Supporting Information

Dense thiol arrays for metal-organic frameworks: boiling water stability, Hg removal beyond 2 ppb and facile crosslinking

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General Procedure. Staring materials, reagents and solvents were purchased from commercial sources and used without further purification. Elemental analysis was obtained with a Vario EL III CHN elemental analyzer. Infrared spectra in the range 400-4000 cm⁻¹ were recorded on a Nicolet Avatar 360 FT-IR spectrophotometer. FT-Raman spectra were obtained using a Perkin-Elmer S2 Spectrum 2000 instrument equipped with a diode pumped Nd:YAG laser PSU and using the standard Spectrum v2.0 software. Solution ¹H NMR and ¹³C NMR spectra were recorded at room temperature on Bruker superconducting-magnet high-field NMR spectrometers with working frequencies of 300 and 400 MHz, using tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are expressed in ppm relative to the residual solvent (e.g. chloroform ¹H: 7.26 ppm, ¹³C: 77.0 ppm) reference. Coupling constants are expressed in hertz. Thermogravimetric analyses (TGA) were carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (STA 6000) with a heating rate of 2 °C/min, with an empty Al₂O₃ crucible being used as the reference. The porosity and surface area analysis was performed using a Quantachrome Autosorb iQ gas sorption analyzer. Samples were outgassed at 0.03 torr with a 2 °C/min ramp to 120 °C and held at 120 °C for 6 or 12 hours. The samples were then held at vacuum until the analysis was run. Pore analysis was performed using N₂ at 77.35 K (P/P₀ range of 2×10^{-7} to 0.995). The amounts of the metal ions were determined by a PerkinElmer Optima[™] 2100 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) analyzer and a PerkinElmer ELAN DRC II Quadrupole Inductively Coupled Plasma Mass Spectrometer (ICP-MS) analyzer. Mercury standard (1000 mg/L) for ICP-MS was purchased from VHG, Manchester, NH, USA. All ICP-MS samples for ICP-MS were prepared using Milli-Q water (18.2 MΩcm Millipore, Billerica, MA, USA). Powder X-ray diffraction data was collected in the reflection mode at room temperature on an Inel Equinox 1000 X-ray diffractometer (Inel, France) equipped with CPS 180 detector using monochromated Cu-K α (λ =1.5418 Å) radiation. The X-ray tube operated at a voltage of 30 kV and a current of 30 mA.

Ligand synthesis



Figure S1. A synthetic scheme for H₄OMTP linker molecule.

Synthesis of Methyl 2,6-bis(benzylthio)-4-bromobenzoate (M2). 4-Bromo-2,6-difluorobenzoic acid (M1, 4.74 g, 0.02 mol) and potassium carbonate (27.6 g, 0.20 mol) were loaded in a two-neck round-bottom flask. *N*-Methyl-2-pyrrolidone (NMP, 100.0 mL) was added to the flask and the mixture was stirred and bubbled with nitrogen at room temperature for 30 minutes. Benzyl

mercaptan (6.0 mL, 0.05 mol) was then added to the mixture under nitrogen. The mixture was stirred at 80 °C for four days. After being cooled to room temperature, methyl iodide (3.0 mL, 48.19 mmol) was added to the mixture, and the mixture was stirred at room temperature under nitrogen for 30 minutes. The resulting mixture was poured into distilled water (800 mL) and extracted with DCM (3×200 mL). The combined organic layer was dried over anhydrous MgSO4 and purified by column chromatography (eluent: DCM/hexanes, 1:5) to afford **M2** (6.96 g, 76% yield based on **M1**). ¹H NMR (300 MHz, CDCl₃): $\delta = 7.34-7.18$ (m, 12H), 4.05 (s, 4H), 3.91 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): $\delta = 167.35$ (s), 138.72 (s), 136.35 (s), 135.67 (s), 133.41 (s), 129.23 (s), 128.69 (s), 127.70 (s), 123.22 (s), 52.70 (s), 40.48 (s). FT-IR (KBr pellet, v/cm⁻¹): 3029 (w), 2949 (w), 1729 (vs), 1550 (s), 1495 (m), 1456 (m), 1437 (m), 1411 (w), 1367 (m), 1276 (s), 1261 (s), 1190 (m), 1136 (m), 1112 (s), 1066 (s), 1029 (w), 855 (m), 832 (m), 763 (m), 713 (s), 704 (s), 694 (s).

4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrakis(2,6-**Synthesis** of tetramethyl bis(benzylthio)benzoate) (M3). Molecule M2 (2.005 g, 4.36 mmol), bis(pinacolato)diboron (1.108 g, 4.36 mmol), and PdCl₂(PPh₃)₂ (77.0 mg, 0.11 mmol) were loaded in a two-neck roundbottom flask and dried under vacuum at room temperature for 4 hours, followed by addition of anhydrous potassium acetate (857 mg, 8.73 mmol) under nitrogen protection. Anhydrous 1,4dioxane (16.0 mL) was bubbled with N₂ for three minutes and added to the flask. The mixture was stirred at 90 °C under nitrogen for 12 hours. After cooling to room temperature, an aqueous solution of K₃PO₄ (2.0 M, 5.2 mL, bubbled with N₂ for few minutes beforehand) was added to the mixture, followed by addition of 1,3,6,8-tetrabromopyrene (522 mg, 1.0 mmol). The mixture was further stirred at 90 °C for 24 hours. After cooling to room temperature, the resulting mixture was poured into cold water (200 mL) and extracted with DCM (3 × 100 mL). The combined organic phase was washed by distilled water $(3 \times 100 \text{ mL})$ and dried over anhydrous MgSO₄, followed by column chromatography (eluent: DCM/hexanes/ethyl acetate, 1:1:0.02) to yield M3 (pale yellow solid, 1.202 g, 54% yield based on 1,3,6,8-tetrabromopyrene). ¹H NMR (300 MHz, CDCl₃): δ = 7.63 (s, 4H), 7.33 (s, 8H), 7.20 (dt, J = 15.2 Hz, 34H), 7.08 (t, J = 6.8 Hz, 8H), 4.15 (s, 16H), 4.06 (s, 12H). ¹³C NMR (75 MHz, CDCl₃): δ = 168.06 (s), 141.97 (s), 140.69 (s), 136.83 (s), 135.37 (s), 134.29 (s), 133.31 (s), 129.21 (s), 129.00 (s), 128.63 (s), 128.10 (s), 127.53 (s), 125.42 (s), 125.27 (s),

52.82 (s), 40.67 (s). FT-IR (KBr pellet, v/cm⁻¹): 1731 (s), 1579 (m), 1528 (m), 1495 (m), 1454 (m), 1425 (m), 1273 (s), 1191 (m), 1135 (s), 1064 (s), 1029 (m), 765 (w), 700 (s).

Synthesis of 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrakis(2,6-bis(benzylthio)benzoic acid) (M5). Molecule M3 (172.0 mg, 0.10 mmol) was dissolved in tetrahydrofuran (THF, 9.0 mL), followed by addition of KOH solution (8.9 M, 9.0 mL in MeOH/H₂O, v:v=1:1). The mixture was stirred at 70 °C for 24 hours. After cooling to room temperature, 10% HCl(aq) was added to the resulting mixture to attain pH=1. A yellow precipitate thus formed was filtered, washed extensively by distilled water, and suction-dried on the filter paper to afford M5 as a yellow solid (164 mg, 98% based on M3). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.73 (s, 4H), 7.57 (s, 2H), 7.44 (s, 8H), 7.29 (d, *J* = 7.3 Hz, 16H), 7.18 (t, *J* = 7.5 Hz, 16H), 7.08 (t, *J* = 7.3 Hz, 8H), 4.32 (s, 16H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 168.61 (s), 141.13 (s), 138.22 (s), 137.40 (s), 135.69 (s), 133.67 (s), 130.81 (s), 129.66 (s), 129.43 (s), 128.82 (s), 127.86 (s), 127.54 (s), 125.56 (s), 125.07 (s), 38.30 (s). FT-IR (KBr pellet, v/cm⁻¹): 3000~3500 (bb), 1706 (s), 1602 (m), 1579 (s), 1527 (m), 1495 (m), 1454 (m), 1276 (m), 1241 (m), 1200 (m), 1142 (m), 1072 (m), 1029 (m), 765 (m), 700 (s).

4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrakis(2,6-dimercaptobenzoic **Synthesis** of acid) (H4OMTP). Molecule M5 (159 mg, 0.10 mmol), anhydrous AlCl₃ (480 mg, 3.6 mmol), dry DCM (10.0 mL) and dry toluene (10.0 mL) was mixed in a reaction tube in a N₂-filled glove box. After the reaction tube was taken out, the mixture was connected to a N2 manifold and stirred under N2 at room temperature for two hours. Afterward, 10% HCl(aq, 10.0 mL) was bubbled with N₂ for few minutes and added to the mixture, followed by stirring at room temperature for 2 hours. The vellow precipitate thus formed was collected by suction filtration and washed by 10% HCl(aq), distilled water, then DCM and dried under a reduced pressure to afford H4OMTP (80 mg, 89% vield based on M5). ¹H NMR (400 MHz, acetone- d_6): $\delta = 8.32$ (s, 4H), 8.09 (s, 2H), 7.63 (s, 8H). ¹³C NMR (100 MHz, acetone- d_6): $\delta = 167.28$ (s), 142.56 (s), 135.52 (s), 135.45 (d, J = 2.5 Hz), 129.48 (s), 129.15 (s), 128.47 (s), 128.27 (s), 125.67 (s), 125.35 (s). FT-IR (KBr pellet, v/cm^{-1}): 3000~3500 (bb), 1796 (w), 1701 (s), 1579 (s), 1525 (m), 1450 (m), 1368 (m), 1281 (m), 1256 (m), 1147 (m), 1060 (m), 1031 (m), 879 (w), 836 (w), 808 (w), 763 (w), 728 (w), 512 (w). Ligands for MOF samples used in activation, water stability and Hg sorption tests were prepared by this method.

4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrakis(2,6-**Synthesis** of tetramethyl bis(acetylthio)benzoate) (M4). In a N₂-filled grove box, a two-neck round-bottom flask was charged with M3 (940 mg, 0.55 mmol) and dry DCM (20.0 mL). After M3 was fully dissolved in DCM by stirring, AlCl₃ (900 mg, 6.75 mmol) and dry toluene (10.0 mL) were added. The flask was then taken out and connected to a N₂-manifold. The mixture was stirred at room temperature for about 20 minutes during which a dark brown mixture was formed. Afterward, the flask was chilled in an ice bath and acetyl chloride (0.6 mL, 8.41 mmol) was added under nitrogen protection. Then, the ice bath was removed and the mixture was stirred at room temperature for 30 minutes. Afterward, crushed ice was added to the resulting mixture and then the mixture was extracted with DCM (3×100 mL). The combined organic phase was washed by distilled water and dried over anhydrous MgSO₄, followed by flash column chromatography (eluent: DCM/hexanes/EA, 1:1:0.25) to yield **M4** (486 mg, 67% yield based on **M3**). ¹H NMR (300 MHz, CDCl₃): $\delta = 8.35$ (s, 4H), 8.05 (s, 2H), 7.84 (s, 8H), 3.92 (s, 12H), 2.40 (s, 24H). ¹³C NMR (75 MHz, CDCl₃): $\delta =$ 191.99 (s), 166.71 (s), 142.71 (s), 141.55 (s), 139.48 (s), 134.88 (s), 129.55 (s), 128.80 (s), 127.13 (s), 126.06 (s), 125.66 (s), 52.75 (s), 30.37 (s). FT-IR (KBr pellet, v/cm^{-1}): 2951 (w), 2925 (w), 2854 (w), 1738 (s), 1709 (s), 1583 (m), 1426 (m), 1276 (s), 1138 (m), 1112 (s), 1072 (m), 1063 (m), 951 (m), 610 (m).

Alternative synthesis of H₄OMTP. Molecule M4 (154 mg) was stirred in 1.0 M dichloromethane solution of BBr₃ (6.0 mL) at room temperature under N₂ for 24 hours. Then crushed ice was added and the mixture was stirred for 1 hour. A yellow solid thus formed was collected by suction filtration, washed by distilled water and DCM to afford H₄OMTP as the linker molecule (100 mg, 92% yield based on M4). The solution ¹H NMR spectrum of this compound produced the same result as that prepared by AlCl₃ protocol. Chemical analysis of the product yielded the following: Calcd [C (56.27%), H (2.79%), S (27.31%)]; Found [C (51.96%), H (2.27%), N (0.32%), S (21.73%)].



Figure S2. The three tetracarboxylic acid linkers H₄TP, H₄OMTP and H₄TEP, with structural information of their respective Zr-MOFs.

Synthesis of ZrOMTP. In a clear glass vial, ZrCl₄ (37.0 mg, 0.159 mmol) and benzoic acid (400 mg, 3.28 mmol) were dissolved in DEF (7.0 mL) and then transferred into a 25-mL glass ampoule. The linker H₄OMTP (30.0 mg, 0.032 mmol) and ethylenedithiol (180 mg, 1.92 mmol) were added and the ampoule was then flame-sealed and heated at 120 °C in a programmable oven for 48 hours. After cooling to room temperature the yellow precipitate was collected by filtration. The solid was then washed by DMF (3 × 10 mL), acetonitrile (2 × 10 mL), and dried by suction under N₂ protection to yield the as-made product (yield: 64.0 mg).

Structure modeling for ZrOMTP.

The structure model of ZrOMTP, including cell parameters and atomic positions, was generated using Materials Studio (v6.1.0) suit of programs by Accelrys. A crude structure model was obtained by substituting the ligand of NU-1100⁴ with tetratopic **OMTP** linker while maintaining a geometrical arrangement of organic linkers and zirconium clusters consistent with the **ftw** topology, followed by Geometry Optimization of Forcite Calculation in Materials Studio by Accelrys. The lattice parameters were modified using the Pawley refinement procedure to match the experimental PXRD, leading to a = 36.4015 Å. Instrumental peak broadening parameters and additional profile parameters, line shift parameters, background, peak asymmetry and crystallite size broadening of sample were also used in the refinement. After lowering the symmetry to P1, the structure was subject to geometry optimization under the constraint of fixed lattice geometry.

The proper symmetry was then found (via "Find Symmetry" from the program) to be Im-3 (No. 204, a = 36.4015 Å), and subsequently imposed on the structure, and the result was exported as a cif file (attached as part of the Supplementary Information).



Figure S3. Pawlay refinement of the experimental diffraction pattern of an as-made sample of ZrOMTP. The difference plot (grey) means that the experimental profile (black dotted) minus the refined profile (red).

Activation of ZrOMTP. An as-made solid sample of ZrOMTP was loaded into a 250-mL twoneck flask and the flask was connected to a N₂-manifold. A mixture of DMF and HCl (50.0 mL of DMF and 2.0 mL of 35% HCl, deaerated by N₂ beforehand) was transferred via cannula into the flask. The mixture was heated at 100 °C under N₂ for 1 day and the supernatant was decanted. The same heating process was repeated by using another fresh mixture of DMF/HCl (50.0 mL of DMF and 2.0 mL of 35% HCl, deaerated by N₂ beforehand). Afterward, the supernatant was decanted and a fresh DMF (50.0 mL, deaerated by N₂ beforehand) was added and heated at 100 °C for 6 hours and then the supernatant was decanted. The same heating procedure using DMF was repeated twice. Next, a fresh MeOH (50.0 mL, deaerated by N₂ beforehand) was added and heated at 75 °C for three days during which the MeOH supernatant was replaced by another batch of fresh MeOH three times per day. Finally, the MOF solid was dried using an oil pump and heated at 120 °C for 24 hours. Elemental analyses found [C (33.21%), H (4.35%), N (0.15%)]. This analysis closely matches the formula $Zr_6O_4(OH)_6(OMTP)_{2.5}(C_3H_7NO)_{0.4}(H_2O)_{53}$ (mw 4035), calcd: [C (33.10%), H (4.24%), N (0.14%)]. The activated ZrOMTP was used for N₂ sorption measurement after vacuum outgassing process (120 °C, 12 hours), see Figure S14 for the isotherm.



Figure S4. Thermogravimetric analysis (TGA) plots for an activated sample of ZrOMTP (5.348 mg; N₂ flow rate: 20 mL/min; heating rate: 2 °C/min). The empirical formula Zr₆O₄(OH)_{16-4n}(OMTP)_n(C₃H₇NO)_m(H₂O)_y was used to fit the elemental analysis and the TGA data. It was found that when n=2.5, the elemental and TGA data can be readily fitted. Moreover, n=2.5 indicates the ligand deficiency in the framework as compared to the formula Zr₆O₄(OH)₆(**OMTP**)_{2.5} (mw 3051) equals 739/3051=24.2%, slightly smaller than the residual weight percentage found in TGA (24.1/0.954%=25.3%). When compared to CHN elemental analysis data, the calculated Zr₆O₄(OH)₆(**OMTP**)_{2.5}(C₃H₇NO)_{0.4}(H₂O)₅₃ (mw 4035) gives [C (33.10%), H (4.24%), N (0.14%)], matching closely the measured data [C (33.21%), H (4.35%), N (0.15%)]. The guest content (e.g., water and DMF) from the calculated formula was 24.4% which was larger than the initial weight loss (100–95.4=4.5%) found in the TGA plot. The different guest content could be due to the different sample handling in the two types of tests (e.g., the sample for CHN analysis was placed in air for about 24 hours, whereas the one for the TGA was placed on the sample holder inside the

TGA machine at 30 °C under a N_2 flow for few hours before the analysis was started). The formula C₃H₇NO corresponds to the molecular formula of DMF guest.



Figure S5. PXRD patterns of: (a) as-made ZrOMTP; (b) sample (a) after being heated at 200 °C under N₂ for 12 hours; (c) sample (b) after being heated at 250 °C under N₂ for 12 hours.



Figure S6. The Raman spectrum of an activated sample of ZrOMTP.

Water stability test for ZrOMTP. An activated ZrOMTP sample (86mg) was mixed with DI water (20 mL) in a two-neck round-bottom flask, and heated to boiling in a 130 °C oil bath for 24 hours. The solid was collected by filtration, dried under vacuum at 100 °C for two hours, and transferred into the gas sorption test tube for outgassing (71 mg after vacuum outgassing at 120 °C for 6 hours) and N₂ sorption measurement (see Figure S15 for the isotherm obtained). Afterward, the MOF solid was also analyzed by PXRD (Figure 2, pattern d) and IR (Fgiure S7) spectroscopy.



Figure S7. The IR spectra of (a) an activated sample of ZrOMTP (sample prepared under N_2 protection, with minimal air exposure); (b) the sample of (a) after treating with boiling water.

Hg(II) sorption kinetics of ZrOMTP. An activated sample of ZrOMTP (10.0 mg) and a freshly prepared aqueous solution of mercury(II) nitrate (6.57 ppm Hg as quantified by ICP-MS, 25.0 mL, pH=6.8 NaH₂PO₄/Na₂HPO₄ buffer) were mixed in a 50-mL centrifuge tube and stirred at room temperature. During the adsorption, the mixture was withdrawn and filtered at intervals through a 0.22-µm membrane filter for all samples (each sample of 0.5 mL), then each of the filtrates was diluted using Milli-Q water (18.2 MΩcm Millipore, Billerica, MA, USA) and quantified by ICP-MS to determine the remaining Hg(II) content.

Correct interpretation of kinetics data in adsorption studies is of topical interests (e.g., see Chao's recent review).¹ The present ZrOMTP network, with its porosity and well-defined binding sites, appears fitting for the Langmuir model. The kinetic data at the initial stage indeed fit the Lagergren's first order equation $\ln(C_t) = -k_1t + \ln(C_t)$ (Figure 3c), which can be rationalized using the Langmuir model $dC_t/dt = kq_tC_t$,² where C_t (mg L⁻¹) refers to the remaining Hg in the solution, q_t the number of unoccupied sites of the sorbent at time t (min), and k (g⁻¹ min⁻¹) the rate constant—with q_t approximated to be a constant.

Such an approximation is justified in the present condition, in which excess adsorbent was used so that the sorption sites greatly outnumber the Hg ions, e.g., in the above test the sorbent (10.0 mg, $q_{\text{max}} = 403 \text{ mg g}^{-1}$) offers sites for 4.03 mg of Hg uptake, over 24 times the Hg ions present (0.164 mg). In general, drinking water treatment usually involves heavy metal pollutants at very low concentrations (e.g., sub-ppm), and the adsorbent is deployed in large excess to fully suppress the residual heavy metal content. In other words, only a small fraction of the binding sites of the adsorbent will be occupied, which further justifies the first order assumption. The linear plot based on the first four data points yields a k_1 of 0.0468 min⁻¹ (Figure 3c), with the corresponding halflife being 14.8 mins.

The kinetic data also fit the pseudo-second-order kinetic model³ $dq_t/dt = k_2(q_e - q_t)^2$ with the following linear fit:

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

where $q_t \pmod{g^{-1}}$ is the amount of Hg adsorbed at time $t \pmod{q_e} \pmod{g^{-1}}$ is the Hg adsorbed at equilibrium, and $k_2 \pmod{g^{-1} \min^{-1}}$ is the adsorption rate constant (Figure S8).

Such a linear fit, however, should be taken with caution.^{1a, c} Theoretically, the pseudo second order model works best when the total number of the metal ions equals that of the adsorption sites, i.e., $C_iV = q_e$, namely $C_tV = C_iV-q_t = q_e-q_t$, so that $(q_e-q_t)^2 = (C_iV-q_t)(q_e-q_t) = (1/V)(C_i-q_t/V)(q_e-q_t) = (1/V)(C_t)(q_e-q_t)$. When excess sorbent was used (as is often the case), we have $C_iV < q_e$ instead and the first order description instead becomes more meaningful.

Second, the linearity between t/q_t and t/q_e is often gratuitous, especially in fast kinetics where $l/(k_2q_e^2)$ is of small, negligible values, rendering $t/q_t \approx t/q_e$. At longer time points, t/q_e becomes ever greater than $l/(k_2q_e^2)$, making the linearity a triviality further devoid of physical significance; also at longer times, the adsorption approaches equilibrium, and the reverse process—the desorption—becomes significant, further invalidating the one-way pseudo second order assumption.^{1a} Indeed, with excess adsorbent (i.e., $C_iV << q_e$), the q_e value derived from the superficially linear plot between t/q_t and t/q_e is simply the total meal ions present, having nothing to do with the number of available adsorption sites physically present.

To properly assess the sorbent kinetics in connection with the removal of trace heavy metal contaminants, we suggest that excess adsorbent be used in order to mimic the actual deployment of the adsorbent, and to simplify the kinetics to the first order regime. Also, data points should be collected at the early stage in order to avoid the complication from desorption. For example, with the distribution quotient $Q_d = (C_i - C_l)V/C_l m < K_d/100$, the desorption rate is no greater than 1% that of adsorption, and can thus be omitted. As adsorption isotherm is routinely measured, the adsorption capacity q_e and K_d derived thereby provide valuable guidance and cross-check for the kinetic studies. For benchmarking the kinetic performance, the first order rate constant k_l can be divided by the amount of sorbent m (g). In the above case, $k_l/m=0.0468/0.010=4.68 \text{ min}^{-1} \text{ g}^{-1}$.



Figure S8. A pseudo-second-order kinetic plot for Hg(II) adsorption using an activated sample of ZrOMTP. Starting from the 5th point (t = 30 min), the value of adsorption rate constant (k_2) is calculated to be 0.079 g mg⁻¹ min⁻¹.

Hg(II) sorption isotherm measurement of ZrOMTP. Mercury(II) nitrate solutions of various Hg(II) concentrations (50, 100, 200, 300, 400, 500, 600, 700, 800 and 1000 mg L⁻¹) were prepared using KH₂PO₄/Na₂HPO₄ buffer solution (pH = 6.8), and used in the following adsorption procedure. An activated sample of ZrOMTP (5.0 mg) was added to each centrifuge tube containing Hg(II) solution (7.0 mL) with different concentrations. The mixtures were stirred at room temperature for 3 hours. The MOF solids were separated by centrifugation and the supernatant was filtered through a 0.22-µm membrane and analyzed using ICP-OES to determine the remaining Hg(II) content. The saturated Hg adsorption capacity (q_{max}) is calculated by the following mathematical expression:

$$\frac{C_e}{q_e} = C_e \times \frac{1}{q_{max}} + \frac{1}{K_L q_{max}}$$

where $q_e \text{ (mg g}^{-1)}$ is the sorption capacity at equilibrium state, $C_e \text{ (mg L}^{-1)}$ is the Hg concentration remaining in the solution at equilibrium state and $K_L \text{ (L mg}^{-1)}$ is a constant related to binding site affinity. Values for q_{max} and K_L can be obtained from the slope and y-intercept, respectively, by plotting C_e/q_e versus C_e , as shown in Figure 3e.

Recyclability test of ZrOMTP for Hg(II) adsorption. An activated sample of ZrOMTP (10.0 mg) and a freshly prepared aqueous solution (25.0 mL) of mercury(II) chloride (which contained

1% HNO₃, 7.3 ppm Hg as quantified by ICP-MS) were mixed in a 50-mL centrifuge tube and stirred at room temperature for 3 hours. The MOF solids were then separated by centrifugation. The supernatant thus obtained was filtered through a 0.22- μ m membrane and analyzed using ICP-MS to determine the residual Hg content. The collected MOF solids were stirred in water (20 mL) for few minutes then separated by centrifugation, and this washing procedure was repeated twice. Afterwards, the MOF solids were reactivated by heating in neat ethane-1,2-dithiol (10 mL) at 80 °C for 4 hours. After cooling to room temperature the MOF solids were separated by centrifugation and the dithiol supernatant was decanted. The above heating procedure was repeated twice. Afterwards, the MOF solids were washed by shaking in methanol and then separated by centrifugation. This washing procedure was repeated ten times to ensure the complete removal of Hg from the MOF host. After being dried by an oil pump, the MOF solids were used for the next cycle. After three runs of the adsorption, the MOF solids were washed by following the above ethane-1,2-dithiol procedure as well as methanol procedure, and analyzed by PXRD. The affinity of a sorbent for a target metal is described by the distribution coefficient (*K*_d). The *K*_d is defined as:

$$K_{\rm d} = \frac{(C_i - C_f)}{C_f} \times \frac{V}{m}$$

where C_i is the initial concentration of the metal ion, C_f is the final equilibrium concentration of the metal ion, V is the volume of the solution (mL) and m is the weight of the sorbent used (g). The K_d values for successive adsorption cycles were calculated to be 1.6×10^8 , 1.2×10^8 and 1.8×10^8 mL g⁻¹.

Table S1. Summary of the high mercury removal efficiency of ZrOMTP in Hg-contaminated water.

	1 st cycle	2 nd cycle	3 rd cycle
Initial Hg conc.	7.3 ppm	7.3 ppm	7.3 ppm
Final Hg conc.	0.114 ppb	0.278 ppb	0.096 ppb
Hg removal efficiency	99.998%	99.996%	99.997%
K _d	$1.6 \times 10^8 \text{ mL g}^{-1}$	$1.2 \times 10^8 \text{ mL g}^{-1}$	$1.8 \times 10^8 \text{ mL g}^{-1}$

Postsynthetic crosslinking by pentafluorobenzaldehyde. An activated sample of ZrOMTP (stored in THF) was pipetted into a 10-ml Schlenk tube and the solvent therewith was dried off by a N₂ stream. To this solid of ZrOMTP (weighed to be 34.0 mg, containing about 0.17 mmol of - SH) was added pentafluorobenzaldehyde (pfb, 19.0 mg, 0.10 mmol), deaerated THF (2.0 mL) and triethylamine (25.0 mg, 0.25 mmol). The mixture was capped and heated to reflux by a 90 °C oil bath for 3 days. Afterward, the mixture was cooled to room temperature and the resulted solid was collected by suction filtration, washed by THF (5×2 mL) and suction-dried. This solid product was further soaked in CH₂Cl₂ (5 ml) for 6 hours and decanted to repeat the soaking cycle, after which the solid was collected by filtration and evacuated by an oil pump to afford the crosslinked product (ZrOMTP-pfb). Energy-dispersive X-ray spectroscopy (EDX) found the molar ratio S:Zr:F to be 1:0.4:1.2.

ZrOMTP-pfb was also prepared by stepwise addition of pfb to help monitor the crosslinking reaction. In the first step, the activated ZrOMTP (86 mg, containing about 0.054 mmol of the OMTP ligand), pfb (20 mg, 0.10 mmol), triethylamine (430 mg, 4.3 mmol) and THF (3 mL) was refluxed for 18 hrs in a sealed Schlenk tube under N₂ protection. Afterward, thin layer chromatography (TLC, by 3:1 *n*-hexane/CH₂Cl₂; see images below) found pfb to be nearly all consumed (i.e., to result in a 2:1 pfb/OMTP ratio in the solid). In the second step, additional pfb (10 mg, 0.051 mmol) was added to react (same way as before) for another 16 hrs; after which TLC indicated the distinct presence of pfb, together with and some (uncharacterized) unsaturated species with slightly smaller Rf values. Together the two steps indicates the pfb/OMTP ratio in the solid to be between 2:1 and 3:1.

The solid in the mixture was then collected by filtration and activated for N₂ sorption test. Specifically, the isolated solid was first repeatedly washed by THF, and then soaked (four times; decanted each time) in 15 mL of chloroform in a two-neck flask at 70 °C for 12 hours. The solid was then isolated by filtration and dried in air. Nitrogen sorption measurement was performed on this solid sample after degassing at 120 °C for 12 hours, see Figure S16 for the N₂ sorption isotherm.



Figure S9. Images of TLC (by 3:1 *n*-hexane/CH₂Cl₂) for the reaction mixture. (a) right after mixing at room temperature (P1: reaction mixture; S: pfb; M: co-spot of P1 and pfb). (b) after refluxing for 18 hours (P4: reaction mixture; M: co-spot of P4 and pfb). (c) after adding 10 mg more of pfb and refluxing for another 16 hours ((P7: reaction mixture; S: pfb; M: co-spot of P7 and pfb). For comparison, the three reaction mixtures in similar amounts were spotted onto the TLC plates.



Figure S10. A scheme showing the idealized post-synthetic crosslinking reaction of ZrOMTP host with pfb guest.



Figure S11. The IR spectra of (a) the pfb molecule; (b) an activated sample of ZrOMTP; (c) the sample of ZrOMTP-pfb; (d) the sample of ZrOMTP-pfb after dezirconiumation. The dotted lines indicate the distinct aldehyde C=O stretch (1707 cm⁻¹) and the thiol SH stretch (2576 cm⁻¹).

NaF resistance test of ZrOMTP-pfb. ZrOMTP-pfb (5.0 mg) was stirred in a 0.5% NaF (w/w, 2.0 mL) solution for 24 hours. The resulted solid was collected by centrifugation, repeatedly washed by DI water, and dried in air. EDX indicated that the molar ratio of S:Zr:F to be 1:0.3:1.2. A larger sample (57 mg) was similarly prepared for N₂ sorption measurement: ZrOMTP-pfb was soaked and stirred in 23 g 0.5% (w/w) NaF solution at room temperature for 24 hours, and the solid was then collected by filtration and washed with DI water (8 mL × 9 times). The resulted solid (ZrOMTP-pfb-NaF) was dried at 90 °C under vacuum for two hours and then transferred into gas sorption sample tube for vacuum outgas (120 °C, 12 hours), see Figure S17 for the N₂ sorption isotherm.

Dezirconiumation of ZrOMTP-pfb. ZrOMTP-pfb (5.0 mg) was first soaked in a 5% (w/w) NaF aqueous solution (1.0 mL) for 3 days, and an HCl solution (10% w/w, 1.0 mL) was then added and mixed together (caution: HF is corrosive, avoid direct contact with the solution!). The resulted mixture was left in air for one day, after which the resulting solid was collected by filtration and repeatedly washed by water, and then dried in air to afford a red solid. EDX on this solid indicated the S:Zr:F ratio to be 1:0.04:0.8, and PXRD indicated an amorphous nature (Figure S12, pattern e). Efforts to investigate the possibility of recovering the crystallinity of the solid (e.g., by metal re-insertion via contact with a ZrCl4 or TiCl4 solution) are ongoing.



Figure S12. PXRD patterns of (a) as-made ZrOMTP; (b) the sample of (a) after being treated with 0.5% NaF (aq); (c) a sample of ZrOMTP after reacting with pentafluorobenzaldehyde (pfb; with proposed reaction schemes shown on top); (d) the sample of (c) after being treated with 0.5% NaF (aq); (e) the sample of (c) after being treated with 5% NaF (aq) for dezirconiumation.



Figure S13. SEM images $(5 \times 10^4 \text{ magnification})$ of (a) an activated sample of ZrOMTP; (b) the sample of ZrOMTP-pfb; (c) the sample of (b) after dezirconiumation by 5% NaF (aq). Scale bar: 500 nm.



Figure S14. (a) N₂ sorption isotherm at 77K and (b) BET plot for an activated ZrOMTP sample (102.3 mg, 12 h, 120 °C under vacuum). The calculated BET surface area is 1443.6 m²/g with a high correlation coefficient of 0.999898. QSDFT analysis on the sorption data showed two major pores of 0.6 nm and 1.1 nm average pore width and a micropore volume of 0.37 cm³·g⁻¹ (see Figs. S18-19 below). Using a model with fully-occupied ligand sites (i.e., no ligand deficiency), the Connolly (at probing radius 1.86 Å) surface area and pore volume was calculated using the Materials Studio software to be 2358 m²/g and 0.568 cm³/g, whereas the accessible solvent surface and volume 1470 m²/g and 0.191 cm³/g, respectively. The ligand deficiency in the ZrOMTP

sample, however, complicates the comparison between observed and calculated values, and entails more sophisticated modeling studies for taking into account the effect of the absent ligands.



Figure S15. (a) N₂ sorption isotherm at 77K and (b) BET plot for a boiling-water-treated ZrOMTP sample. The calculated BET surface area is 1290.2 m^2/g with a high correlation coefficient of 0.999955.



Figure S16. (a) N_2 sorption isotherm at 77K and (b) BET plot for a pfb-treated ZrOMTP sample (i.e., ZrOMTP-pfb). The calculated BET surface area is 822.6 m²/g with a high correlation coefficient of 0.999990.



Figure S17. (a) N₂ sorption isotherm at 77K and (b) BET plot for a ZrOMTP-pfb sample after being treated by 0.5 % NaF aqueous solution. The calculated BET surface area is $652.5 \text{ m}^2/\text{g}$ with a high correlation coefficient of 0.999990.



Figure S18. Pore Width distribution of: (a) ZrOMTP; (b) boiling-water-treated ZrOMTP; (c) pfb-treated ZrOMTP (i.e., ZrOMTP-pfb); and (d) 0.5%-NaF-treated ZrOMTP-pfb.



Figure S19. Cumulative pore volume plots of: (a) ZrOMTP; (b) boiling-water-treated ZrOMTP; (c) pfb-treated ZrOMTP (i.e., ZrOMTP-pfb); and (d) 0.5%-NaF-treated ZrOMTP-pfb.



Figure S20. Cumulative surface area plots of: (a) ZrOMTP; (b) boiling-water-treated ZrOMTP; (c) pfb-treated ZrOMTP (i.e., ZrOMTP-pfb); and (d) 0.5%-NaF-treated ZrOMTP-pfb.

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