 °C with stirring overnight. After overnight reaction, a dark green slurry was obtained, which was poured into ice water, filtered, and the filter residue was washed with water and methanol. The filter residue was taken and mixed with H₂O (40 mL), ethanol (40 mL) and concentrated sulfuric acid (4 mL), the mixture was refluxed and stirred overnight, and the target product was obtained by filtration, which was directly used in the next step without further purification. Yield: 2.65 g (30%). ¹H NMR (400 MHz, d₆-DMSO, 298K, TMS): δ 10.14 (s, 2H), 8.07 (s, 2H) ppm.

(2) 2,5-divinylterephthalaldehyde: 2,5-dibromobenzene-1,4-dicarbaldehyde (4.0 g, 13.7 mmol), potassium vinyltrifluoroborate (4.57 g, 33.1 mmol), K₂CO₃ (11.3 g, 82.2 mmol) and Pd(PPh₃)₄ (0.456 g, 0.411 mmol) were dissolved in a mixed solvent of toluene (50 mL), THF (50 mL) and H₂O (10 mL). The resulting mixture was heated and stirred at 90 °C under reflux for 24 h with N₂ atmosphere protection. The reaction solution was extracted with ethyl acetate, washed with brine, dried over Na₂SO₄, and the solvent was spin-dried under reduced pressure to obtain the crude product, which was separated and purified by column chromatography, using n-hexane:ethyl acetate=5:1 as the eluent to obtain the target product, The product was a light yellow solid. Yield: 2.10 g (82%). ¹H NMR (400 MHz, d₆-DMSO, 298K, TMS): δ 10.34 (s, 2H), 8.18 (s, 2H), 7.59-7.66 (m, 2H), 5.97 (d, 2H, J = 17.6 Hz), 5.59 (d, 2H, J = 11.2 Hz) ppm.

1.3 Synthetic procedure for COFs

Synthesis of COF_{TAPT-Dva}

A 10 ml glass bottle was preloaded with 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (0.04 mmol, 14.17 mg) and 2,5-divinylterephthalaldehyde (0.06 mmol, 11.18 mg). 5 mL acetonitrile was then added and sonicated for 15 min to fully dissolve the reactants in the bottle. After that, 0.4 mL of acetic acid (HOAc, 15 M) was added to the bottle. Subsequently, the mixture was vigorously shaken and sonicated for 1 min, then stood at room temperature for 72 h. The obtained yellow precipitates were collected by centrifugation and washed three times with dry tetrahydrofuran (THF) and ethanol, respectively. Eventually, the powders were dried under vacuum at 60 °C for 24 h.

Synthesis of COF_{S-CH₃} and COF_{S-SH}

To a mixture of COF_{TAPT-Dva} (100 mg) and azobisisobutyronitrile (AIBN, 10 mg) in a 25 mL Schlenk tube, ethanethiol (4.0 mL) was introduced under N₂ atmosphere. After stirring at 80 °C for 48 h, the obtained product, COF_{S-CH₃} was isolated by filtration, washed with acetone, and dried under vacuum at 50 °C overnight. COF_{S-SH} was synthesized by following the similar procedure except ethanedithiol (4.0 mL) was introduced as a modifying agent.

Synthesis of COF_{S-CH₃@CPE} and COF_{S-SH@CPE}

Graphite powder (75 mg) and COF_{S-CH₃} (25 mg) were preloaded in a 5 ml glass bottle,

subsequently 3 mL acetone was added. The mixture was sonicated for 30 min to evenly disperse the powder in the solvent. After that, the sample bottle was placed in a vacuum oven and dried at 50 °C overnight. The obtained mixture and 30 μ L paraffin oil were thoroughly hand-mixed in a mortar using a pestle for 20 min, and then filled into the pre-prepared Teflon tube with an internal diameter of 3 mm. A copper wire was used for electrode connection. COF_{S-SH} modified carbon paste electrode (COF_{S-SH}@CPE) and the pristine CPE were prepared by following the same procedure. The surface of the working electrode was polished by smoothing the electrode with a weighing paper and dried under an infrared lamp for further usage.

1.4 Instrumental

Fourier Transform Infrared Spectra (FTIR) were recorded on a VARIAN 1000 FT-IR spectrometer (Varian, Inc., Palo Alto, CA, USA) over a range of 400-4000 cm^{-1} . And the samples were prepared by the potassium bromide (KBr) tablet method. Scanning electron microscope (SEM, JSM-7610F JEOL, Japan) was used to capture the morphologies and microstructures of the samples. The N₂ adsorption-desorption isotherms were obtained over an Autosorb-iQ2-MP gas sorption analyzer (Quantachrome, USA). The surfaces areas were calculated using the Brunauer-Emmett-Teller (BET) model of N₂ adsorption isotherms. The pore size distribution curves were performed from the N₂ adsorption isotherms using nonlocalized density function theory (NLDFT). The X-ray diffraction (XRD) pattern was carried out on a Bruker Advance D8 (Bruker, Germany) using Cu/K α rays ($\lambda=1.5418 \text{ \AA}$), with a scan speed of 5° min^{-1} and 2 θ range 2-30°. Elemental analysis (EA, CHNS mode) was operated on a Vario EL Cube elemental analyzer to determine the carbon, nitrogen, hydrogen and sulfur content of the samples. Cyclic voltammograms and Nyquist diagrams of electrochemical impedance spectra were performed on an electrochemical workstation (CHI 760E, CH Instrument Corp, Shanghai) using a standard three-electrode cell. The zeta potential was measured through a potential and nanometer particle size analyzer (Nano ZSE, Zetasizer, U.K.) at different pH values.

1.5 General procedures for electro-sensing of trace mercury ions

Square wave anodic stripping voltammetry (SWASV) was employed to investigate the sensitivity detection. For all measurements, the three electrodes were immersed in a 50 mL beaker containing testing solution, and the solution was stirred using a magnetic stirrer. The pH of the solution containing Hg²⁺ was adjusted to 3.4 by HOAc-NaAc buffer solution. The preconcentration step was performed in a stirred solution for 360 s at a potential of -0.60 V. The stirring was then stopped and after a resting time of 30 s to settle the solution and eliminate the background current. The anodic stripping voltammetric potential range from -0.60 to 0.60 V was performed with the SW frequency of 15 Hz, the pulse amplitude of 50 mV and the dc voltage step height of 4 mV. The electrochemical measurements were carried out at the ambient temperature.

Section 2. NMR spectra of monomers

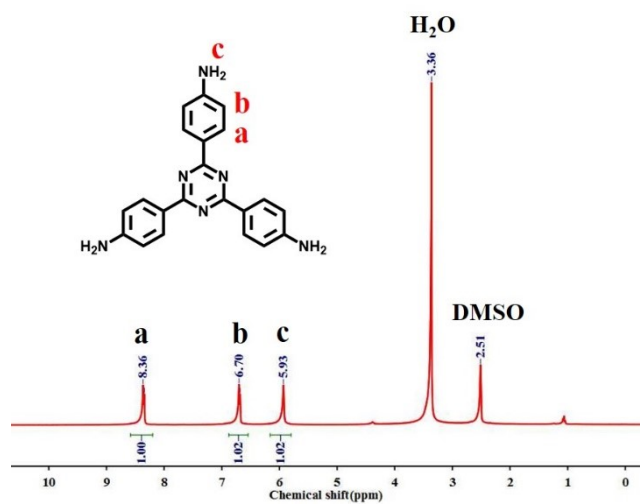


Fig. S3. ^1H NMR spectrum of TAPT.

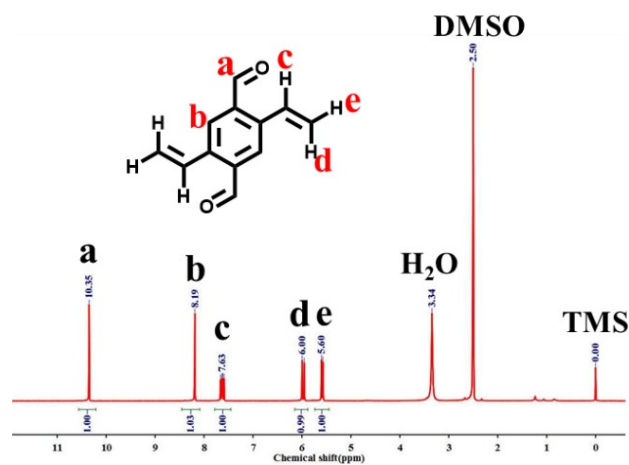


Fig. S4. ^1H NMR spectrum of Dva.

Section 3. Characterizations

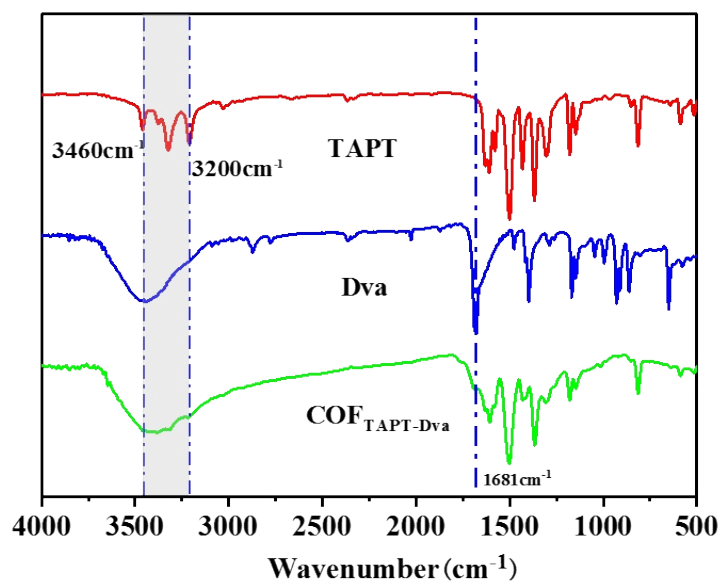


Fig. S5. FT-IR spectra of TAPT, Dva and $\text{COF}_{\text{TAPT-Dva}}$.

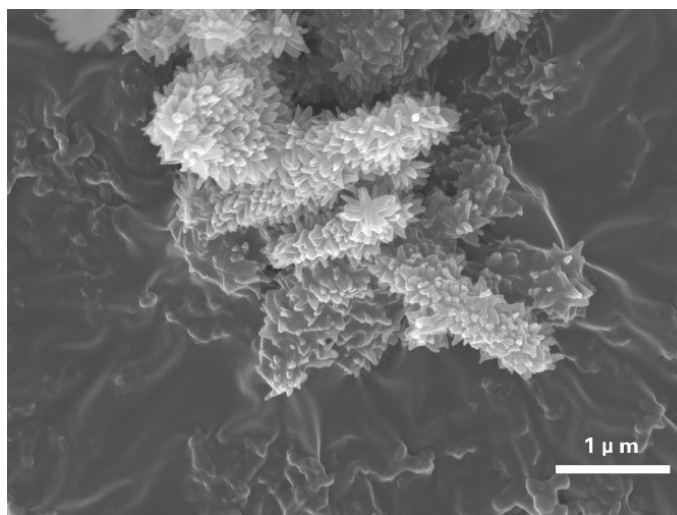


Fig. S6. SEM images of $\text{COF}_{\text{TAPT-Dva}}$.

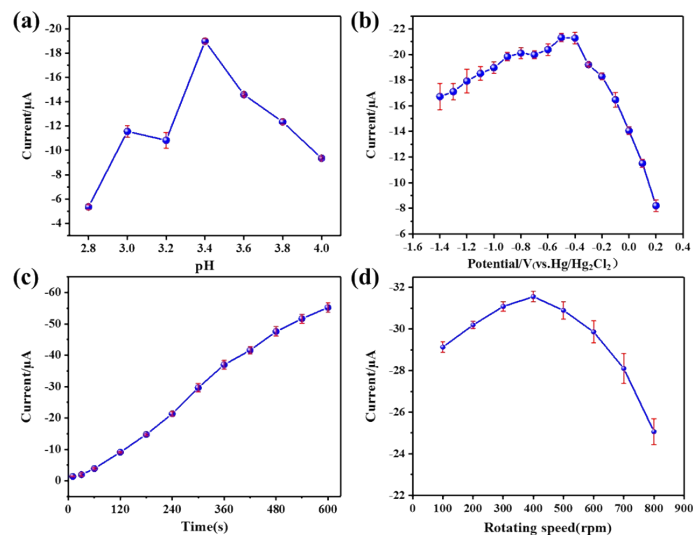


Fig. S7. The effects of (a) pH of acetate buffer solution (b) accumulation potential (c) accumulation time (d) rotating speed on the current signal of Hg^{2+} .

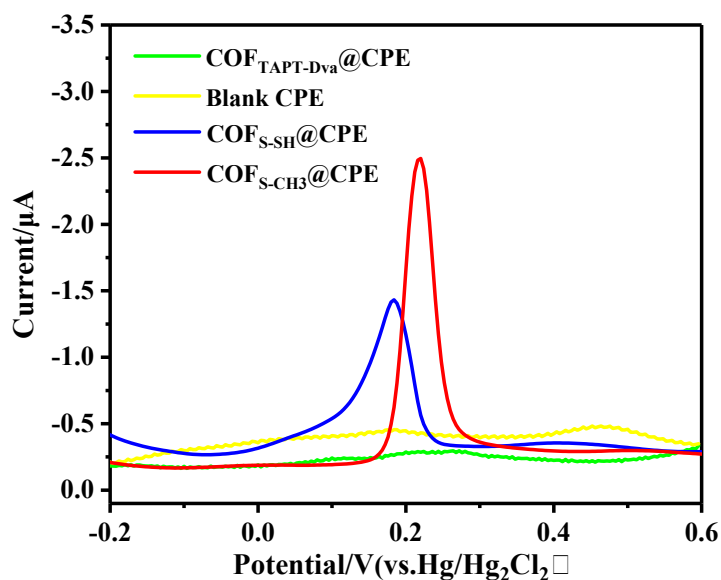


Fig. S8. Square wave anodic stripping voltammetric measurements with bare and modified CPE.

Table S1 Zeta potential data of $\text{COF}_{\text{S-CH}_3}$ and $\text{COF}_{\text{S-SH}}$

Samples	Zeta Potential (mV)	
	pH = 3	pH = 7
$\text{COF}_{\text{S-CH}_3}$	14.96	-0.97
$\text{COF}_{\text{S-SH}}$	--5.35	-16.22

Section 4. Tables showing the Elemental analysis data and Porosity parameters of COFs

Table S2 Elemental analysis data of COF_{TAPT-Dva}, COF_{S-CH3} and COF_{S-SH}

Sample	N (%)	C (%)	H (%)	S (%)
COF _{S-CH3}	13.19	72.19	5.05	9.57
COF _{S-SH}	10.26	58.72	4.08	20.16

Table S3 Porosity parameters of COF_{TAPT-Dva}, COF_{S-CH3} and COF_{S-SH}

Sample	S _{BET} (m ² g ⁻¹)	V _{Total} (cm ³ g ⁻¹)	V _{Micro} (cm ³ g ⁻¹)	V _{Micro} / V _{Total} (%)	Dominant Pore Size (nm)
COF _{TAPT-Dva}	1299.1	0.811	0.328	40	3.43
COF _{S-CH3}	166.4	0.453	0.055	12	1.49, 3.43, 4.72
COF _{S-SH}	84.4	0.219	0.022	10	3.43, 4.51

Section 5. Performance comparison for determination of Hg²⁺

Table S4 Comparison of various modified electrodes for determination of Hg²⁺

Working electrodes	Detection method	Detection limit	Linear range
NanoCB SPE ¹	Amperometry	5 nM	0.05-14.77 ppm
Cu ₂ O@NCs ²	EIS	0.15 nM	1-100 nmol L ⁻¹
Chemical modified CPE ³	ASWASV	0.05 ng mL ⁻¹	0.6-1100 ng mL ⁻¹
Y-DNA ⁴	CV	0.094 nM	1-5 μM
NH ₃ -pn-MWCNT ⁵	SWASV	0.1439 nM	0.02-0.6 μM
MgSiO ₃ modified GCEs ⁶	SWASV	0.375 nM	0.8-2.0 μM
B-doped DLC ⁷	SWASV	4.99 nM	2-25 μg L ⁻¹
Invertase Conductometry ⁸	Conductometry	25 nM	0.1-100 μM
Carbon NPs SPE ⁹	SWASV	5 nM	1-10 μg L ⁻¹
uNPs amplified DNA-Gold electrode ¹⁰	DPV	0.5 nM	1-100 nM
MB tag ¹¹	Amperometry	0.2 nM	0-80 nM
DNA linked luminol AuNPs ¹²	ECL	1.05*10 ⁻¹⁰ M	2-1000 pM
COF_{s-CH3}@CPE	SWASV	0.05 nM	0.1-1.0 ppb
COF_{s-SH}@CPE	SWASV	0.1 nM	0.05-2.4 ppb

Section 6. Table showing the anti-interference experimental data of COF

Table S5 Effect of interfering ions on the detection of 0.25 ppb Hg²⁺ by COF_{S-SH}@CPE

Interfering ions	Concentration (ppb)	RSD (%)
K ⁺	25	-0.97
Mg ²⁺	25	2.93
Al ³⁺	25	2.86
Li ⁺	25	-1.64
Sr ⁺	25	-1.82
Fe ³⁺	25	-1.19
Co ²⁺	25	2.84
Mn ²⁺	25	-1.25
Zn ²⁺	25	-2.17

Section 7. Table showing determination of Hg^{2+} in real water samples

Table S6. Determination of Hg^{2+} in different water samples using $\text{COF}_{\text{S-CH}_3}$ @CPE by SWASV.

Sample	Added (ppb)	Found (ppb)	Recovery (%)	RSD % (n=3)
Lake water	0	-	-	-
	0.2	0.195	97.7	2.5
	0.4	0.417	104.3	2.1
Tap water	0	-	-	-
	0.2	0.191	95.6	3.1
	0.4	0.411	102.7	1.7

Section 8. References

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