

Efficient Mercury Capture Using Functionalized Porous Organic Polymer

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The primary challenge in materials design and synthesis is achieving the balance between performance and economy for real-world application. This issue is addressed by creating a thiol functionalized porous organic polymer (POP) using simple free radical polymerization techniques to prepare a cost-effective material with a high density of chelating sites designed for mercury capture and therefore environmental remediation. The resulting POP is able to remove aqueous and airborne mercury with uptake capacities of 1216 and 630 mg g⁻¹, respectively. The material demonstrates rapid kinetics, capable of dropping the mercury concentration from 5 ppm to 1 ppb, lower than the US Environmental Protection Agency's drinking water limit (2 ppb), within 10 min. Furthermore, the material has the added benefits of recyclability, stability in a broad pH range, and selectivity for toxic metals. These results are attributed to the material's physical properties, which include hierarchical porosity, a high density of chelating sites, and the material's robustness, which improve the thiol availability to bind with mercury as determined by X-ray photoelectron spectroscopy and X-ray absorption fine structure studies. The work provides promising results for POPs as an economical material for multiple environmental remediation applications.

Rapid industrial progress has become a byproduct of the recent advances in technology and the competitive nature of the research community. However, such innovations come with adverse effects as the growth of industry, with more coal-powered fuel stations and waste incinerators, consequently increases the release of toxic heavy metals into the environment.^[1] Mercury, Hg⁰ and Hg²⁺, is one of the most hazardous heavy metals being reported with more than 6000 tons

emitted into the atmosphere per year.^[2] Mercury is uniquely dangerous due to the natural processes that convert the organic and inorganic forms of mercury into its highly volatile elemental form. This creates a constant cycle of mercury entering and reentering the atmosphere, soil, and water, ultimately accumulating in our food supply as methylmercury, a potent neurotoxin.^[3] Mercury exposure is the cause of many serious health issues for humans, including damage to the nervous system and lungs; also of concern are potential birth defects in expectant mothers after exposure.^[4] The threat of mercury has become a global issue that has warranted intervention, with the Minamata Convention recently held to forge an agreement to reduce emissions from common anthropogenic sources such as coal burning, cement production, oil refining, and artisanal and small-scale gold mining.^[5] Until the emissions can be greatly reduced, it is imperative to develop

new technologies to decrease the mercury found in the atmosphere and industrial wastewater run-off.

The immediate need for remediation of toxic metals has spurred research interest in the field of materials design.^[6] Preliminary methods like ion-exchange resins were explored but were found to be expensive and ineffective.^[7] Further research employed the strong soft-soft interactions between the thiol group (-SH) and mercury,^[8] and much work has been done on thiol-functionalized adsorbent materials including clays,^[9] activated carbon,^[10] mesoporous silica,^[11] cross-linked polyethyleneimine,^[12] and others.^[13] However, these materials display low surface areas, small pore sizes, and a low density of functional groups. Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) offer an amenable design strategy to create a high density of chelating sites with promising uptake capacities but suffer from stability issues which inhibits their use in a wide range of conditions.^[8b,14] These limitations have necessitated the exploration of new adsorbent materials to enhance mercury capture and to create a viable option for real-world applications.

Taking the aforementioned challenges into account, the use of porous organic polymers (POPs) has been investigated as a promising adsorbent for heavy metal decontamination. POPs are a burgeoning class of porous material, which offer structural

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diversity, tunable pore size, high surface area, and chemical stability.^[15] Pioneering work done using a functionalized POP (PAF-1-SH) set the standard as a stable material for effective mercury decontamination; however, stoichiometric amounts of catalyst are required for the synthesis of the PAF-1 framework and a multistep postsynthetic modification is required, contributing to the impracticality in large-scale applications. In addition, the resulting material is microporous, which may lower the efficiency of wastewater treatment.^[16] To add applicability of the adsorbent material, there is a need for a cost-effective and simple method to synthesize a hierarchical porous organic polymer with a high density of chelating sites.

To tackle these challenges a *de novo* strategy and a free radical polymerization method with readily available reagents are utilized to make a thiol functionalized POP, namely POP-SH. Using this method gives rise to an exceptionally high density of available chelating sites and it was found to have a high saturation uptake capacity of over 600 and 1200 mg g⁻¹ (with an equilibrium concentration of 200 ppm) for Hg⁰ and Hg²⁺, respectively. The material was discovered to have rapid kinetics, reaching ppb level within 10 min. Additionally, POP-SH was fully recyclable, stable at different pH values, and selective for mercury in the presence of other cations. This work reveals the promise of POPs as an adsorbent for mercury removal and potentially many other toxic metals detrimental to the environment.

The aforementioned POP-SH was synthesized via free radical polymerization of 3,5-divinylbenzyl chloride with azobisisobutyronitrile (AIBN), a free radical initiator, dissolved in dimethylformamide (DMF) and heated to 100 °C in a solvothermal autoclave for 16 hr. The thiol group cannot be incorporated into the monomer unit, as it is a free radical quencher;

therefore, further treatment of the obtained solid is required with sodium hydrosulfide in ethanol under nitrogen, heated to 75 °C for 3 days, which gave the thiol-functionalized polymer, POP-SH.

To confirm the thiol conversion, solid-state ¹³C NMR studies and elemental analysis were performed. The ¹³C NMR spectra showed the chemical shift for the methyl chloride bond in POP-Cl at ≈46 ppm. After conversion the peak was slightly shifted downfield to 30 ppm, indicative of the methyl sulfur bond of POP-SH (Figure S3, Supporting Information).^[17] Through elemental analysis the sulfur content was found to be 16.3 wt%, corresponding to 5.09 mmol g⁻¹ sulfur species. This value accounts for ≈90% substitution of the chloride groups by thiol groups and is proposed to occur due to the high accessibility within the porous matrix.

For the final amorphous product, nitrogen sorption isotherms were collected at 77 K with the calculated Brunauer–Emmett–Teller (BET) surface area equaling 1061 m² g⁻¹ (Figure 1a). The hysteresis loop shown in the isotherms and the calculated nonlocal density functional theory (NLDFT) pore size distribution are indicative of the hierarchical porosity, from 1 to 10 nm, present in POP-SH that provides high accessibility to the chelating sites (Figure 1b). To further confirm the hierarchical porosity of POP-SH, scanning electron micrograph (SEM) and transmission electron micrograph (TEM) images were taken (Figure 1c,d). Thermogravimetric analysis revealed minimal weight loss below 300 °C corresponding to residual solvent loss, substantiating the high stability of POP-SH (Figure S4a, Supporting Information).

As a preliminary study, experimental work was done to determine the maximum uptake capacity of POP-SH to remove Hg²⁺ from an aqueous solution. The adsorption isotherm shown

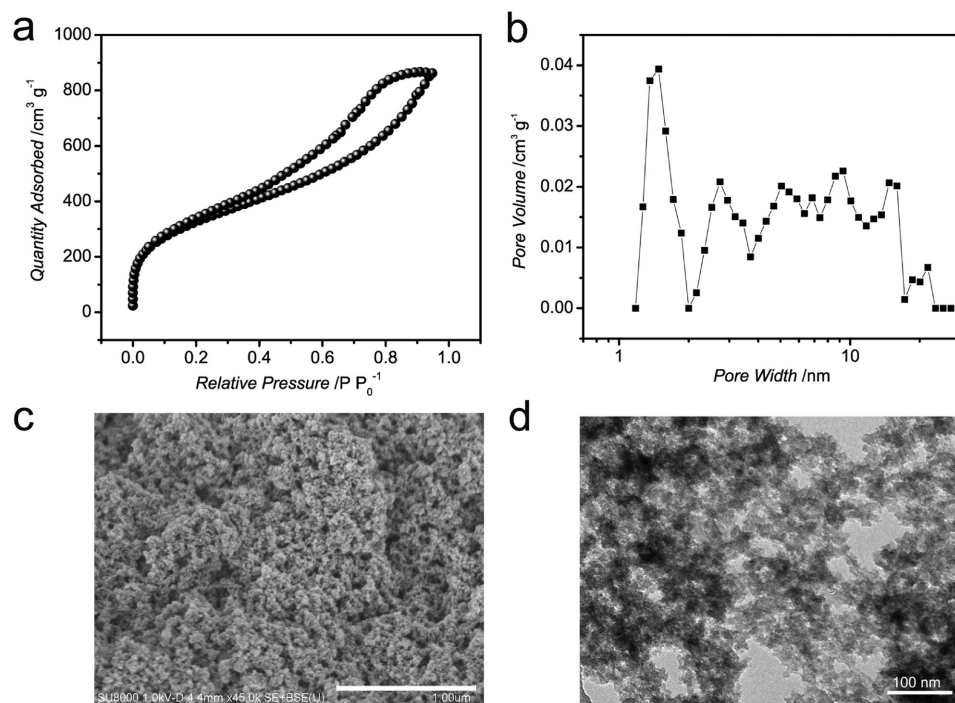


Figure 1. a) Nitrogen sorption isotherms of POP-SH collected at 77 K with BET surface area calculated to be 1061 m² g⁻¹. b) Pore size distribution of POP-SH, calculation based on NLDFT. c) SEM image of POP-SH (scale bar 1 µm). d) TEM image of POP-SH (scale bar 100 nm).

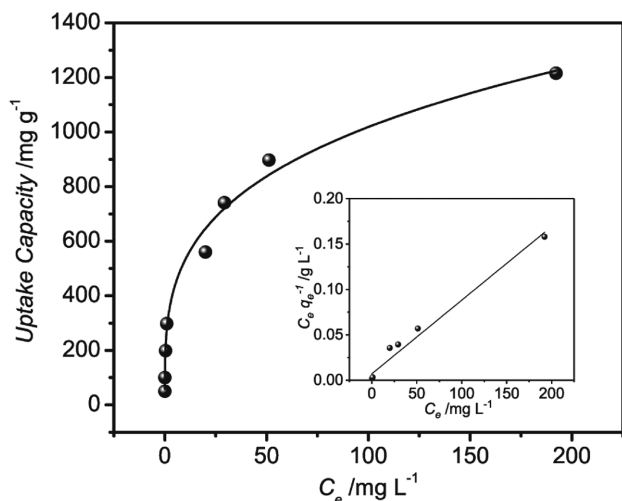


Figure 2. Hg^{2+} adsorption isotherm for POP-SH. Inset shows the linear regression by fitting the equilibrium data with the Langmuir adsorption model.

in **Figure 2** displays equilibrium data obtained for aqueous solutions with initial Hg^{2+} concentrations ranging from 25 to 800 ppm after treatment with POP-SH. The equilibrium adsorption data were well fitted with the Langmuir model, with a correlation coefficient equal to 0.989. The uptake capacities for each point were calculated and the maximum was found to be 1216 mg g^{-1} (with an equilibrium concentration

of 200 ppm), outperforming many previously reported materials.^[7–16] Furthermore, with only a simple washing procedure POP-SH could be fully regenerated, achieving a similar uptake capacity of 1250 mg g^{-1} . The full retention of the uptake capacity is due to the stability of the framework and the thiol functionality, leading to no disulfide bond formation, which compromise the mercury removal performance. This is evidenced by the absence of the S–S stretching band at $\approx 500 \text{ cm}^{-1}$ in the Raman spectrum of the regenerated POP-SH sample (Figure S5, Supporting Information).^[18] Based on the sulfur content of POP-SH, the theoretical uptake capacity was calculated to be 1018 mg g^{-1} . The increased capacity found experimentally can be attributed to the conjugated nature of POP-SH, resulting in cation– π interactions between the benzene rings of POP-SH and mercury cations. To further support this claim, UV–vis spectra have been collected and an apparent redshift was observed at the characteristic band ascribed to benzene after introduction of mercury (Figure S6, Supporting Information).^[19]

Kinetic studies were performed on POP-SH in removing mercury from solutions, as rapid decontamination of heavy metals is vital for a material to have prospects in any practical applications. Beginning with a 5 ppm solution of Hg^{2+} , aliquots were taken at different time intervals following treatment with POP-SH and analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) for their remaining Hg^{2+} concentrations (**Figure 3a**). Within 10 min the concentration was lowered to 1 ppb, already less than the US Environmental Protection

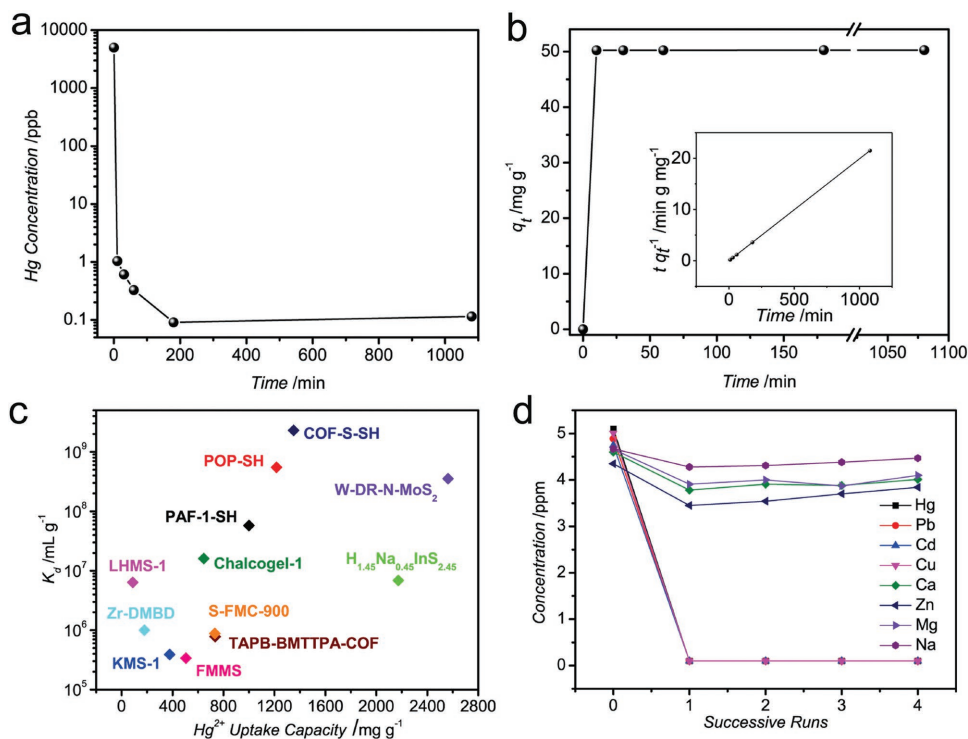


Figure 3. a) Hg^{2+} sorption kinetics of POP-SH with Hg^{2+} initial concentration of 5 ppm. b) Adsorption curve of Hg^{2+} versus contact time in aqueous solution using POP-SH. Inset shows the pseudo-second order kinetic plot for the adsorption. c) Comparison of Hg^{2+} saturation uptake amount and K_d value for POP-SH with other benchmark porous materials, PAF-1-SH,^[16] LHMS-1,^[13h] FMMS,^[11f] Chalcogel-1,^[13] S-FMC-900,^[11b] Zr-DMBD,^[14e] KMS-1,^[13j] COF-S-SH,^[14f] W-DR-N-MoS₂,^[13f] H_{1.45}Na_{0.45}InS_{2.45},^[13g] TAPB-BMTTPA-COF.^[14h] d) Concentrations of metal ions after the breakthrough experiment with POP-SH, collected at 4 mL intervals. The initial concentration of various metals is ≈ 5 ppm.

Agency (EPA) acceptable limit of 2 ppb,^[20] and after 3 hr the concentration was as low as 0.1 ppb, reaching the detection limit of the instrument. The experimental kinetic data were fitted to a pseudo-second order kinetic model using Equation (1), where k_2 is the adsorption rate constant ($\text{g mg}^{-1} \text{min}^{-1}$), t is time (min), and q_t and q_e are the uptake capacities (mg g^{-1}) at time (t) and equilibrium, respectively.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (1)$$

From Figure 3b, the adsorption rate constant, k_2 , was found to be $10.76 \text{ g mg}^{-1} \text{min}^{-1}$, illustrating the rapid removal of mercury from aqueous solutions. Previous work has suggested applicability of pseudo-second order kinetics to adsorption by porous materials implies that the rate is limited by intraparticle diffusion.^[21] Therefore, the fast kinetics can be ascribed to the inherent properties of the material, namely the hierarchical porosity as well as the high density of chelating sites. Together these offer readily available thiol groups to bind with mercury.

To quantify the affinity of an adsorbent for mercury, distribution coefficient (K_d) values were thus calculated using Equation (2), where C_0 and C_e are the initial and equilibrium concentrations, respectively, V is the volume of solution (mL), and m is the mass of adsorbent used (g)

$$K_d = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{m} \quad (2)$$

For POP-SH, the K_d value was calculated to equal $5.5 \times 10^8 \text{ mL g}^{-1}$, which is comparable to the best thiol functionalized adsorbents reported thus far, as seen in Figure 3c, with the added benefit of simple synthetic procedures for large-scale applications. Though the metal sulfide materials demonstrate superior uptake capacities, they lack the ability to be recycled for multiple uses.^[13f,g] It is interesting to note that even when the mercury solution was adjusted to pH levels of three and ten, the K_d values were still as high as 2.1×10^7 and $1.3 \times 10^6 \text{ mL g}^{-1}$, respectively. Both of these values still indicate exceptional affinity toward mercury.^[10b] The ability of POP-SH to successfully capture mercury at different pH values is important due to the varying acidity levels of the diverse wastewater composition.

As a final marker for an adsorbent's capabilities, it must selectively remove mercury in the presence of other ions. Initial batch studies were performed with a solution containing Hg^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Ca^{2+} , Zn^{2+} , Mg^{2+} , and Na^+ with nearly equal concentrations. After treatment with POP-SH, not only was mercury removed with over 98% efficiency, but the other toxic metals— Pb^{2+} , Cd^{2+} , and Cu^{2+} —were also captured while the nontoxic ions were relatively unchanged (Table S2, Supporting Information). To simulate a flow-through system for water purification purposes a breakthrough study was also performed with the same mixed ion solution. As seen in Figure 3d, even after four successive runs, the toxic metals were dropped to ppb level while the nontoxic metals were minimally affected. Further testing of the mercury content revealed a residual concentration of 0.3 ppb, almost ten times lower than the EPA standard. These results can be attributed

to the soft–soft interactions between the thiol group and the soft metal cations, Hg^{2+} , Cd^{2+} , and Cu^{2+} , and borderline Pb^{2+} ,^[8a] further confirming the importance of the thiol functionality on the POP. Mercury spiked solutions of ground and potable water were also tested. After 30 min of treatment the concentration was dropped to 0.44 and 0.25 ppb, respectively, demonstrating the true applicability of POP-SH for water treatment.

With such promising results for POP-SH to remove mercury from various aqueous solutions, its ability to remove mercury by vapor adsorption was also examined. One of the main causes of mercury release into the environment is from industrial flue gas. Previous adsorbents were unable to withstand such harsh conditions, but with the high stability of POP-SH this issue is circumvented.^[22] Following a previously reported procedure,^[14e] elemental mercury was placed in a small vial surrounded by the material; the apparatus was then sealed and heated to $140 \text{ }^\circ\text{C}$. After 8 days the adsorbent was removed, dissolved in aqua regia, and analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) for its mercury content. It was found that POP-SH achieved a Hg^0 uptake capacity of 630 mg g^{-1} , greatly outperforming a thiol-functionalized MOF (83.6 mg g^{-1})^[14e] and activated carbon (47 mg g^{-1} , BET = $1011 \text{ m}^2 \text{ g}^{-1}$) under identical conditions. The ability of POP-SH to retain thiol functionality and mercury capture at elevated temperatures highlights its possibilities in many applications.

The performance seen for POP-SH in capturing mercury under diverse conditions is due to the strong binding interactions between the thiol group in POP-SH and mercury, confirmed by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy studies. XPS samples were prepared following a previously reported procedure.^[23] The S 2p core level emissions revealed at $\approx 168 \text{ eV}$, for pristine POP-SH and POP-SH@Hg. The peak slightly shifts and becomes more symmetrical, compared to POP-SH, which indicates the sulfur was bound to the mercury in POP-SH@Hg. The Hg 4f spectrum has a doublet resulting in $4f_{7/2}$ and $4f_{5/2}$ peaks at 110 and 106 eV, respectively (Figure S7, Supporting Information).^[24] Additionally, the Raman spectrum of POP-SH@Hg displayed peaks at 276 and 290 cm^{-1} , associated with the Hg–S stretching vibrations ($\nu_s = 276$ and $\nu_{as} = 290 \text{ cm}^{-1}$) (Figure S5, Supporting Information) further confirming the coordination between sulfur and mercury.^[25]

To achieve further understanding of the mercury-thiol coordination environment within the porous framework, the Hg L_{III} -absorption edge (12.284 keV) of POP-SH@Hg was analyzed using X-ray absorption fine structure (XAFS) spectroscopy (see the Supporting Information for experimental details and data analysis). The fit of the extended XAFS (EXAFS) data obtained for POP-SH@Hg is shown in Figure 4. Importantly, fits to Hg–O^[26] and Hg–Cl were significantly inferior to Hg–S models, which suggest neither precipitation of HgO nor nonspecific adsorption of the Hg starting material occurs. Two Hg–S scattering paths were required, with 69% and 31% contribution at 2.37 and 2.26 Å, respectively, providing the best fit for POP-SH@Hg. A multimodal distribution of Hg–S distances is anticipated for an amorphous material with a rigid polymeric backbone in conjunction with flexible benzyl thiols. The cooperative interplay of the variation in structural constraints contributes to the overall robustness of POP-SH and its high mercury adsorption capacity.

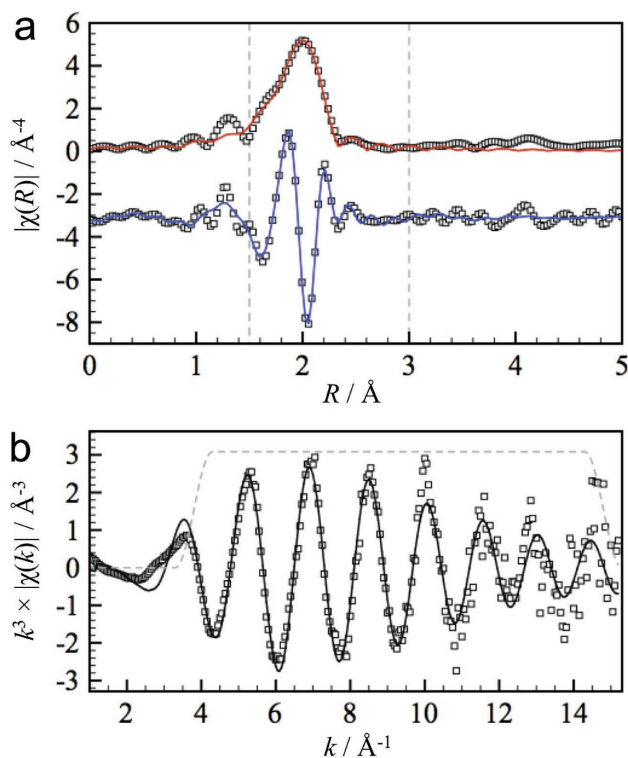


Figure 4. a) Fourier transform of the Hg L_{III} -edge EXAFS spectrum of POP-SH in R-space fit with two Hg-S scattering paths. The real component and fit are presented below. Gray dashed lines indicate the fit window. b) EXAFS spectrum of POP-SH in k-space fit (black trace) with two Hg-S scattering paths. Gray dashed lines indicate the fit window.

This study explored the use of a functional porous organic polymer, POP-SH, for its ability to remove mercury for environmental remediation purposes. POP-SH demonstrated exceptionally high Hg^0 and Hg^{2+} uptake capacities of 630 and 1216 $mg\ g^{-1}$, respectively. Efficient mercury removal was rapid due to the hierarchical pore structure and readily available thiol groups, which resulted in high concentrations of mercury being reduced to ppb level within minutes. Furthermore, POP-SH was fully recyclable, stable at a broad pH range, and highly selective for mercury in the presence of other cations. These results demonstrate the feasibility of POPs as adsorbent materials for heavy metal capture in several applications from wastewater run-off to industrial flue gas.

Experimental Section

Synthesis of POP-SH: To a solvothermal autoclave, 3,5-divinylbenzyl chloride (1 g) was added with azobisisobutyronitrile (25 mg) and dimethylformamide (10 mL). The autoclave was placed in an oven and heated to 100 °C for 24 hr. The resulting product was collected by filtration, washed with acetone, and dried under vacuum to produce POP-Cl.^[27] Following, POP-Cl (250 mg) and sodium hydrosulfide (1.3 g) were placed in a 100 mL Schlenk tube, with ethanol (50 mL) being introduced under N_2 atmosphere and stirred at 75 °C for 3 days. The resulting product was collected by filtration, washed extensively with deionized water and ethanol, and dried under vacuum, producing POP-SH as a white powder. To confirm all the reactant was excluded,

thermogravimetric analysis under air was performed, showing no remaining weight percentage (Figure S4b, Supporting Information), indicating no sodium hydrosulfide remained in the final POP-SH sample.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

environmental remediation, heavy metal removal, mercury capture, porous organic polymers, thiol functionality

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