

Rapid Removal of HgCl_2 from Actual Industrial Wastewater by Covalent Organic Framework

Tingqiong Ma

tianqiongma@nju.edu.cn

Nanjing University

MingYang Li

Nanjing University

Yuanxin Gu

Nanjing University

Xiangyu Pei

Nanjing University School of Chemistry,

Wenguang Du

Nanjing University School of Chemistry,

Rongming Xu

Nanjing university

Hongshuai Wu

Nanjing University School of Chemistry,

Manyi Yang

Nanjing University

Weiming Zhang

Nanjing University

Article

Keywords:

Posted Date: September 17th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11017526/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.
[Read Full License](#)

Additional Declarations: There is **NO** Competing Interest.

1 Rapid Removal of HgCl₂ from Actual Industrial Wastewater by Covalent
2 Organic Framework

3
4 Mingyang Li^{1,2,3,4†}, Yuanxin Gu^{3,5,6†}, Xiangyu Pei^{2,3,4}, Wenguan Du^{2,3,4}, Rongming Xu¹,
5 Hongshuai Wu^{2,3,4}, Manyi Yang^{3,5,6*}, Weiming Zhang^{1*} and Tianqiong Ma^{2,3,4*}

6
7 Affiliations

8 ¹State Key Laboratory of Water Pollution Control and Green Resource Recycling, School of
9 Environment, Nanjing University, Nanjing 210023, China.

10 ²School of Chemistry, Nanjing University, Nanjing 210023, China.

11 ³State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210023,
12 China.

13 ⁴Key Laboratory of High Performance Polymer Materials and Technology, Ministry of
14 Education, Nanjing University, Nanjing 210023, China.

15 ⁵Jiangsu Key Laboratory of Green Energy Catalysis and Intelligent Chemical Engineering,
16 Nanjing University, Nanjing 210023, China.

17 ⁶The Institute of Green Chemistry and Engineering, Nanjing University, Suzhou, Jiangsu
18 215163, China

19 Corresponding authors: Manyi Yang (manyi.yang@nju.edu.cn), Weiming Zhang
20 (wmzhang@nju.edu.cn), Tianqiong Ma (tianqiongma@nju.edu.cn)

22 **Abstract**

23 Mercury contamination imposes long-lasting ecosystem risks due to its high
24 diffusivity and persistent toxicity, underscoring an urgent need for rapid
25 pollutant removal in emergency heavy metal remediation scenarios.
26 Conventional negatively-charged adsorbents sequester ionic Hg(II) via
27 electrostatic attraction yet lose efficacy in chloride-laden real-world industrial
28 wastewater, where abundant chloride drives Hg(II) conversion to neutral HgCl₂
29 that evades electrostatic capture. Here, we design a superhydrophilic
30 methylthio-functionalized β -ketoenamine-linked covalent organic framework
31 (TP-S-COF) for ultrafast HgCl₂ elimination. TP-S-COF removes 98% HgCl₂
32 from 10 mg L⁻¹ solutions within 10 s and meets the 0.001 mg L⁻¹ effluent
33 standard in 30 s, while attaining 84% removal from complex high-salinity
34 industrial wastewater over the same 10 s timeframe; its kinetics outstrip
35 conventional adsorbents by orders of magnitude. Mechanistic analyses uncover
36 synergistic effects of β -ketoenamine carbonyl-oxygen and methylthio groups,
37 which break H₂O-HgCl₂ clusters to boost HgCl₂ diffusion and adsorption.
38

39 Maintext

40 Rapid response to heavy metal leakage incidents is critical for controlling
41 long-term pollutant diffusion, thereby preventing escalated complications and
42 costs from multi-regional remediation efforts. This is particularly vital for
43 highly toxic, highly diffusive, and bioaccumulative mercury(II) ion. The
44 traditional approach to removing mercury(II) ion from wastewater involves
45 using solid adsorbents like activated carbon¹, resins^{2,3} and zeolites^{4,5}, however,
46 these methods often suffer from limited capacity and slow adsorption rates. To
47 improve mercury(II) ion removal efficiency, adsorbents with high surface areas
48 and ordered pore structures are essential, as they offer more adsorption sites and
49 diffusion channels to increase the adsorption capacity and enhance kinetics.

50 Covalent organic frameworks (COFs)⁶ represent a novel class of
51 crystalline porous materials characterized by their design flexibility and
52 precisely tunable pore environments, making them promising candidates for
53 mercury removal⁷. While most existing research predominantly addresses Hg(II)
54 removal from high-concentration solutions using Hg(NO₃)₂ as the mercury
55 source^{8,9}, there is a lack of studies focusing on the removal of HgCl₂ at lower
56 concentrations, which are more prevalent in real-world scenarios. In real
57 industrial wastewater, elevated chloride concentrations promote stable mercury
58 chloride complex formation (e.g., HgCl₂)^{10,11}. These molecular complexes
59 reduce electrostatic interactions between mercury species and adsorption sites,
60 making the removal more challenging than free Hg(II) ions from Hg(NO₃)₂.
61 Additionally, HgCl₂ undergoes spontaneous hydration to form H₂O-HgCl₂
62 clusters, which impair molecular mobility and consequently result in
63 insufficient adsorption kinetics, thereby significantly hindering effective
64 mercury remediation¹²⁻¹⁵.

65 We herein develop a methylthio-functionalized COF (TP-S-COF) with
66 remarkable HgCl₂-trapping capacity. Starting from 10 mg L⁻¹ HgCl₂, the
67 material removes 98% of the contaminant in 10 s (residual: 200 µg L⁻¹) and

attains the 0.001 mg L^{-1} effluent limit at 30 s, exhibiting far faster adsorption kinetics than conventional adsorbents. As shown in Fig. 1, TP-S-COF was synthesized by using 1,3,5-triformylphloroglucinol (TP) and 2,5-bis(methylsulfanyl)benzene-1,4-diamine (S-PDA) as building blocks. The methylthio groups in S-PDA were designed as the adsorption sites, which could strongly interact with mercury through Hard and Soft Acids and Bases (HSAB) interaction and meanwhile more stable than thiol groups¹⁶ in actual wastewater treatment under acidic conditions. The keto-enamine linkages formed in TP-S-COF provide stable framework in acidic wastewater, while the carbonyl groups facilitate the breaking down of $\text{H}_2\text{O-HgCl}_2$ cluster through H-bonds formation during HgCl_2 capture, thereby synergistically enhancing HgCl_2 sequestration. The ultrafast HgCl_2 capture kinetics of TP-S-COF was conclusively validated in real industrial wastewater matrices, thereby demonstrating its unparalleled potential for emergency Hg-contaminated water treatment through kinetic superiority.

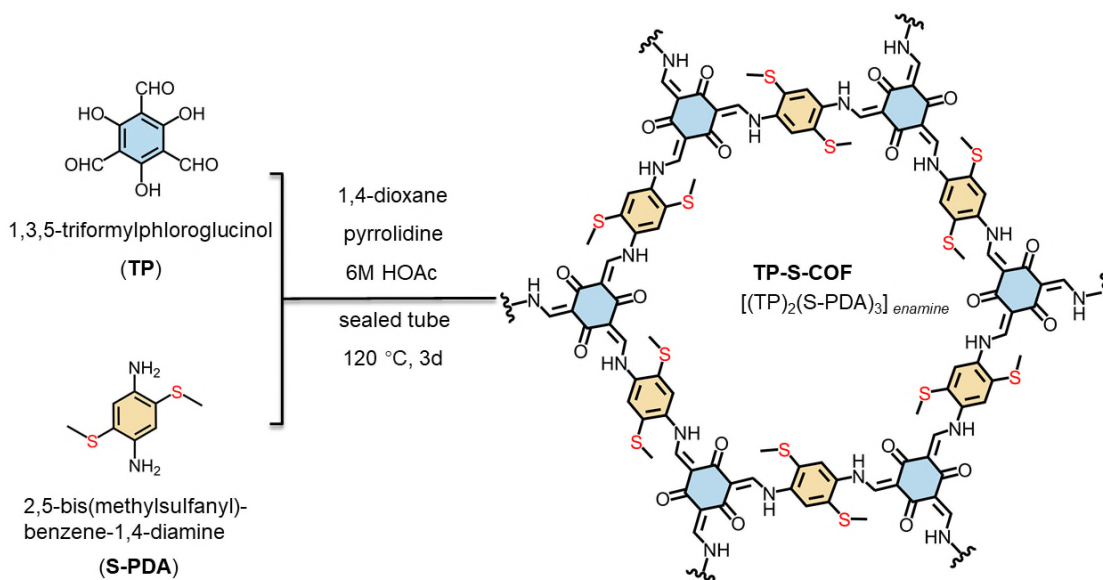


Fig. 1| Synthetic route of TP-S-COF. TP-S-COF was synthesized *via* Schiff base reaction between aldehyde linker TP and amino linker S-PDA.

Results and Discussion

Synthesis and structure characterization of TP-S-COF

A Pyrex tube was charged with 1,3,5-triformylphloroglucinol (TP, 0.1 mmol, 21 mg), 2,5-bis(methylsulfanyl)benzene-1,4-diamine (S-PDA, 0.15 mmol, 30 mg), 1,4-dioxane (1.0 mL), pyrrolidine (0.02 mL) and aqueous acetic acid (6 M, 0.1 mL). The mixture was flash-frozen at 77 K, degassed through three freeze–pump–thaw cycles, sealed under vacuum and heated at 120 °C for 3 days. The precipitate was isolated by filtration, washed with tetrahydrofuran (THF) and acetone. After vacuum drying at 80 °C for 24 h, a deep red powder was obtained and further identified as TP-S-COF. The formation of keto-enamine linkages of TP-S-COF was first confirmed by Fourier-transform infrared (FT-IR) spectroscopy (Fig. 2a). Compared with those of TP and S-PDA, the FT-IR spectrum of TP-S-COF shows the emergence of a characteristic C–N stretching band¹⁷ at 1256 cm^{−1}, together with pronounced attenuation of the aldehyde C=O stretching vibration at 1654 cm^{−1} and the amine N–H stretching band at 3332 cm^{−1}, confirming the successful condensation between monomers. ¹³C cross-polarization/magic angle spinning (CP-MAS) solid-state nuclear magnetic resonance (ssNMR) spectroscopy^{16,17} further validates the formation of TP-S-COF (Fig. 2b). Compared to the monomers, the resonance signals assigned to the aldehyde carbon (192 ppm) and the carbon atoms adjacent to the amino group (118 ppm) in S-PDA are strongly attenuated, corroborating keto-enamine condensation between aldehyde and amine linkers¹⁷. The formation of β -ketoenamine is evidenced by the resonance signals at 145 ppm (enamine carbon in =C–NH), 115 ppm (α -enamine carbon), and 180 ppm (ketone carbon).

The crystallinity of TP-S-COF was characterized by powder X-ray diffraction (PXRD). The PXRD pattern of TP-S-COF shows diffraction peaks distinct from those of the monomers, indicating the formation of a new crystalline phase (Fig. 2c, Supplementary Fig. 1). On the basis of the structural characteristics of two-dimensional COFs, an AA stacking structural model was

constructed, and the corresponding simulated PXRD pattern matches well with the experimental profile (Supplementary Fig. 2 and Supplementary Table 1). Pawley refinement¹⁸ further validates the structural model, providing unit cell parameters of $a = b = 22.55(6)$ Å, $c = 6.80(0)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ in $P6/m$ space group, with the unweighted residual factor $R_p = 3.16\%$ and the weighted residual factor $R_{wp} = 4.08\%$ (Fig. 2c). The PXRD peaks at $2\theta = 4.8^\circ$, 8.3° , and 26.9° for TP-S-COF can be assigned to the lattice planes of (100), (110), and (001), respectively. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) reveal uniform aggregates composed of small particles (Supplementary Figs. 3 and 4). Energy-dispersive X-ray spectroscopy (EDS) elemental mapping further confirmed the homogeneous distribution of sulfur within the framework (Supplementary Fig. 5). N₂ sorption isotherm was recorded at 77 K to characterize the porosity of TP-S-COF. The Brunauer-Emmett-Teller (BET) surface area of TP-S-COF was calculated to be 445.3 m² g⁻¹ (Fig. 2d). Pore-size distributions derived from nonlocal density functional theory (NLDFT) showed a pore width centered at 13.2 Å, which is similar to the theoretical pore size obtained from structural model (13.8 Å, Fig. 2e).

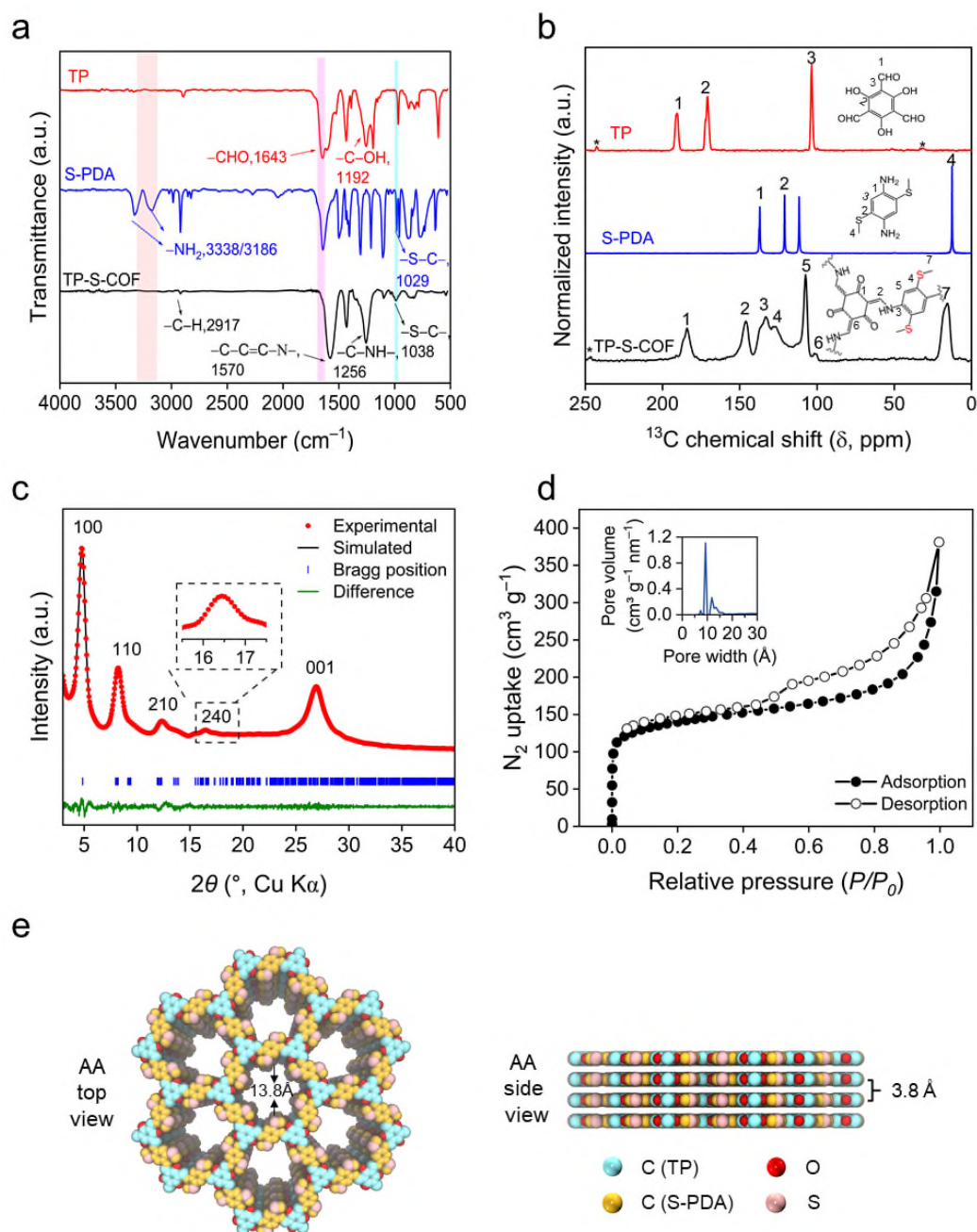


Fig. 2| Structural characterization of TP-S-COF. **a**, Comparison of FT-IR spectra of TP (red), S-PDA (blue) and TP-S-COF (black). **b**, Comparison of ¹³C CP-MAS ssNMR spectra of TP (red), S-PDA (blue) and TP-S-COF (black). The spinning sidebands are denoted with asterisks. **c**, Experimental PXRD pattern of TP-S-COF (red), Pawley-refined profile (black), difference curve (green). **d**, N₂ sorption isotherm measured at 77 K. Inset: pore-size distribution. **e**, Structural model illustrating the pore architecture of TP-S-COF.

HgCl₂ adsorption performance

The HgCl₂ adsorption capability of TP-S-COF in aqueous solution was first evaluated through equilibrium adsorption experiments. For each HgCl₂ concentration (5~300 mg L⁻¹), TP-S-COF (5 mg) was added to 20 mL solution, stirred at 25 °C for 2 h to achieve adsorption equilibrium. The residual HgCl₂ concentrations were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES). The resulting equilibrium isotherm (Fig. 3a) fits well to the Langmuir model, indicating a monolayer adsorption mechanism for HgCl₂ on TP-S-COF. As a result, TP-S-COF exhibited a maximum adsorption capacity of 1079.2 mg g⁻¹, which surpassed almost every other benchmark material in the removal of HgCl₂ (Supplementary Fig. 7 and Supplementary Tables 2 and 3)².

Given the acidic nature of industrial wastewater^{10,11}, the HgCl₂ removal performance of TP-S-COF was investigated at pH 2~7 (Fig. 3b). TP-S-COF maintained an average HgCl₂ removal efficiency of ~95% across this range, demonstrating remarkable chemical stability under acidic conditions. Notably, PXRD shows no detectable structural degradation after TP-S-COF was immersed in solution at pH 0 for 24 h (Supplementary Fig. 8). This stability is attributed to the keto–enol tautomerism, which converts imine linkages into more stable C–N bonds¹⁷.

To evaluate TP-S-COF's adsorption selectivity for HgCl₂ in complex environmental matrices, competitive adsorption experiments were conducted in simulated wastewater containing 10 mg L⁻¹ HgCl₂ and equal mass concentrations (10 mg L⁻¹ each) of competing ions: Na(I), K(I), Ca(II), Mg(II), Zn(II), Ni(II), Cu(II), Cd(II), and Pb(II) (Fig. 3c). TP-S-COF achieved a HgCl₂ removal efficiency of 98.2%, while exhibiting negligible adsorption toward Na(I), K(I), Ca(II), Mg(II), and Zn(II), and limited uptake of Cu(II) (23.6%) and Pb(II) (31.3%). Even at elevated concentrations of Na(I) (1000 mg L⁻¹) and Ca(II) (200 mg L⁻¹), the HgCl₂ removal efficiency remained above 98% (Fig.

3c inset and Supplementary Fig. 9). This exceptional selectivity arises from the tailored framework architecture and the strong binding affinity between sulfur functionalities and mercury species, demonstrating the adsorption potential of TP-S-COF under complex environmental conditions.

Moreover, TP-S-COF exhibited excellent recyclability, maintaining an HgCl_2 removal efficiency above 93.5% over 15 consecutive adsorption-desorption cycles (Fig. 3d). Negligible changes can be observed in PXRD patterns of TP-S-COF after cycling experiments (Supplementary Fig. 10). The structural stability of this framework demonstrates exceptional potential for industrial-scale wastewater remediation.

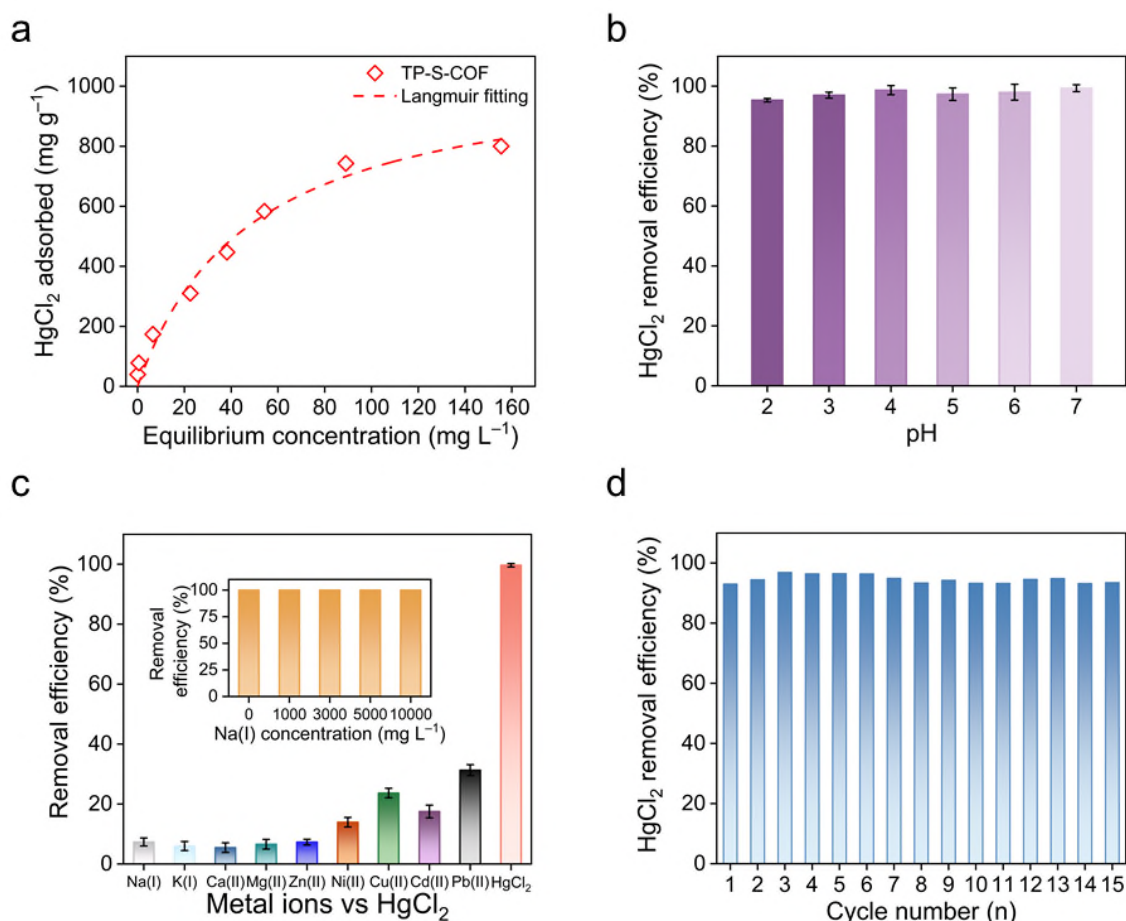


Fig. 3| Adsorption performance of TP-S-COF toward HgCl_2 . **a**, HgCl_2 adsorption isotherms at pH 5 (2 h) with nonlinear Langmuir fitting. **b**, HgCl_2 removal efficiency across different pH conditions. **c**, Removal efficiency for HgCl_2 and competing metal ions in a mixed-ions system (10 mg L^{-1} each) and the effect of elevated Na(I)

concentration on HgCl_2 removal (inset). **d**, Recycling performance of TP-S-COF for HgCl_2 removal.

Fast kinetics and real-world wastewater treatment

The ability to achieve ultrafast adsorption kinetics is crucial for wastewater treatment in practical application, as it is essential for responding to mercury (II) ion leakage incidents¹⁹⁻²¹. We therefore investigated the adsorption kinetics of TP-S-COF under low HgCl_2 concentration (10 mg L^{-1}) (Fig. 4a and Supplementary Fig. 11). TP-S-COF exhibited exceptionally rapid adsorption kinetics, removing 98% of HgCl_2 from a 10 mg L^{-1} solution within 10 s and lowering the residual concentration to below 0.001 mg L^{-1} within 30 s, thereby meeting the applicable effluent standard. Kinetic fitting using the pseudo-second-order model yielded an $R^2 > 0.99998$ and a rate constant (k_2) of $37.2 \text{ g mg}^{-1} \text{ min}^{-1}$ (Fig. 4a inset and Supplementary Fig. 12), surpassing reported porous adsorbents by factors of 3.5 to over 200 (Supplementary Fig. 13 and Supplementary Table 4).

The rapid uptake is consistent with the pronounced hydrophilicity of TP-S-COF, as supported by water contact-angle (CA) measurements^{22, 23}. A water droplet was completely absorbed within 1.4 s ($\text{CA} = 0^\circ$), indicating a superhydrophilic wetting and efficient water transport²³ (Fig. 4c and Supplementary video 1). In addition, the abundant keto groups ordered pore channels are expected to promote interfacial interactions and accelerate mass transfer during HgCl_2 capture.

The wetting and dispersibility of TP-S-COF were further corroborated by dispersion tests. Upon addition of 20 mg TP-S-COF to aqueous media such as water, rapid sedimentation occurred under static conditions without mechanical agitation (Fig. 4d–e and Supplementary videos 2 and 3). By contrast, conventional carbon-based adsorbents—including resins and activated carbon—remained persistently suspended under identical static processing protocols (Fig. 4f). After vigorous shaking, TP-S-COF maintained excellent

dispersibility, while other materials exhibited a tendency to agglomerate. Together, these results highlight the favorable interfacial properties and dispersion characteristics of TP-S-COF, which facilitate accelerated HgCl₂ uptake and enable time-critical treatment.

To assess practical applicability, TP-S-COF was further tested in real industrial wastewater. A wastewater sample obtained from Jiangsu NJU Environmental Technology Co., Ltd. was spiked with HgCl₂ to simulating mercury-contaminated effluent (see Methods). Owing to its complex composition, the wastewater exhibited high ionic strength, containing Ca(II) (120 mg L⁻¹), Mg(II) (140 mg L⁻¹), and Cu(II) (25 mg L⁻¹), corresponding to 12, 14 and 2.5 times higher than those used in laboratory mixed-ion experiments (Fig. 4b inset). Upon introducing TP-S-COF (5 mg) into 20 mL of contaminated wastewater, the HgCl₂ concentration decreased from 15.6 mg L⁻¹ to below 2.5 mg L⁻¹ within 10 s, corresponding to an 84% removal efficiency. Equilibrium was achieved within 30 s, with over 99% removal and residual concentration to below 0.1 mg L⁻¹ (Fig. 4b). Moreover, TP-S-COF maintained its performance over 10 adsorption-desorption cycles without observable degradation (Supplementary Fig. 14), underscoring its robustness. The fast adsorption kinetics and high stability indicated the strong potential of TP-S-COF for emergency response to water pollution under real-world conditions.

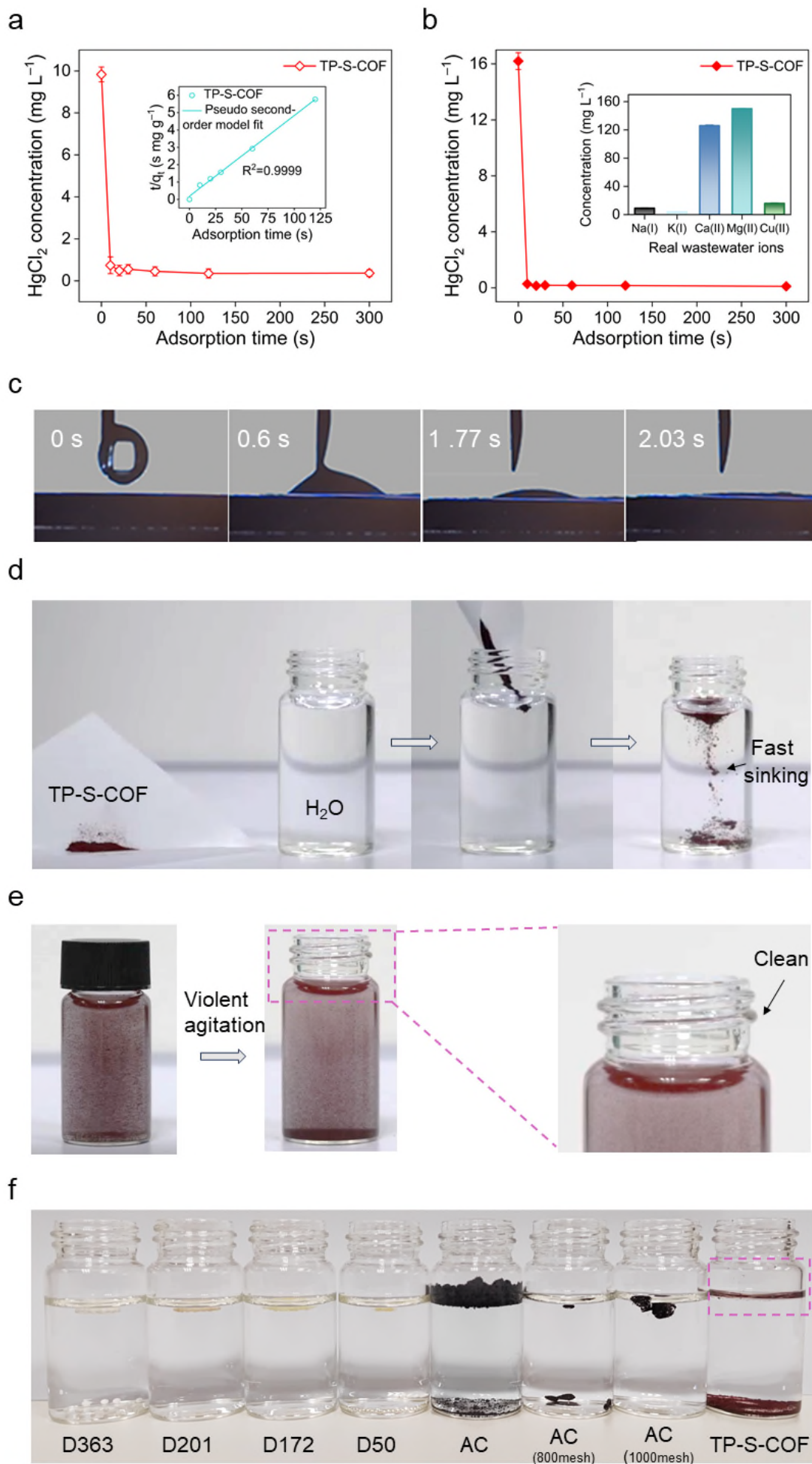


Fig. 4| Hydrophilicity and dispersion behavior of TP-S-COF. **a**, HgCl₂ adsorption kinetics at an initial HgCl₂ of 10 mg L⁻¹ (pH 5, 25 °C). Inset: Pseudo-second-order kinetic fit. **b**, HgCl₂ adsorption kinetics in real industrial wastewater (HgCl₂ concentration: 15.6 mg L⁻¹, pH 4, 25 °C). **c**, Time-resolved water contact-angle measurements on TP-S-COF, showing rapid wetting. **d**, Settling behavior of TP-S-COF in water. **e**, Adhesion behavior of TP-S-COF on glass surfaces under agitation. **f**, Settling behavior of conventional carbon-based adsorbents in water.

Mechanism insights for rapid removal

Combined computational and experimental approaches elucidated the molecular mechanism behind TP-S-COF's ultrafast HgCl₂ adsorption in water. Molecular dynamics (MD) simulations were first carried out to decipher how framework functional groups modulate the HgCl₂ hydration shell and drive interfacial adsorption at the molecular level, with four systems investigated: bulk water (H₂O), TP-S-COF, TPPA-COF, and TFP-S-COF (Supplementary Fig. 15). In these models, TPPA-COF was designed without methylthio groups, while TFP-S-COF lacked keto functionalities (Fig. 5a–c). This setup enabled a systematic assessment of the individual and cooperative contributions of the sulfur and oxygen moieties to HgCl₂ adsorption.

In our initial design, the carbonyl oxygen sites in TP-S-COF were engineered to disrupt the H₂O-HgCl₂ hydration shell through hydrogen bonding, thereby accelerating and enhancing HgCl₂ adsorption. To quantitatively evaluate the disruption of the H₂O-HgCl₂ cluster, radial distribution functions (RDFs) between Hg and water oxygen atoms (g_{Hg-ow}) were calculated. The RDFs revealed a first Hg–Ow coordination shell centered at 0.26 nm, extending to 0.36 nm. Integration to this cutoff gave coordination numbers of 3.82, 3.28, 1.54, and 1.28 water molecules for HgCl₂ in bulk water, TPPA-COF, TFP-S-COF, and TP-S-COF, respectively (Fig. 5d). These results indicate a substantial reduction in Hg-water coordination in the presence of COF frameworks, with methylthio groups exerting a stronger disruptive effect than

keto groups. The dual-functional TP-S-COF achieved the lowest Hg–water coordination number, highlighting the synergistic interplay between methylthio and keto moieties, which underpins high-affinity HgCl₂ adsorption and guides future sorbent design.

To further elucidate this synergistic effect, the RDFs for Hg–S (g_{Hg-S} , Fig. 5e) and Hg–O (g_{Hg-O} , Fig. 5f) were analyzed. The Hg–S RDFs exhibited two distinct coordination shells centered at 0.32 nm and ~0.47 nm, with corresponding coordination numbers of 0.31 and 2.93 for TP-S-COF, compared with 0.12 and 2.00 for TFP-S-COF (Fig. 5e). These results indicate stronger and more extensive Hg–S binding in TP-S-COF, suggesting that the incorporation of keto oxygen sites enhances Hg–S interactions through synergistic effects. For Hg–O interactions (Fig. 5f), both TP-S-COF and TPPA-COF displayed first coordination shells centered at 0.28 nm. However, TP-S-COF exhibited a significantly higher coordination number (0.84 vs. 0.29), suggesting that keto oxygen atoms provide additional stabilization of Hg species after S-induced desolvation. The Hg–N RDFs (g_{Hg-N}) provided in the Supplementary Information (Supplementary Fig. 16) support these conclusions. Collectively, these RDF results are consistent with a cooperative adsorption mechanism in which methylthio sulfur sites promote disruption of the HgCl₂ hydration shell, thereby increasing the probability of close Hg–framework contacts, while keto oxygen atoms provide auxiliary stabilization to the adsorbed Hg species. This dual functionality perturbs the hydration shell more effectively than either moiety alone, as reflected by the reduced Hg–O_w coordination and enhanced Hg–framework coordination in TP-S-COF.

To quantify the relative contributions of sulfur and oxygen functionalities, distance-based classification and diffusion coefficient analyses were performed on Hg atoms in the COF-HgCl₂ systems (Fig. 5g and Supplementary Figs. 17–20). Adsorption was defined as Hg atoms residing within the first RDF-derived cutoff distance relative to framework O atoms (Supplementary Fig. 17a) or

within the second Hg–S contact-shell cutoff relative to S (Supplementary Fig. 17b). The classification results yielded adsorbed-Hg efficiencies of 29.0% for TPPA-COF, 60.4% for TFP-S-COF, and 89.4% for TP-S-COF, supporting the cooperative contribution of sulfur and oxygen sites. Complementary diffusion coefficient analysis further substantiated this conclusion. HgCl₂ exhibited high mobility in bulk water, with a diffusion coefficient of $2640.5 \pm 373.9 \mu\text{m}^2 \text{s}^{-1}$, whereas diffusivity was markedly reduced in the COF systems: $1500.3 \pm 191.2 \mu\text{m}^2 \text{s}^{-1}$ for TPPA-COF, $645.2 \pm 16.4 \mu\text{m}^2 \text{s}^{-1}$ for TFP-S-COF, and $297.0 \pm 29.6 \mu\text{m}^2 \text{s}^{-1}$ for TP-S-COF. The lowest diffusivity in TP-S-COF reflects the combined effects of pore confinement and stronger Hg–framework interactions.

To evaluate the presence of chemical bonding upon adsorption, Mayer bond order (MBO) analysis was conducted on representative adsorption configurations extracted from the MD simulations (see Methods for details, Supplementary Fig. 21). MBO values quantify the degree of electron sharing between atoms. As a commonly used qualitative criterion, MBO values below 0.1 generally indicate negligible bonding interactions, whereas values approaching or exceeding 1.0 are characteristic of strong covalent interactions^{24–35}. Calculations revealed that the coordination strength between Hg and S is notably higher than that between Hg and O, as reflected by the larger MBO values for Hg–S contacts. For Hg–S pairs within the RDF-derived contact region ($r < 3.20 \text{ \AA}$), MBO values ranged from 0.12 to 0.25, suggesting weak but discernible Hg–S coordination with partial covalent character. In contrast, Hg–O contacts within the first shell-cutoff ($< 2.80 \text{ \AA}$) exhibited much smaller MBO values, all below 0.12, indicating negligible-to-weak covalent character. Together with the Hg–O RDF analysis, the MBO results suggest that keto oxygen atoms mainly provide secondary, largely non-covalent stabilization to the adsorbed Hg species, whereas sulfur atoms act as the primary binding sites through weak but discernible Hg–S coordination with partial covalent

character. These computational findings are consistent with XPS and ssNMR results (Supplementary Figs. 22–24), which showed pronounced S 2*p* binding energy shifts (1.4 eV) consistent with Hg–S bond formation, whereas O 1*s* spectra exhibited minimal chemical shift (<0.1 eV), confirming the absence of strong Hg–O covalent bonding. These computational findings are consistent with the spectroscopic evidence (Supplementary Figs. 22–24). XPS analysis revealed a pronounced S 2*p* binding-energy shift of 1.4 eV after HgCl₂ adsorption, supporting the formation of Hg–S interactions, whereas the O 1*s* spectra exhibited only a minimal chemical shift of less than 0.1 eV, consistent with the absence of appreciable covalent Hg–O bonding. The solid-state NMR results further corroborated changes in the local chemical environment of the COF framework upon HgCl₂ uptake.

Collectively, molecular-level insights from RDF, molecular clustering, diffusion, and MBO analyses demonstrate that the integration of methylthio and keto functional groups is essential for the high-affinity capture of neutral HgCl₂. Such synergistic functionality governs the superior adsorption kinetics of TP-S-COF and delivers a rational design guideline for advanced mercury sorbents. To experimentally verify this synergistic mechanism, TFP-S-COF and TPPA-COF were synthesized and evaluated for HgCl₂ adsorption under identical conditions. Within 10 s, TFP-S-COF and TPPA-COF only achieved 46.1% and 29.4% HgCl₂ removal efficiencies, respectively, which are substantially lower than the 95.9% removal rate of TP-S-COF. These experiments confirm that neither single functional group can afford the ultrafast HgCl₂ removal performance, solidifying the cooperative adsorption mechanism between methylthio sulfur and keto oxygen active sites.

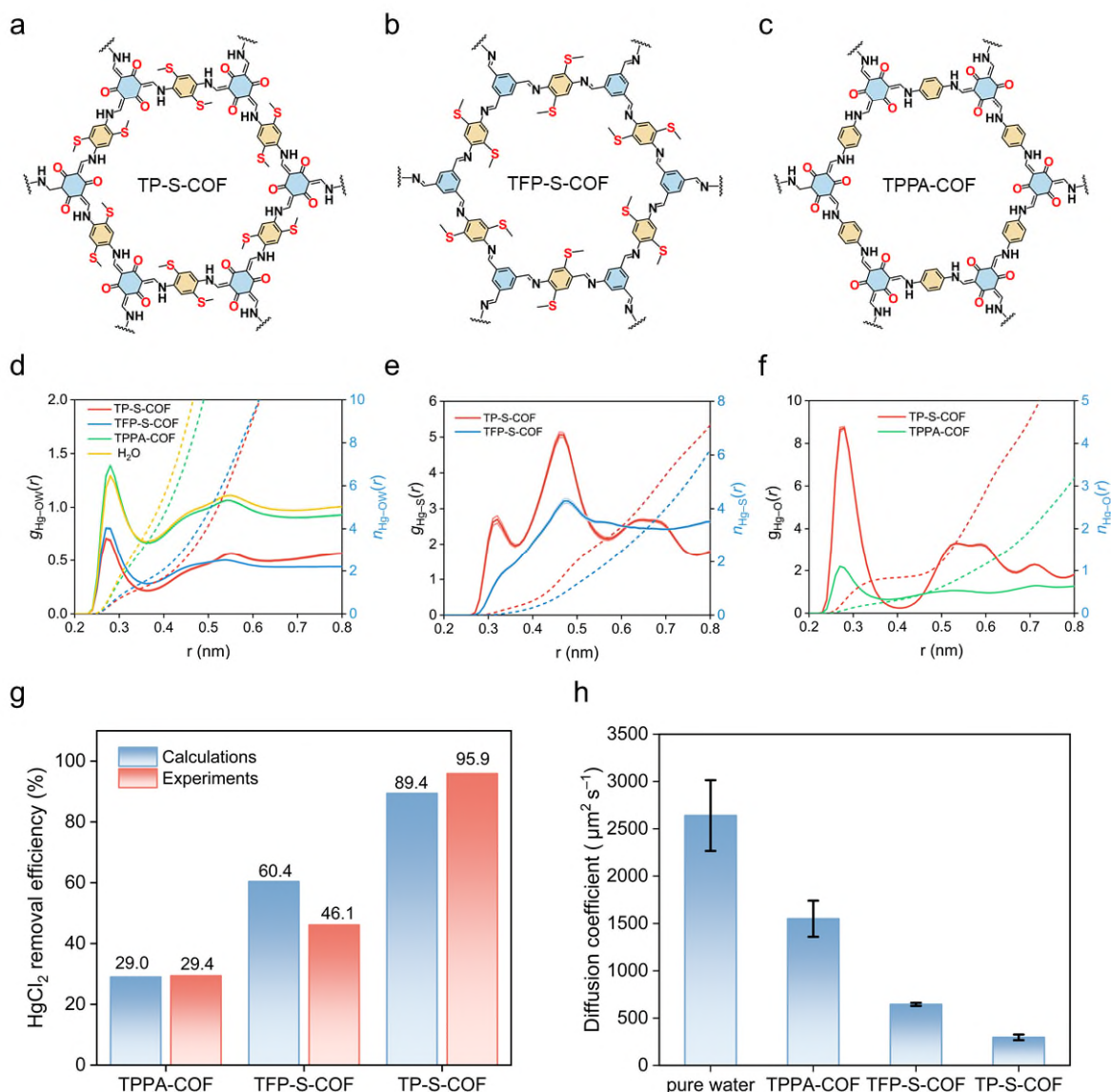


Fig. 5| Mechanistic insights into rapid HgCl_2 adsorption process. **a-c**, Structures of TP-S-COF, TFP-S-COF, and TPPA-COF. **d**, Radial distribution function (RDF) between Hg and O atoms from water molecules in the simulated systems ($g_{\text{Hg-ow}}$). **e**, RDF profiles of Hg with S atoms in TP-S-COF and TFP-S-COF ($g_{\text{Hg-S}}$). **f**, RDF profiles of Hg with O atoms in TP-S-COF and TPPA-COF ($g_{\text{Hg-O}}$). **g**, Comparison between theoretical predictions and experimental adsorption efficiencies of different COFs toward HgCl_2 . The experimental data correspond to the amount of HgCl_2 adsorbed after 10 s of reaction. **h**, Diffusion-coefficient. For all RDF plots, the left y -axis (black) represents the RDF values, and the right y -axis (blue) denotes the cumulative coordination number of Hg with specific atoms. Error bars for all RDFs were estimated using the weighted block averaging method (number of blocks = 4).

Shaded areas indicate the uncertainty ranges, most of which are smaller than the line width.

Conclusion

In conclusion, this work establishes TP-S-COF as a highly efficient adsorbent for rapid and selective removal of low-concentration HgCl_2 from contaminated water. Beyond its demonstrated fast adsorption kinetics and high selectivity in complex ion systems, the material exhibits robust stability across acidic pH conditions and maintains performance through multiple reuse cycles, addressing practical requirements for industrial applications. Mechanistic investigations integrate computational modeling with experimental validation using synthetically designed contrast COFs, confirming synergistic interactions between carbonyl oxygen and methylthio groups that disrupt water- HgCl_2 clustering to enhance adsorption. This integrated approach—combining targeted design, precise synthesis, application testing, and mechanistic validation—exemplifies the strength of COFs as versatile platform materials. It provides a blueprint for developing next-generation adsorbents capable of addressing real-world heavy metal pollution challenges while supporting effective emergency response and long-term environmental remediation strategies.

Methods

Synthesis of TP-S-COF

A Pyrex tube was charged with 1,3,5-triformylphloroglucinol (TP, 0.1 mmol, 21 mg), 2,5-bis(methylsulfanyl)benzene-1,4-diamine (S-PDA, 0.15 mmol, 30 mg), 1,4-dioxane (1.0 mL), pyrrolidine (0.02 mL) and aqueous acetic acid (6 M, 0.1 mL). The mixture was flash-frozen at 77 K, degassed through three freeze–pump–thaw cycles, sealed under vacuum and heated at 120 °C for 3 days. The precipitate was isolated by filtration, washed with tetrahydrofuran (THF) and acetone, and dried under vacuum at 80 °C for 24 h to afford TP-S-COF as a deep red powder (yield: 80 %, 40.8 mg).

Characterization

Solution-state nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 400 spectrometer (400 MHz for ^1H , 101 MHz for ^{13}C). Fourier-transform infrared spectroscopy (FT-IR) spectra were collected in the range of 4000~400 cm^{-1} on a Bruker Alpha Platinum ATR-FT-IR spectrometer. ^{13}C cross-polarization/magic-angle spinning (CP-MAS) ssNMR spectra were performed on a Bruker Avance III 400WB spectrometer operation at 9.4 T with frequencies of 100.62 MHz. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) operated at 40 kV and 40 mA in reflection mode. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectrometer (EDS) elemental mapping were obtained on a Hitachi S-3400 N microscope at an accelerating voltage of 10.0 kV. Transmission electron microscopy (TEM) images were conducted on a JEOL JEM-2800 instrument operated at 200 kV. N_2 adsorption-desorption isotherms were measured at 77 K using a Quantachrome Nova 3000 instrument, and pore size distributions were calculated using nonlocal density functional theory (NLDFT).

HgCl₂ adsorption experiments

Sorption Isotherm: For adsorption isotherm measurements, TP-S-COF (5 mg) was dispersed in HgCl_2 solutions (20 mL) with initial concentrations of 5 to 300 mg L^{-1} at pH 5. The suspensions were stirred at 25 $^\circ\text{C}$ for 2 h to reach equilibrium and then filtered through a 0.22 μm membrane. The filtrates were acidified with two drops of concentrated HNO_3 and the residual mercury concentration was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).

Selectivity tests: For selectivity evaluation, a mixed-solution containing Na(I), K(I), Ca(II), Mg(II), Zn(II), Ni(II), Cu(II), Cd(II), Pb(II) and HgCl_2 was prepared, with each metal ion maintained at 10 mg L^{-1} . TP-S-COF (5 mg) was added to the mixed solution (20 mL, pH 5) and stirred at 25 $^\circ\text{C}$ for 5 min. The

suspensions were filtered through a 0.22 μm membrane, and the filtrates were acidified with concentrated HNO_3 . Residual ion concentrations were determined by ICP–OES.

Effect of pH: To evaluate the influence of pH, TP-S-COF (5 mg) was added to HgCl_2 solution (20 mL) adjusted pH 2~7 and stirred at 25 $^\circ\text{C}$ for 5 min. The suspensions were filtered through a 0.22 μm membrane and the filtrates were acidified with two drops of concentrated HNO_3 prior and analyzed by ICP–OES.

Wastewater sample: Vinyl chloride monomer (VCM) can be produced via a calcium carbide-based suspension process, in which an alkaline scrubbing step is used to remove residual HCl from the process stream. This operation generates alkaline wastewater containing trace mercury species originating from the Hg -based catalyst and entrained by the process gas, with a typical Hg concentration of $\sim 1.0 \text{ mg L}^{-1}$.

Calculation Methods

Molecular dynamics (MD) simulations were carried out for four systems: (a) TP-S-COF, (b) TFP-S-COF, (c) TPPA-COF, and (d) a control system consisting of bulk water containing HgCl_2 (Supporting Information, Supplementary Fig. 16). Prior to MD simulations, geometry optimizations of HgCl_2 and the three COF monomers were performed using the QUICKSTEP module in the CP2K (version 2024.3) package²⁶. The Perdew–Burke–Ernzerhof (PBE) functional²⁷ within the generalized gradient approximation (GGA) was employed to describe exchange–correlation effects, applying a plane–wave (GPW) and mixed Gaussian basis set. Core electrons were treated with Goedecker–Teter–Hutter (GTH) pseudopotentials²⁸. Atomic partial charges were derived by fitting to the DFT electrostatic potentials using the restrained electrostatic potential (RESP) method²⁹.

All MD simulations were performed using GROMACS (version 2024.3)³⁰. The COF frameworks were parameterized using the General Amber Force Field

(GAFF)³¹. Parameters for HgCl₂ were taken from Ref. [32], and water molecules were modeled using the TIP3P potential.

Simulation boxes were constructed based on the DFT-optimized structures. The box dimensions were 39.41 × 22.67 × 60.00 Å³ for TP-S-COF, 40.22 × 23.22 × 60.00 Å³ for TFP-S-COF, 39.34 × 22.56 × 60.00 Å³ for TPPA-COF, and 35.00 × 38.00 × 60.00 Å³ for the bulk water system. To ensure the same HgCl₂ loading across all systems, eight HgCl₂ molecules were placed in each simulation box. For COF systems (a-c), a six-layer COF slab periodic in the *xy*-plane was centered in the box, with four HgCl₂ molecules initially positioned on either side of the slab. The boxes were then solvated with 1275, 1443, 1393, and 2531 TIP3P water molecules for systems (a)-(d), respectively. Periodic boundary conditions were applied along all three dimensions.

After energy minimization using the steepest descent algorithm, 1 μs production simulations were conducted in the NPT ensemble at 298 K and 1 bar. Temperature and pressure were controlled using the V-rescale thermostat³³ and the Parrinello–Rahman barostat³⁴, respectively. A 0.5 fs time step was used throughout. The cutoff for nonbonded interactions was set to 1.1 nm, and long-range electrostatics were treated using the Particle Mesh Ewald (PME) method³⁵. All analyses presented in this work were performed based on the trajectories from the final 500 ns, during which the systems were equilibrated.

Data availability

The data supporting the findings of this study are available within the paper and its Supplementary Information. Source data are provided with this paper.

References

1. Fang, R. et al. Puffed rice carbon with coupled sulfur and metal iron for high-efficiency mercury removal in aqueous solution. *Environ. Sci. Technol.* **54**, 2539-2547 (2020).
2. Chiarle, S., Ratto, M. & Rovatti, M. Mercury removal from water by ion-exchange resins adsorption. *Water Res.* **34**, 2971-2978 (2000).

3. Gong, Y., Liu, Y., Xiong, Z. & Zhao, D. Immobilization of mercury by carboxymethyl cellulose stabilized iron sulfide nanoparticles: reaction mechanisms and effects of stabilizer and water chemistry. *Environ. Sci. Technol.* **48**, 3986-3994 (2014).
4. Bibby, A. & Mercier, L. Mercury(II) ion adsorption behavior in thiol-functionalized mesoporous silica microspheres. *Chem. Mater.* **14**, 1591-1597 (2002).
5. Brown, J., Mercier, L. & Pinnavaia, T. Selective adsorption of Hg^{2+} by thiol-functionalized nanoporous silica. *Chem. Commun.* **1**, 69-70 (1999).
6. Yaghi, O. M., Kalmutzki, M.J. & Diercks, C.S. *Introduction to reticular chemistry: metal-organic frameworks and covalent organic frameworks* (Wiley-VCH, 2019).
7. Ding, S. et al. Thioether-based fluorescent covalent organic framework for selective detection and facile removal of mercury(II). *J. Am. Chem. Soc.* **138**, 3031-3037 (2016).
8. Wang, J., Zhuang, S. Covalent organic frameworks (COFs) for environmental applications. *Coord. Chem. Rev.* **400**, 213046 (2019).
9. Gendy, EA. et al. Removal of heavy metals by covalent organic frameworks (COFs): A review on its mechanism and adsorption properties. *J. Environ. Chem. Eng.* **9**, 105687 (2021).
10. Yuan, L. et al. Insights into the adsorptive separation of iron from pickling waste acid: The overlooked role of FeCl_3 species. *Chem. Eng. J.* **477**, 146637 (2023).
11. Li, X. et al. Unexpected chloride-triggered organics removal in the zirconium oxide activated peroxymonosulfate system. *J. Hazard. Mater.* **482**, 136621 (2025).
12. Ciavatta, L. & Grimaldi M. The hydrolysis of mercury(II) chloride, HgCl_2 . *J. Inorg. Nucl. Chem.* **30**, 563-581 (1968).
13. López-Muñoz, M., Aguado, J., Arencibia, A. & Pascual, R. Mercury removal from aqueous solutions of HgCl_2 by heterogeneous photocatalysis with TiO_2 . *Appl. Catal. B Environ.* **104**, 220-228 (2011).
14. Busato, M., Fazio, G., Tavani, F., Pollastri, S. & D'Angelo, P. Solubilization and coordination of the HgCl_2 molecule in water, methanol, acetone, and acetonitrile: an SSNMR absorption investigation. *Phys. Chem. Chem. Phys.* **24**, 18094-18102 (2022).
15. Wang, Z. et al. Revealing the interaction forms between Hg(II) and group types (-Cl, -CN, - NH_2 , -OH, -COOH) in functionalized poly(pyrrole methane)s for efficient mercury removal. *Environ. Pollut.* **351**, 124049 (2024).

16. Huang, N., Zhai, L., Xu, H. & Jiang, D. Stable covalent organic frameworks for exceptional mercury removal from aqueous solutions. *J. Am. Chem. Soc.* **139**, 2428-2434 (2017).
17. Kandambeth, S. et al. Construction of crystalline 2D covalent organic frameworks with remarkable chemical (acid/base) stability via a combined reversible and irreversible route. *J. Am. Chem. Soc.* **134**, 19524-19527 (2012).
18. Pawley, G. Unit-cell refinement from powder diffraction scans. *J. Appl. Crystallogr.* **14**, 357-361 (1981).
19. Pressly, L. et al. How mercury poisons gold miners and enters the food chain. *BBC*. <https://www.bbc.com/news/magazine-24127661> (2023).
20. Fraser, B. et al. Peru's gold rush prompts public-health emergency. *Nature* **534**, 162 (2016).
21. Webber, T. Dozens potentially exposed to toxic mercury in Houston spill. *AP*. <https://apnews.com/general-news-a8e44f8bfdcf7224a5b97ab708353f39> (2019).
22. Huhtamäki, T., Tian, X., Korhonen, J. T. & Ras, R. H. A. Surface wetting characterization using contact-angle measurements. *Nat. Protoc.* **13**, 1521-1538 (2018).
23. Yan, X. et al. Superhydrophilic 2D covalent organic frameworks as broadband absorbers for efficient solar steam generation. *Angew. Chem. Int. Ed.* **61**, e202201900 (2022).
24. Chen, X., Zhang, Y., Zhang, M. & Zeng, M. Bond order analysis, packing ratio, and electronic structures of two structural polymorphs based on manganese complexes. *Chin. J. Chem.* **35** 927-930 (2017).
25. Fu, Q. et al. Pyridine-based covalent organic framework for efficient and selective removal of Hg(II) from water: adsorption behavior and adsorption mechanism investigations. *Chem. Eng. J.* **454** 140154 (2023).
26. Hutter, J., Iannuzzi, M., Schiffmann, F. & VandeVondele, J. CP2K: atomistic simulations of condensed matter systems. *WIREs Comput. Mol. Sci.* **4**, 15-25 (2014).
27. Perdew, J., Burke, K., & Wang, Y. Generalized gradient approximation for the exchange-correlation hole of a many-electron system. *Phys. Rev. B.* **54**, 16533-6539 (1996).
28. Goedecker, S., Teter, M. & Hutter, J. Separable dual-space Gaussian pseudopotentials. *Phys. Rev. B: Condens. Matter.* **54**, 1703-1710 (1995).
29. Bayly, C. I., Cieplak, P., Cornell, W. & Kollman, P. A. A well-behaved electrostatic

- potential based method using charge restraints for deriving atomic charges: the RESP model. *J. Phys. Chem.* **97**, 10269-10280 (1993).
30. Abraham, M. J. et al. GROMACS: high performance molecular simulations through multi-level parallelism from laptops to supercomputers. *SoftwareX.* **1**, 19-25(2015).
31. Wang, J., Wolf, R. M., Caldwell, J. W., Kollman, P. A. & Case, D. A. Development and testing of a general AMBER force field. *J. Comput. Chem.* **25**, 1157-1174 (2004).
32. Castro, L., Dommergue, A., Renard, A., Ferrari, C., Ramirez-Solis, A. & Maron, L. Theoretical study of the solvation of HgCl_2 , HgClOH , $\text{Hg}(\text{OH})_2$ and HgCl_3^- : a density functional theory cluster approach. *Phys. Chem. Chem. Phys.* **13**, 16772-16779 (2011).
33. Bussi, G., Donadio, D. & Parrinello, M. Canonical sampling through velocity rescaling. *J. Chem. Phys.* **126**, 014101 (2007).
34. Parrinello, M. & Rahman, A. Polymorphic transitions in single crystals: a new molecular dynamics method. *J. Appl. Phys.* **52**, 7182-7190 (1981).
35. Darden, T., York, D. & Pedersen, L. Particle mesh Ewald: An $N\log(N)$ method for Ewald sums in large systems. *J. Chem. Phys.* **98**, 10089-10092 (1993).

Acknowledgements

This research was supported by National Natural Science Foundation of China (Grants No. 22501136 and U22A20403), the Fundamental Research Funds for the Central Universities (No. 14380325 and 491916003301), the Natural Science Foundation of Jiangsu Province (Grant No. BK20241192) and the Suzhou Innovative Leading Talent Project (Project No. ZXL2025318). The authors acknowledge Shimadzu Enterprise Management (China) Co., Ltd. Shanghai Branch for their technical support in XPS measurements. Calculations were performed at the High-Performance Computing Center (HPCC) of Nanjing University.

Author contributions

W.Z. and T.M. conceived the project and supervised the experimental work.

M.L. was responsible for the synthesis of the materials, and conducted structural characterizations including PXRD, SEM, and TEM. Y.G. and M.Y. performed the theoretical calculations, analyzed the computational results, contributed to the mechanistic interpretation, and drafted the computational section of the manuscript. X.P. conducted the FT-IR and BET experiments. X.K. conducted the ssNMR experiments. L.P. helped with the ssNMR analysis. R.X. assisted with the ion adsorption experiments. W.D. assisted with the formatting, and H.W. assisted with the material synthesis. M.L., W.Z., and T.M. analyzed the data and prepared the initial draft. T.M. finalized the manuscript. All authors read and discussed the manuscript.

Competing financial interests

The authors declare no competing financial interests.

Corresponding authors

Correspondence and requests for materials should be addressed to W.Z. (email: wmzhang@nju.edu.cn), M.Y. (manyi.yang@nju.edu.cn) and T.M. (email: tianqiongma@nju.edu.cn)

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplementaryInformation.docx](#)
- [Supplementaryvideo1.mp4](#)
- [Supplementaryvideo2.mp4](#)
- [Supplementaryvideo3.mp4](#)