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Improving Stability to Desolvation and Mercury Removal in Zr(IV)-carboxylate Frameworks by Bulky Sulfur Functions

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Supporting Information

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Experimental details

General procedure. Compound **SM6** and **SM11** were prepared by our reported methods[1], sodium 4-methoxy-benzenethiolate (96%), sodium thiomethoxide (96%) and pentaerythrityl tetrabromide (96%) were purchased from Aldrich and used without further purification. Bis(triphenylphosphine)palladium(II) chloride and trimethylsilylacetylene were purchased from Meryer and used without further purification. Nuclear magnetic resonance (NMR) spectra were recorded at 298 K on Mercury VX-300 spectrometers, with working frequencies of 300 and 400 MHz for ^{1}H and 75 and 100 MHz for ^{13}C nuclei. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents, with tetramethylsilane (TMS) as the internal standard.

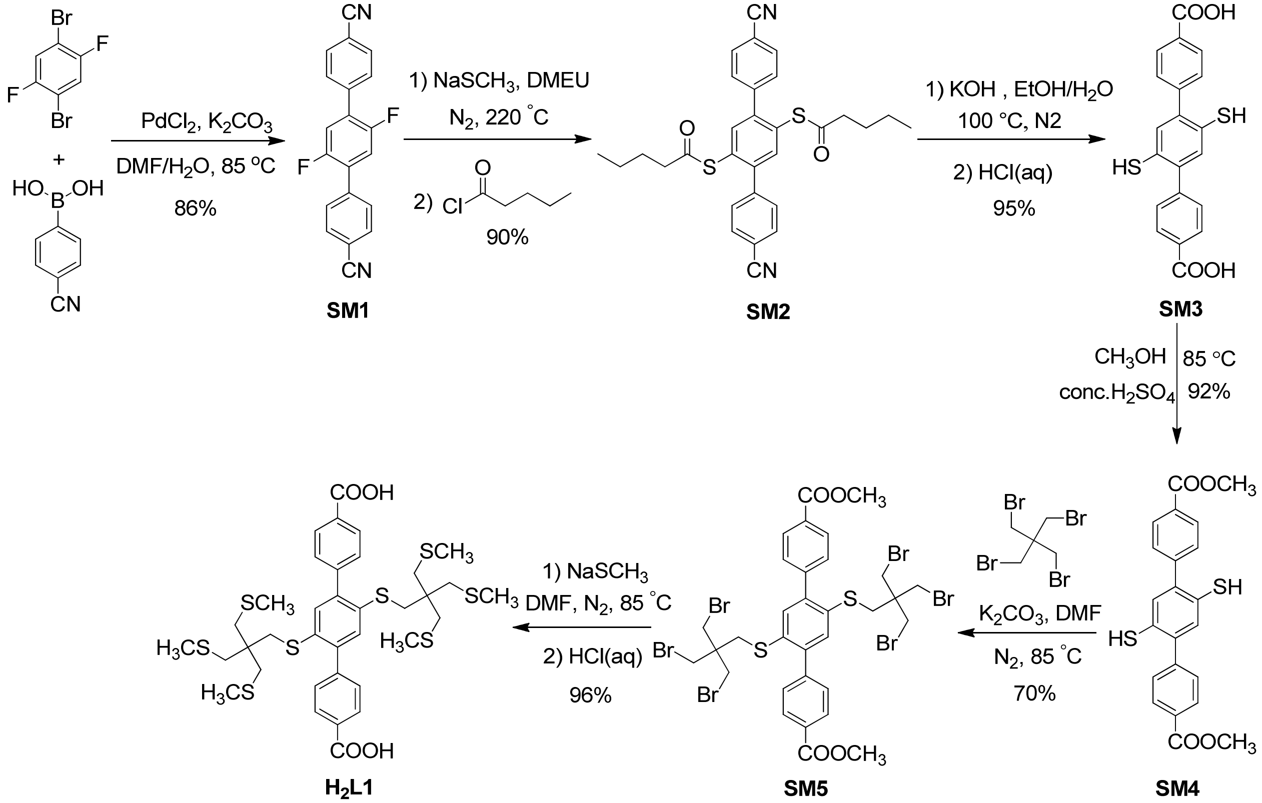


Figure S1. The synthetic steps for H_2**L1**.

Synthesis of SM1. 1,4-Dibromo-2,5-difluorobenzene (0.816 g, 3.00 mmol), (4-cyanophenyl)boronic acid (0.970 g, 6.60 mmol), palladium (II) chloride (0.032 g, 0.18 mmol), potassium carbonate (1.656 g, 11.98 mmol) and a solution mixture of *N*,*N*-dimethylformamide (DMF)/water (80.0 mL, 1:1, v:v) were added to a round-bottom flask charged with a stirring bar and heated at 85 ^{o}C for 72 hours. After cooling to room temperature, the resulting mixture was poured into distilled water (400 mL) and the precipitate was collected by suction filtration, washed by distilled water (3 × 100 mL), dissolved in dichloromethane (DCM, 300 mL), and dried over anhydrous $MgSO_4$. After solvent removal, the solid residue was purified by flash column chromatography (eluent: petroleum ether/DCM, 2:1) to yield **SM1** as a white solid (0.816 g, 86% based on 1,4-dibromo-2,5-difluorobenzene). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.03-8.01 (d, *J* = 8.5 Hz, 4H, CHAr), 7.88-7.86 (d, *J* = 8.3 Hz, 4H, CHAr), 7.77-7.73 (t, *J* = 8.9 Hz, 2H, CHAr).

Synthesis of SM2. A mixture of **SM1** (0.816 g, 2.580 mmol) and sodium thiomethoxide (2.528 g, 36.12 mmol) were added to a Schlenk tube charged with a stirring bar under N_2 protection, 1,3-dimethyl-2-imidazolidinone (DMEU, 20.0 mL) were degassed and injected into the tube via cannula under N_2. The reaction mixture was then stirred at 220 ^{o}C under nitrogen for 48 hours. Upon cooling in crashed ice, valeryl chloride (4.3 mL, 36.2 mmol) was injected into the tube by syringe, and the mixture was stirred at room temperature under nitrogen for 24 hours. Afterward, the mixture was then poured into distilled water (400 mL) and the precipitate was collected by suction filtration, washed by distilled water (3 × 100 mL), dissolved in DCM (300 mL), dried over anhydrous $MgSO_4$. After solvent removal, the solid residue was purified by flash column chromatography (eluent: petroleum ether/DCM, 1:2) to afford **SM2** as a white solid (1.191 g, 90% based on **SM1**). ^{1}H NMR (400 MHz, $CDCl_3$):): δ = 7.69-7.67 (d, *J* = 8.4 Hz, 4H, CHAr), 7.53 (s, 2H, CHAr), 7.48-7.46 (d, *J* = 8.4 Hz, 4H, CHAr), 2.48-2.45 (t, *J* = 7.4 Hz, 4H, CH_2), 1.51-1.43

(m, J = 15.0 Hz, 4H, CH_2), 1.22-1.12 (m, J = 14.6 Hz, 4H, CH_2), 0.84-0.81 (t, J = 7.3 Hz, 6H, CH_3).

Synthesis of SM3. Molecule **SM2** (1.191 g, 2.322 mmol) added to a Schlenk tube charged with a stirring bar under N_2 protection. Then a solution mixture of KOH (1.6 M, 30.0 mL in EtOH/H_2O, 1:1, v:v) was degassed and injected into the tube via cannula under N_2. Then the mixture was heated at 100 °C for 60 hours. After being cooled to room temperature, 30% HCl was injected into the tube by syringe under N_2 protection with vigorous stirring. After the pH value of the mixture became lower than 2, the precipitate was collected by suction filtration, washed extensively with distilled water to provide **SM3** as a light yellow powder (0.846 g, 95% based on **SM2**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.08 (s, 2H, COOH), 8.05-8.03 (d, J = 8.1 Hz, 4H, CHAr), 7.58-7.56 (d, J = 8.1 Hz, 4H, CHAr), 7.47 (s, 2H, CHAr), 5.37 (s, 2H, SH).

Synthesis of SM4. A round-bottom flask was loaded with a stirring bar, the molecule **SM3** (0.846 g, 2.215 mmol), methanol (20.0 mL) and concentrated H_2SO_4 (1.0 mL). The flask was connected to a water condenser and refluxed at 85 ^{o}C for 48 hours. Upon cooling to room temperature, the resulting mixture was poured into distilled water (400 mL) and the precipitate was collected by suction filtration, washed extensively with distilled water to yield **SM4** as a white solid (0.836 g, 92% based on **SM3**). ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 8.14-8.12 (d, J = 8.2, 4H, CHAr), 7.64-7.62 (d, J = 8.2, 4H, CHAr), 7.46 (s, 2H, CHAr), 4.27 (s, 2H, SH), 3.93 (s, 6H, CH_3).

Synthesis of SM5. A mixture of **SM4** (0.836 g, 2.038 mmol), pentaerythrityl tetrabromide (1.659 g, 4.280 mmol) and potassium carbonate (1.274 g, 8.152 mmol) were added to a Schlenk tube charged with a stirring bar under N_2 protection. DMF (20.0 mL, bubbled by N_2 for 20 minutes beforehand) was injected into the tube via cannula under N_2. Then the mixture was heated at 85 °C overnight. After being cooled to room temperature, the mixture was then poured into distilled water (200 mL) and the precipitate was collected by suction filtration, washed extensively with water, dissolved in DCM (300 mL), dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (eluent: petroleum ether/DCM, 1:2) to yield **SM5** as a white solid (1.461 g, 70% based on **SM4**). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09-8.07 (d, *J* = 8.4 Hz, 4H, CHAr), 7.50-7.47 (d, *J* = 8.4 Hz, 4H, CHAr), 7.45 (s, 2H, CHAr), 3.91 (s, 6H, CH_3), 3.29 (s, 12H, CH_2), 2.88 (s, 4H, CH_2).

Synthesis of H_2L1. Molecule **SM5** (0.816 g, 2.58 mmol) and sodium thiomethoxide (2.528 g, 36.12 mmol) were added to a Schlenk tube charged with a stirring bar under N_2 protection, DMF (20.0 mL, bubbled by N_2 for 20 minutes beforehand) was transferred to the tube via cannula under N_2. The reaction mixture was then stirred at 85 °C under nitrogen for 48 hours. After being cooled to room temperature, the mixture was poured into distilled water (200 mL), and 30% HCl was added with vigorous stirring. After the pH value of the mixture became lower than 2, the precipitate was collected by suction filtration, washed extensively with distilled water to yield H_2**L1** as a light yellow powder (1.09 g, 96% based on **SM5**). ^{1}H NMR (400 MHz, DMSO-d_6/DCl): δ = 8.04-8.02 (d, *J* = 8.1 Hz, 4H, CHAr), 7.58-7.56 (d, *J* = 8.1 Hz, 4H, CHAr), 7.46 (s, 2H, CHAr), 2.91 (s, 4H, CH_2), 2.46 (s, 12H, CH_2), 1.94 (s, 18H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.56, 144.19, 142.16, 133.54, 132.21, 130.54, 130.09, 129.62, 45.07, 40.98, 40.87, 17.28.

Crystallization of Zr-L1. $ZrCl_4$ (7.2 mg, 0.031 mmol), H_2**L1** (24.0 mg, 0.030 mmol), benzoic acid (80.0 mg, 0.656 mmol, about 21 molar equivalents to $ZrCl_4$; used as a modulator to promote the crystal growth process), and DMF (1.0 mL) were loaded in a Pyrex glass tube. The tube was then sealed and heated at 130 °C in an oven for 72 hours, followed by natural cooling to room temperature, during which colorless octahedron shape single crystals suitable for single-crystal X-ray diffraction were formed (12.1 mg, 65% based on H_2**L1**). The crystals thus obtained were suspended in DMF (5.0 mL) and then dried in air to give the as-made product as colorless octahedron crystals. Elemental analysis found [C (45.43%), H (5.15%), N (1.53%)]; a fitting formula can be determined to be $Zr_6O_4(OH)_6(C_{36}H_{44}O_4S_8)_5(C_3H_7NO)_5(H_2O)_5$ (mw 5155), which gives a calculated profile as [C (45.43%), H (5.30%), N (1.36%)]. The quantification of the C_3H_7NO (DMF) and the water guests are also supported by the ^1H NMR spectrum (see figure S5 and thermogravimetric analysis (TGA, see Figure S6). The ^1H NMR spectrum of a solution obtained from dissolving crystals of Zr-**L1** in DCl (38% in D_2O)/DMSO-d_6 (1:4, v:v), consequently heating at 50°C under sonication for about 5 min.

Activation of crystals of Zr-L1. The freshly prepared crystal (5.0 mg) was stored in a 10 mL glass vial with DMF (4.0 mL) at 80 ℃ for 6 hours. The DMF solution was decanted and the crystals were washed with acetonitrile (5.0 mL x 3 — each time, the crystals were allowed to soak for 4 hours before the CH_3CN was decanted).

Extraction of $HgCl_2$ from crystals of Zr-L1-$HgCl_2$. In a clear glass vial, an acetonitrile solution (0.2 mL) of as-made Zr-L1-$HgCl_2$ crystals (5.0 mg) and 2-mercaptoethanol (18.0 mg) was stirred slowly at room temperature for about 24 hours. The solid was isolated by centrifugation and washed extensively with acetonitrile (ca. 20.0 mL). The amount of $HgCl_2$ remained in the 2-mercaptoethanol treated sample was determined by ICP-OES, which revealed that only 3.2% of the original Hg content was found to remain.

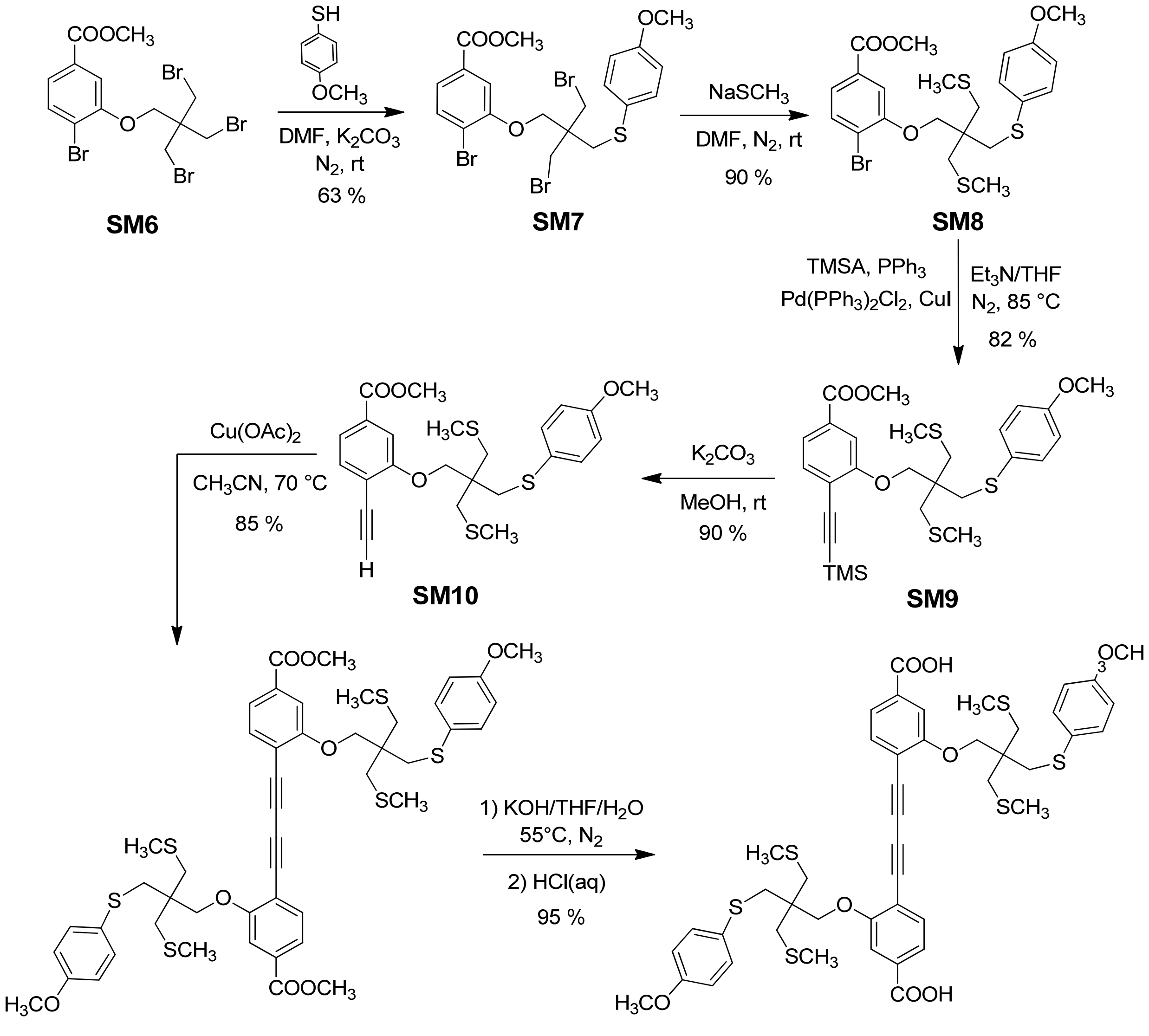


Figure S2. The synthetic route of the molecule H2**L3**.

Synthesis of SM7. Compound **SM6** (2.15 g, 4.0 mmol) was dissolved in dry DMF (14.0 mL) and added to a two-neck round-bottom flask under a nitrogen atmosphere. Anhydrous potassium carbonate (0.80 g, 5.80 mmol) and a solution of 4-methoxy-benzenethiol (0.41 g, 2.90 mmol) in dry DMF (10.0 mL) was added into the flask. The mixture was then stirred at room temperature under nitrogen overnight. Afterward, distilled water (120 mL) was added and the resulting mixture was extracted with DCM (3 × 100 mL), washed by distilled water (3 × 100 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by flash column chromatography (eluent: hexanes/DCM, 2:1) to afford **SM7** as a white oily liquid (1.10 g, 63% based on sodium 4-methoxy-benzenethiolate). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.53 (d, *J* = 8.2 Hz, 1H, CHAr), 7.49-7.47 (d, *J* = 8.2 Hz, 1H, CHAr), 7.37-7.34 (d, *J* = 8.3 Hz, 2H, CHAr), 7.24 (s, 1H, CHAr), 6.63-6.61 (d, *J* = 8.3 Hz, 2H, CHAr), 4.00 (s, 2H, CH_2OAr), 3.93 (s, 3H, $COOCH_3$), 3.72 (s, 4H, CH_2Br), 3.65 (s, 3H, CH_3OAr), 3.26 (s, 2H, CH_2SAr). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.19, 159.14, 154.02, 133.74, 132.99, 130.37, 125.47, 123.20, 117.81, 114.56, 113.07, 67.96, 55.12, 52.43, 45.15, 38.67, 35.72.

Synthesis of SM8. Compound **SM7** (1.10 g, 1.84 mmol) was dissolved in dry DMF (10.0 mL) and added to a two-neck round-bottom flask under a nitrogen atmosphere. A solution of sodium thiomethoxide (0.27 g, 3.9 mmol) in dry DMF (2.0 mL) was added slowly into mixture while the flask was chilled in an ice bath. The mixture was then stirred at room temperature under nitrogen for 1 hour. Afterward, distilled water (120 mL) was added and the resulting mixture was extracted with DCM (3 × 100 mL), washed by distilled water (3 × 100 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by flash column chromatography (eluent: hexanes/DCM, 1:1) to obtain **SM8** as a white oily liquid (0.87 g, 90% based on **SM7**). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54-7.52 (d, *J* = 8.2 Hz, 1H, CHAr), 7.47-7.45 (d, *J* = 8.2 Hz, 1H, CHAr), 7.35-7.33 (d, *J* = 8.4 Hz, 2H, CHAr), 7.29 (s, 1H, CHAr), 6.64-6.62 (d, *J* = 8.3 Hz, 2H, CHAr), 3.97 (s, 2H, CH_2OAr), 3.92 (s, 3H, $COOCH_3$), 3.65 (s, 3H, CH_3OAr), 3.22 (s, 2H, CH_2SAr), 2.89 (s, 4H, CH_2SCH_3), 2.10 (s, 6H, CH_2SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.30, 158.80, 154.22, 133.30, 132.94, 130.36, 126.49, 122.84, 117.74, 114.41, 112.95, 69.34, 55.13, 52.39, 45.72, 40.42, 38.66, 17.76.

Synthesis of SM9. A mixture of **SM8** (0.360 g, 0.67 mmol), bis(triphenylphosphine)palladium(II) chloride (50.0 mg, 0.067 mmol), triphenylphosphine (18.0 mg, 0.067 mmol) and copper(I) iodide (20.0 mg, 0.1 mmol) were added to a 10-mL Schlenk tube and the tube was connected to a nitrogen manifold. Diisopropylamine (2.0 mL) and THF (1.0 mL) were bubbled by nitrogen for 5 minutes and then transferred into the tube via a cannula. After trimethylsilylacetylene (0.38 mL, 2.7 mmol) was injected, the tube was screw-capped and stirred at 85 ^{o}C in an oil bath under nitrogen for 12 hours. After cooling to room temperature, the solvents were removed by a rotary evaporator and the resulting residue was purified by flash column chromatography (eluent: hexanes/DCM, 2:1) to yield **SM9** as an orange oily liquid (300 mg, 82% based on **SM8**). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43-7.41 (d, *J* = 7.9 Hz, 1H, CHAr), 7.29-7.27 (d, *J* = 7.9 Hz, 1H, CHAr), 7.25-7.22 (d, *J* = 8.5 Hz, 2H, CHAr), 7.16 (s, 1H, CHAr), 6.54-6.51 (d, *J* = 8.6 Hz, 2H, CHAr), 3.85 (s, 2H, CH_2OAr), 3.80 (s, 3H, $COOCH_3$), 3.55 (s, 3H, CH_3OAr), 3.11 (s, 2H, CH_2SAr), 2.77 (s, 4H, CH_2SCH_3), 1.99 (s, 6H, CH_2SCH_3), 0.15 (s. 9H, $Si(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.37, 158.86, 158.75, 133.28, 132.85, 130.88, 126.46, 121.58, 117.18, 114.43, 111.79, 101.60, 100.50, 68.79, 55.14, 52.34, 45.71, 40.33, 38.68, 17.78, 0.04.

Synthesis of SM10. A mixture of **SM9** (300.0 mg, 0.55 mmol) and anhydrous potassium carbonate (0.380 g, 2.80 mmol) in a solution of DCM (2.0 mL) and methanol (2.0 mL) was stirred at room temperature for 1 hours. After removal of the solvent, the product was extracted with DCM (3 × 30 mL), filtered, and the resulting organic filtrate was washed by distilled water (3 × 30 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, an orange solid thus obtained was used directly in the next step (236.0 mg, 90% based on **SM9**).

Synthesis of Me_2L3. A round-bottom flask charged with compound **SM10** (236.0 mg, 0.50 mmol), copper(II) acetate monohydrate (270 mg, 0.48 mmol) and acetonitrile (7.0 mL) was stirred at 70

°C in an oil bath for 5 hours. Afterward, the solvents were removed by a rotary evaporator and distilled water (50 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 30 mL) and the combined organic layers were washed by distilled water (3 × 30 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by flash column chromatography (eluent: hexanes/ethyl acetate, 4:1) to provide Me_2**L3** as a light yellow powder (200 mg, 85% based on **SM10**). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58-7.56 (d, *J* = 7.8 Hz, 1H, CHAr), 7.48-7.45 (d, *J* = 7.9 Hz, 1H, CHAr), 7.37-7.35 (d, *J* = 8.9 Hz, 2H, CHAr), 7.32 (s, 1H, CHAr), 6.64-6.62 (d, *J* = 8.3 Hz, 2H, CHAr), 3.99 (s, 2H, CH_2OAr), 3.94 (s, 3H, $COOCH_3$), 3.63 (s, 3H, CH_3OAr), 3.23 (s, 2H, CH_2SAr), 2.89 (s, 4H, CH_2SCH_3), 2.11 (s, 6H, CH_2SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.16, 159.77, 158.76, 133.65, 133.49, 133.23, 131.72, 126.50, 121.77, 116.15, 115.73, 112.09, 78.96, 69.02, 55.11, 52.47, 45.72, 40.60, 38.73, 29.71.

Synthesis of H_2L3. Compound Me_2**L3** (200.0 mg, 0.21 mmol) was added to a two-neck round-bottom flask charged with a magnetic stirring bar and connected to a nitrogen manifold. An aqueous solution mixture of KOH (0.4 M, 4.5 mL in THF/H_2O, 2:1, v:v) was bubbled by N_2 for 5 minutes and then transferred to the flask via cannula under N_2 protection. The mixture was stirred at 60 °C for 5 hours. After cooling to room temperature, THF was removed by a rotary evaporator and distilled water (50 mL) was added, the resulting mixture was acidified with 10% HCl to attain a pH value lower than 2. An orange red precipitate was formed, collected by filtration, and washed extensively with distilled water, yielding H_2**L3** as a yellow red solid (185 mg, 95% based on Me_2**L3**). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.62-7.60 (d, *J* = 7.9 Hz, 2H, CHAr), 7.53-7.51 (d, *J* = 8.0 Hz, 2H, CHAr), 7.36-7.33 (m, 6H, CHAr), 6.68-6.66 (d, *J* = 8.4 Hz, 4H, CHAr), 3.97 (s, 4H, CH_2OAr), 3.58 (s, 6H, CH_3OAr), 3.15 (s, 4H, CH_2SAr), 2.80 (s, 8H, CH_2SCH_3), 2.04 (s, 12H,

CH_2SCH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 183.66, 166.87, 159.89, 158.85, 134.25, 133.57, 133.19, 126.18, 122.23, 114.95, 114.43, 112.36, 79.49, 69.12, 55.37, 46.19, 45.63, 38.55, 17.54.

Crystallization of Zr-L3. Molecule H_2**L3** (15.9 mg, 0.017 mmol) and a *N*,*N*-diethylformamide (DEF, 0.3 mL) solution of $ZrOCl_2$ (3.9 mg, 0.012 mmol) and benzoic acid (42.0 mg, 0.34 mmol, about 30 molar equivalents to $ZrOCl_2$) were added in a Pyrex glass tube (soda lime, 10 mm OD, 6 mm ID). The tube was flame-sealed and heated at 120 °C in an oven for 36 hours, followed by programmed cooling to room temperature over 18 hours to afford yellow octahedron-shaped single crystals. For elemental analysis, the crystals were washed by DMF (3 × 2 mL) and soaked in acetonitrile (3 × 3 mL, replaced by fresh acetonitrile every hour). The resulting crystals were further washed by acetone (3 × 2 mL), filtered and then evacuated at 60 °C for 8 hours. Elemental analysis found [C (47.12%), H (4.46%), N (0.07%)]; a fitting formula can be determined to be $Zr_6O_4(OH)_8(H_2O)_4(C_{46}H_{48}O_8S_6)_4(H_2O)_9$ (mw 4667), which gives a calculated profile as [C (47.36%), H (4.88%)]. The Zr-**L3** solid sample was also characterized by TGA (see Figure S8).

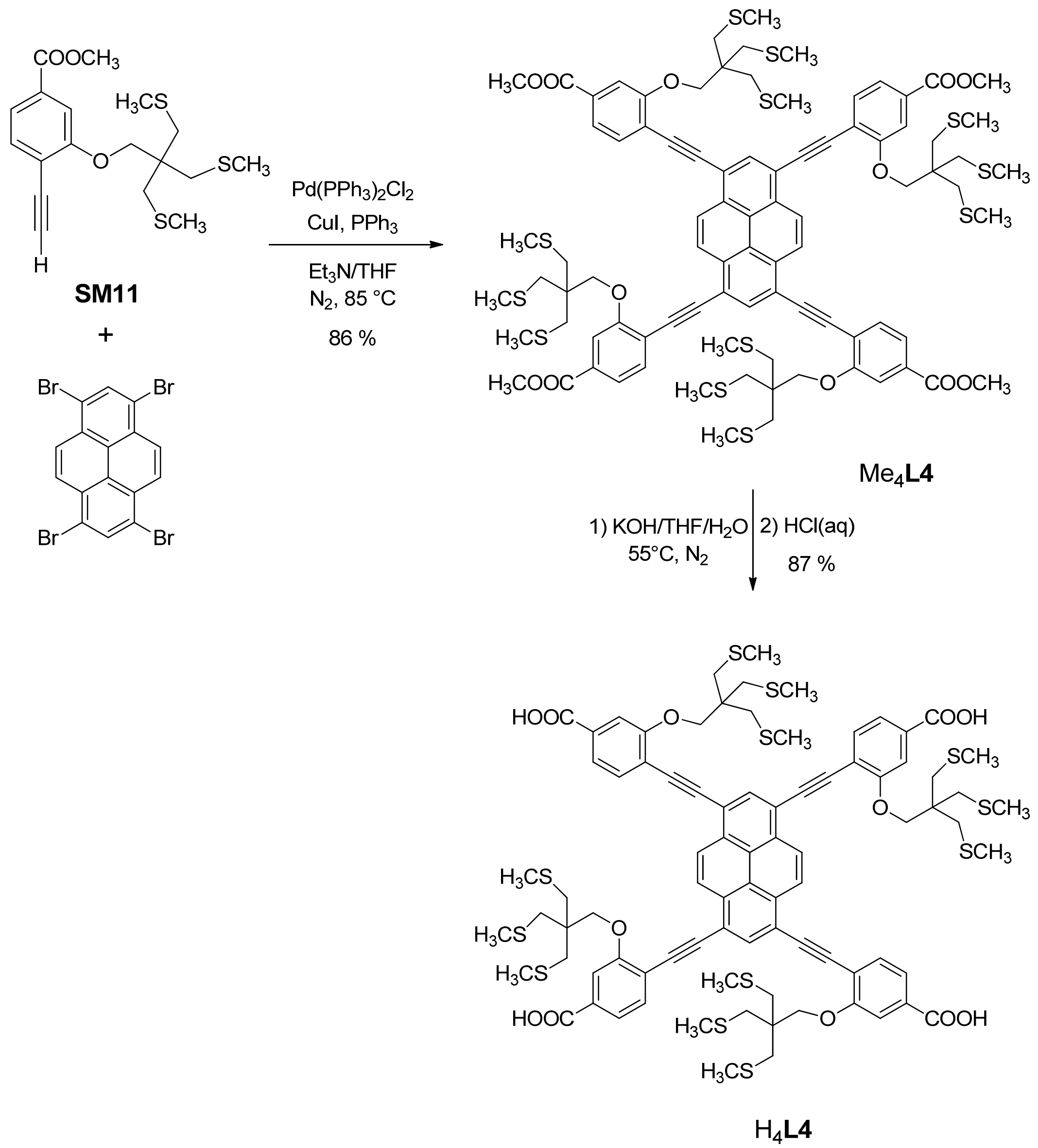


Figure S3. The synthetic route of the molecule H$_4$**L4**.

Synthesis of Me$_4$L4. A mixture of **SM11** (1.38 g, 3.6 mmol), 1,3,6,8-tetrabromopyrene (312 mg, 0.6 mmol), bis(triphenylphosphine)palladium(II) chloride (220 mg, 0.29 mmol), triphenylphosphine (400 mg, 1.5 mmol) and copper(I) iodide (50 mg, 0.25 mmol) were added to a 10-mL Schlenk tube under a nitrogen atmosphere. Diisopropylamine (20.0 mL) and THF (10.0 mL) were bubbled by nitrogen for 5 minutes and then transferred into the tube via a cannula. The tube was screw-capped and stirred at 85 °C in an oil bath under nitrogen for 18 hours. After cooling to room temperature, the solvents were removed in vacuum and the residue was purified by column chromatography (eluent: hexanes/EA, 2:1) to afford Me_4**L4** as a red solid (900 mg, 86% based on **SM11**). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.89 (s, 4H, CHAr), 8.45 (s, 2H, CHAr), 7.76-7.69 (m, 12H, CHAr), 4.23 (s, 8H, CH_2OAr), 3.98 (s, 12H, $COOCH_3$), 2.98 (s, 24H, CH_2S), 2.10 (s, 36H, SCH_3).

Synthesis of H_4L4. Compound Me_4**L4** (200.0 mg, 0.115 mmol) was added to a two-neck round-bottom flask charged with a magnetic stirring bar and connected to a nitrogen manifold. An aqueous solution mixture of KOH (0.4 M, 14.0 mL in THF/EtOH/H_2O, 7:2:5, v:v:v) was bubbled by N_2 for 5 minutes and then transferred to the flask via cannula under N_2 protection. The mixture was stirred at 60 °C for 24 hours. After cooling to room temperature, THF was removed by a rotary evaporator and distilled water (80 mL) was added, the resulting mixture was acidified with 10% HCl to attain a pH value lower than 2. An orange red precipitate was formed, collected by filtration, and washed extensively with distilled water, yielding H_4**L4** as a yellow red solid (167 mg, 87% based on Me_4**L4**). ^1H NMR (300 MHz, DMSO-d_6): δ = 8.48 (s, 4H, CHAr), 8.16 (s, 2H, CHAr), 7.67-7.51 (m, 12H, CHAr), 4.13 (s, 8H, CH_2OAr), 2.83 (s, 24H, CH_2S), 1.98 (s, 36H, SCH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 166.93, 158.99, 153.97, 133.64, 133.11, 132.78, 131.13, 126.84, 122.91, 122.39, 118.81, 116.18, 112.97, 93.49, 92.99, 70.79, 45.27, 17.59.

Crystallization of Zr-L4. Molecule H_4**L4** (15.0 mg, 0.010 mmol) and DEF (0.9 mL) solution of $ZrOCl_2·8H_2O$ (5.7 mg, 0.018 mmol) and benzoic acid (300.0 mg, 2.46 mmol, about 140 molar equivalents to $ZrOCl_2·8H_2O$) were added in a Pyrex glass tube (soda lime, 10 mm OD, 6 mm ID). The tube was flame-sealed and heated at 120 °C in an oven for 96 hours, followed by programmed cooling to room temperature over 18 hours to afford red crystals. For elemental analysis, the crystals were washed by DMF (3 × 2 mL) and soaked in acetonitrile (3 × 3 mL, replaced by fresh acetonitrile every hour). The resulting crystals were further washed by acetone (3 × 2 mL), filtered and then evacuated at 60 °C for 8 hours. Elemental analysis found [C (46.93%), H (4.65%), N (0.12%)]; a fitting formula can be determined to be $Zr_6O_4(OH)_8(C_{84}H_{86}O_{12}S_{12})_2(H_2O)_{11}$ (mw 4290), which gives a calculated profile as [C (47.03%), H (4.75%)]. The Zr-**L4** solid sample was also characterized by TGA (see Figure S10).

Hg(II) removal from water by Zr-L1, Zr-L3 and Zr-L4. A sample solution of mercury(II) chloride (1.3% HNO_3 (v/v), mass concentration of Hg = 8.0 ppm) was freshly prepared. A crystal sample of Zr-**L3** (*ca.* 7 mg) was shaken with the mercury sample solution (3.0 mL) at 150 rpm and room temperature for 20 hours using an IKA KS 501 Digital Orbital shaker. Afterward, the solid was isolated by centrifugation, washed by acetonitrile (3 × 1.0 mL), and analyzed by powder X-ray diffraction. The Hg content in the supernatant was found to be 0.70 ppm for Zr-**L3** using ICP-OES. Similar sorption tests were done for Zr-**L1** and Zr-**L4**. For Zr-**L1** (3.0 mg), the Hg content of a sample solution (3.0 mL) was reduced from 10 ppm to 3.4 ppm. For Zr-**L4** (6.0 mg), the Hg content of a sample solution (6.0 mL) was reduced from 10 ppm to 0.40 ppm. The distribution coefficient (K_d) is defined as $K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{m}$, where C_i is the initial metal ion concentration, C_f is the equilibrium metal ion concentration, V is the volume of the sample solution (mL) and m is the amount of the sorbent (g).[2] The K_d of Zr-**L1,** Zr-**L3** and Zr-**L4** were calculated to be 1.95×10^3 mL g^{-1}, 4.47×10^3 mL g^{-1} and 2.4×10^4 mL g^{-1}, respectively.

Hg(II) sorption isotherm measurement of Zr-L1, Zr-L3 and Zr-L4. Mercury(II) chloride solutions of various concentrations (50, 100, 200, 300, 400, 500, 600, 800, 1000 mg L^{-1}) were prepared using KH_2PO_4/Na_2HPO_4 buffer solution (pH = 6.8), and used in the following adsorption procedure. A freshly made sample of Zr-**L3** (7.0 mg) was washed by DMF (3 × 1.0 mL) and soaked in acetonitrile (3 × 3 mL, replaced by fresh acetonitrile every hour). The acetonitrile was then decanted, and the crystals were washed twice by distilled water to remove the residual acetonitrile, and then immediately mixed with the $HgCl_2$ solution (3.0 mL). After the mixture was shaken at 150 rpm and room temperature for 48 hours using an IKA KS 501 Digital Orbital shaker, the crystals were separated by centrifugation and the concentration of the remaining Hg in the supernatant was determined by ICP-OES. The above procedure was repeated for Zr-**L1** and Zr-**L4**. Based on the Langmuir adsorption equation (see below),[3] the saturated Hg (II) adsorption capacity q_{max} of Zr-**L1**, Zr-**L3** and Zr-**L4** was calculated to be 193 mg g^{-1} ($R^2 = 0.9994$), 245 mg g^{-1} ($R^2 = 0.9989$) and 322 mg g^{-1} ($R^2 = 0.9940$), respectively.

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

where a plot of C_e/q_e to C_e (see Fig. 6 inset) yields the sorption capacity q_{max} (mg g^{-1}) as the reciprocal of the slope.

Test of recyclability. In a clear glass vial, a sample of Zr-**L3** and Zr-**L4** (~3.0 mg) was shaken with a freshly prepared mercury solution (50 ppm, 2.0 mL) at 150 rpm and room temperature for 10 hours using an IKA KS 501 Digital Orbital shaker. Afterward, the solid was isolated by centrifugation, washed with 2-mercaptoethanol aqueous solution (10%) and water (5 × 1.0 mL), and used for next cycle. After three runs, the solid recovered was sequentially washed with water and DMF, and analyzed by powder X-ray diffraction. After these cycling steps, the Hg content in the supernatant can still be consistently reduced down to 3.18 ppm by Zr-**L3** and 2.07 ppm by Zr-**L4** (i.e., 96 % of the total Hg was removed; ICP-OES results).

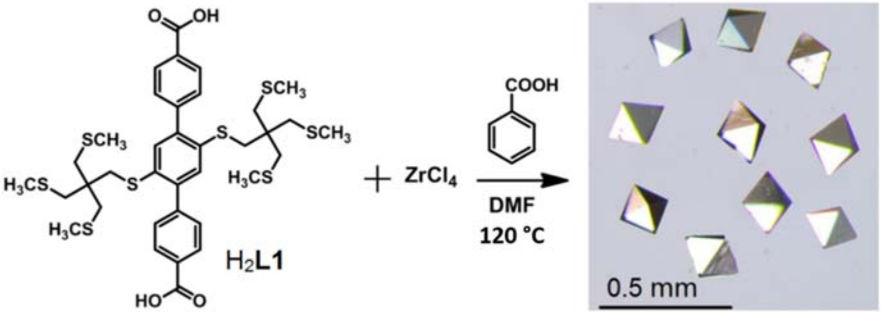


Figure S4. A reaction scheme for the crystallization of Zr-**L1**, with a photograph of the crystals on the right.

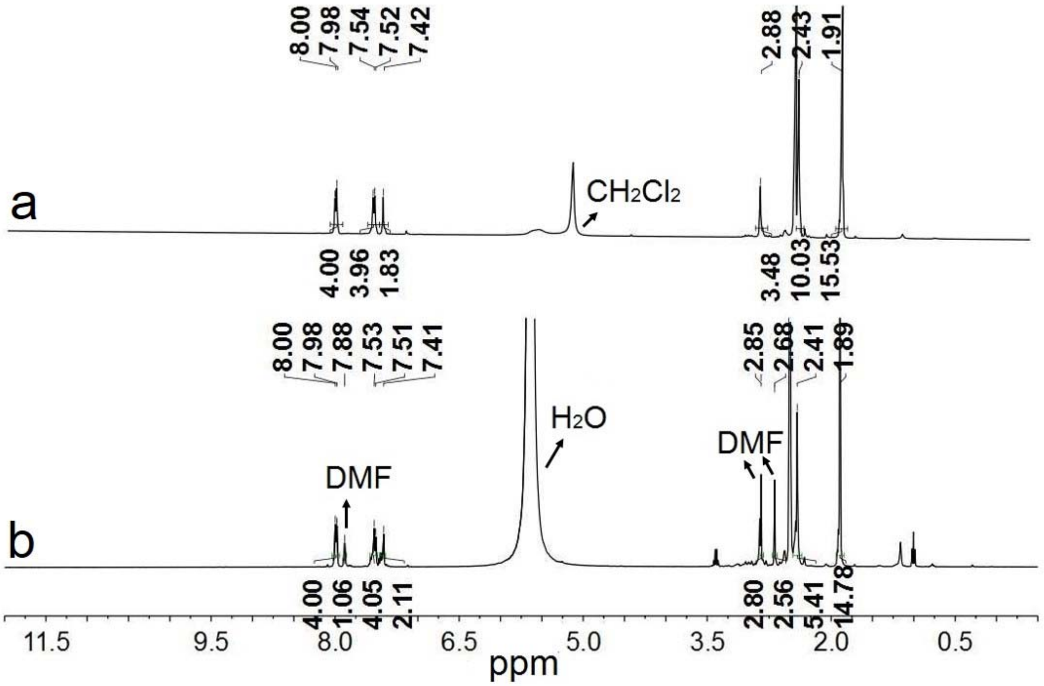


Figure S5. Solution ^{1}H-NMR spectra of the ligand H_2**L1** in DMSO-d_6 + DCl (38% in D_2O) (a) and the as-made sample of Zr-**L1** dissolved in DCl (38% in D_2O)/DMSO-d_6 (1:4, v:v), consequently heating at 50°C under sonication for about 5 min (b).

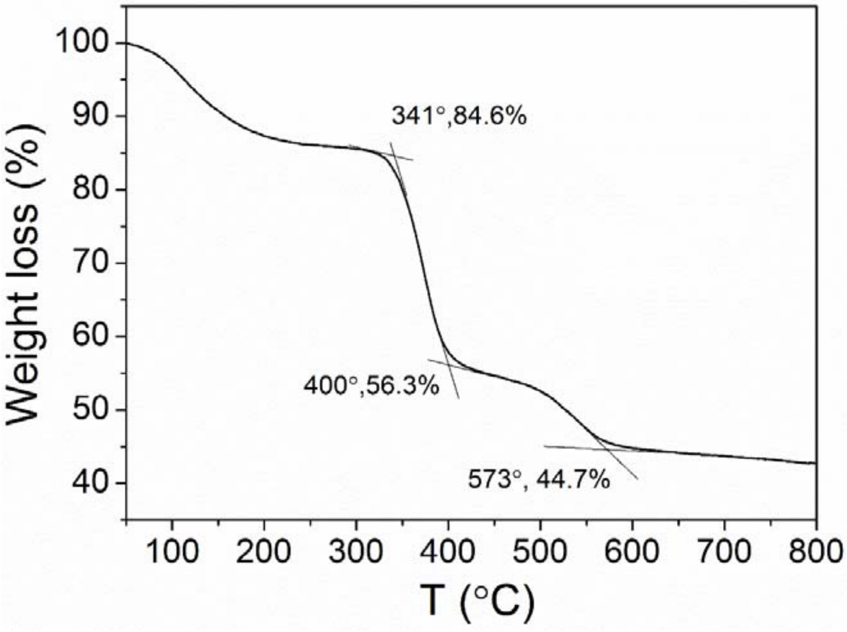
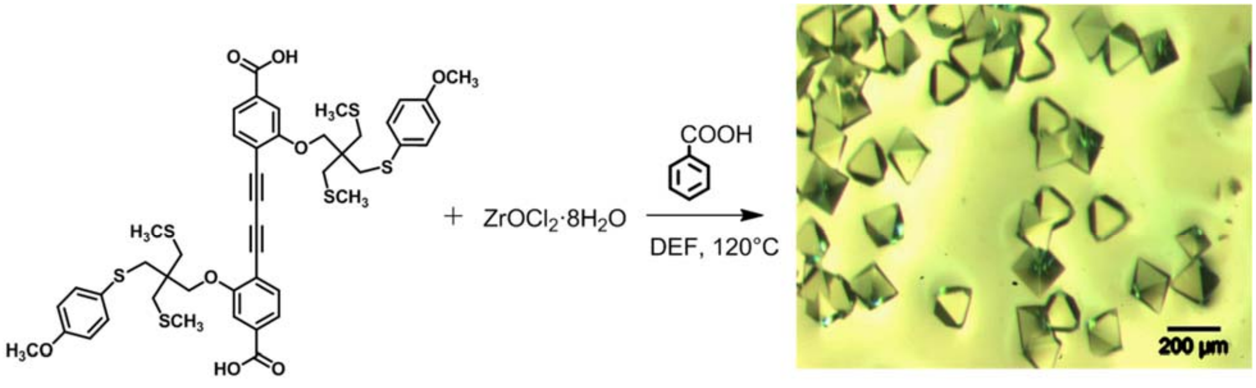


Figure S6. The thermogravimetric analysis (TGA) plot of an as-made sample of Zr-**L1**. The initial weight loss (e.g., under 200 °C) of about 12.7% can be ascribed to the departure of the guests of DMF and water. The inflection points at 400 °C, corresponding to the weight loss of 28.3% (from 341°C to 400°C), can be ascribed to the decomposition of SCH_3 (calculated to be 27.4% from the formula $Zr_6O_4(OH)_6(H_2O)_2(C_{36}H_{44}O_4S_8)_5(C_3H_7NO)_5(H_2O)_3$ (mw 5155) fitted from the elemental analysis). The inflection points at 573°C, corresponding to the weight loss of 39.9% (from 341°C to 573°C) is responsible for decomposition of $C(CH_2)_4(SCH_3)_3$ (calculated to be 40.6% from the above formula).

Table S1. Crystallographic data of Zr-**L1**

Empirical formula	$C_{30}H_{30}O_{10}S_8Zr$
Formula weight	898.68
Temperature/K	270(2)
Wavelength/Å	0.7107
Crystal system	cubic
Space group	Fm-3m
a/Å	32.800(2)
V/Å^3	35287(6)
Z	4
α/°	90
Dc/g.cm^{-3}	1.353
μ/mm^{-1}	0.672
F(000)	1424.0
wR_2 (all data)	0.2576
R_1[a][I>2σ (I)]	0.0904
GOF	1.107

[a] $R_1=\sum(||F_0|-|F_c||)/\sum|F_0|$; [b] $wR_2=[\sum w(F_0^2-F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$



H_2**L3**

Zr-**L3**

Figure S7. A reaction scheme for the crystallization of Zr-**L3**, with a photograph of the crystals on the right (scale bar: 200 μm).

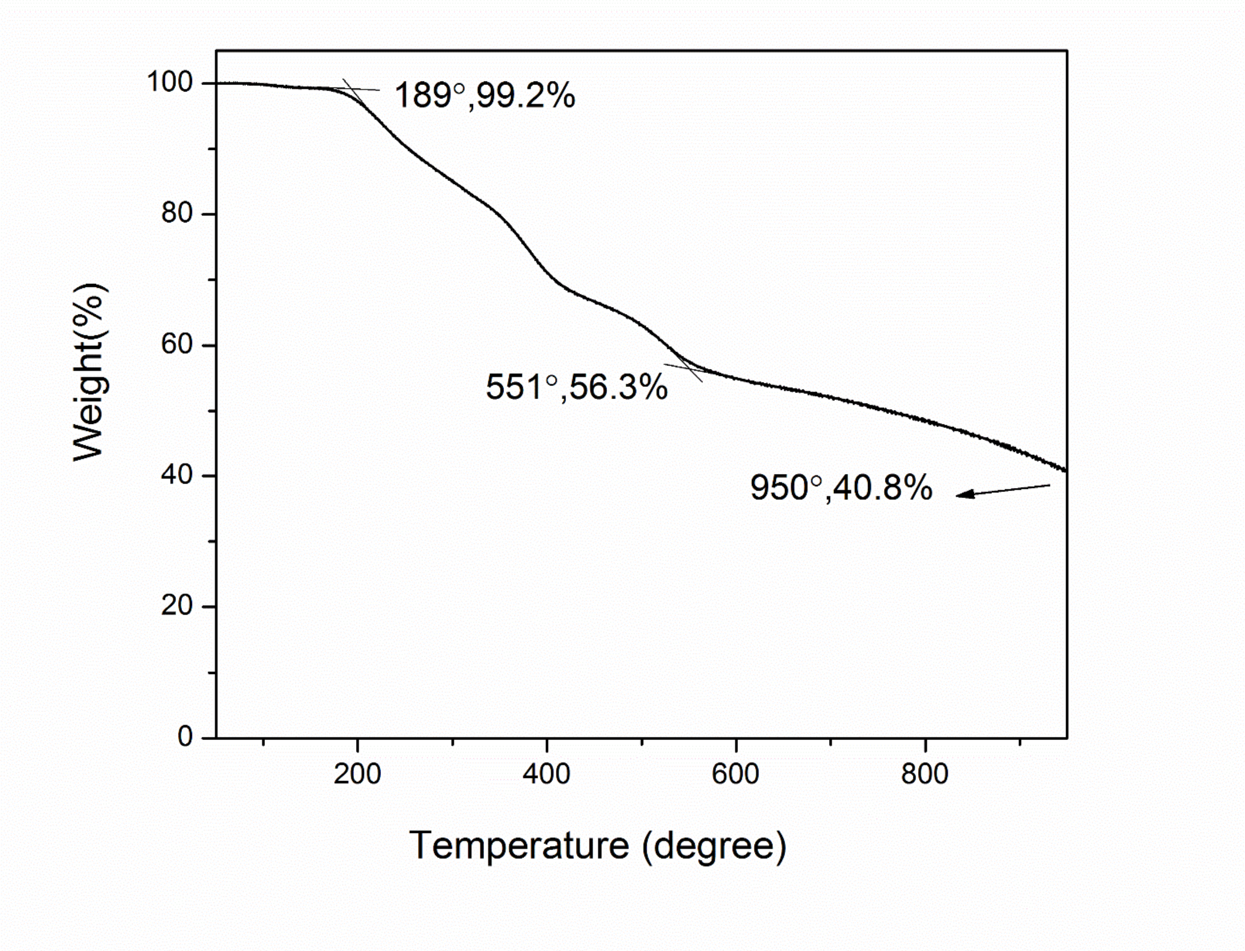
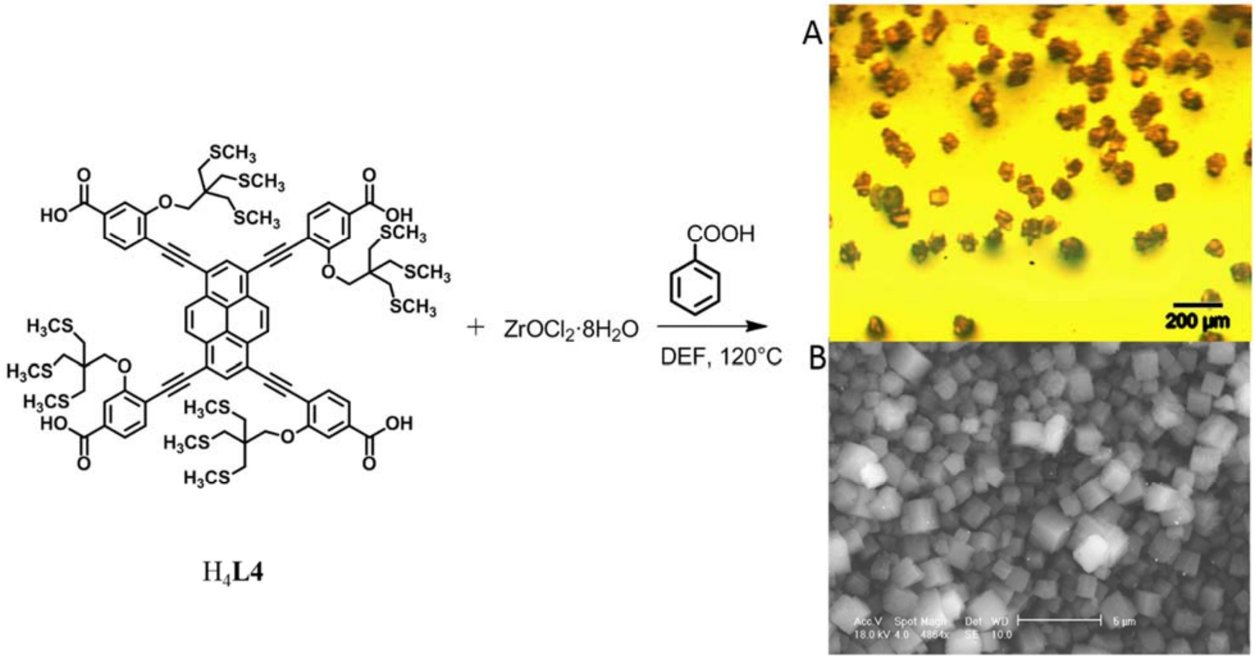


Figure S8. Thermogravimetric analysis (TGA) plots of the activated sample of Zr-**L3**. The sample was hold at 50°C for 20 minutes, heating rate: 5 °C/min. The initial weight loss of < 0.7% (under 150 °C) can be ascribed to the departure of the water guests in TGA profile. The inflection point at 189 °C, corresponding to the weight loss of 42.9% (from 189°C to 551°C), can be ascribed to the decomposition of SCH_3 and $SC_6H_4OCH_3$, which are calculated to be 42.1% from the formula $Zr_6O_4(OH)_8(H_2O)_4(C_{46}H_{48}O_8S_6)_4$ (mw 4504) fitted from the elemental analysis.



H_4**L4**

Zr-**L4**

Figure S9. A reaction scheme for the crystallization of Zr-**L4**; on the right are a photograph of the crystals (scale bar: 200 μm) taken under an optical microscope (A) and an SEM image of the crystallites (scale bar: 5 μm) (B).

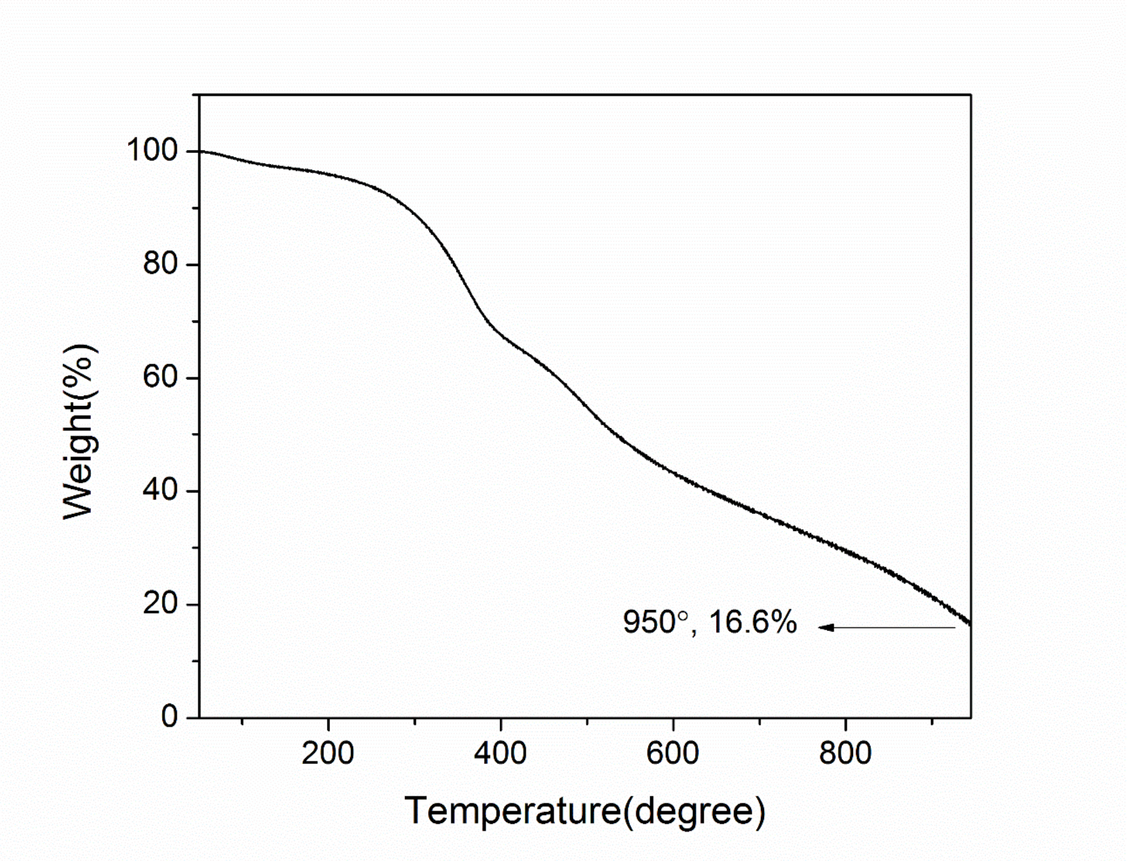


Figure S10. Thermogravimetric analysis (TGA) plots of as-made sample of Zr-**L4**. Heating rate: 5 °C/min, the initial step was conducted by holding sample at 50°C for 30 minutes, followed by immediate heating. The initial weight loss is about 2.9%, corresponding to the departure of the water guests; and the residual weight of 16.6% at 950°C can be ascribed to the formation of ZrO_2, which is consistent with the calculated ZrO_2 of 17.2% from the formula $Zr_6O_4(OH)_8(H_2O)_4(C_{84}H_{86}O_{12}S_{12})_2(H_2O)_7$ (mw 4290) fitted from the elemental analysis.

X-ray single crystal diffraction studies. The intensity data for Zr-**L1** was collected on a Bruker AXS D8 Quest CMOS diffractometer with Mo Kα radiation (λ = 0.71073 Å) monochromated using a laterally graded multilayer (Goebel) mirror. Crystals were mounted on MiTeGen micromesh mounts with a trace of mineral oil and were in situ cooled to 100K. Data were collected, unit cells determined, and the data integrated using the Apex2 suite of programs.[a] All absorption corrections were performed using multi-scan methods as implemented in the SADABS program.[b] The space group was assigned and the structure was solved by direct methods using the SHELXTL suite of programs[c] and refined by full-matrix least squares on F^2 using Shelxl2014[d] and the graphical interface Shelxle[e].

a. Apex2 v2013.4-1 (Bruker, 2013) Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA.

b. Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). J. Appl. Crystallogr. 48.

c. i) SHELXTL (Version 6.14) (2000-2003) Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA. ii) Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

d. i) Sheldrick, G. M. (2013). University of Göttingen, Germany. ii) Sheldrick, G.M. (2008). Acta Cryst., A64, 112--122.

e. Hübschle, C. B., Sheldrick, G. M. and Dittrich, B. (2011). J. Appl. Cryst., 44, 1281--1284.

Crystals loose diffraction intensity and quality upon cooling to temperatures substantially below freezing. Data were collected at 270 K.

Oxo and hydroxy groups are 1:1 disordered.

The central of the three benzene rings of the ligand is systematically disordered over two positions related by symmetry elements. The sulfur atoms in the 2 and 5 positions are in addition 1:1 disordered with a hydrogen atom (which has been omitted from the refinement).

The alkyl substituents attached to the sulfur arms are too disordered to be resolved in the difference electron density and were omitted from the refinement.

All ligand atoms show substantial thermal vibration. No attempts were made to refine large asymmetric ADPs as additional disorder.

A DMF solvate molecule was refined as disordered around a three-fold rotation axis. Its geometry was restrained to be as expected using distance and similarity restraints for its atom positions. The molecule was also restrained to be flat, and the ADPs of its atoms to have similar Uij components if closer than 1.7 Angstroms, and to be close to isotropic. The oxygen atom's position was restrained to be in hydrogen bonding distance to the metal cluster hydroxyl group. A global rigid bond restraint was applied for all atoms.

References

1. Y.-L. Hou, K.-K. Yee, Y.-L. Wong, M. Zha, J. He, M. Zeller, A. D. Hunter, K. Yang and Z. Xu, J. Am. Chem. Soc, 2016, 138, 14852.

2. B. Li, Y. Zhang, D. Ma, Z. Shi, S. Ma, Nat. Commun., 2014, 5, 5537.

3. K.-K. Yee, N. Reimer, J. Liu, S.-Y. Cheng, S.-M. Yiu, J. Weber, N. Stock, Z. Xu, J. Am. Chem. Soc., 2013, 135, 7795.

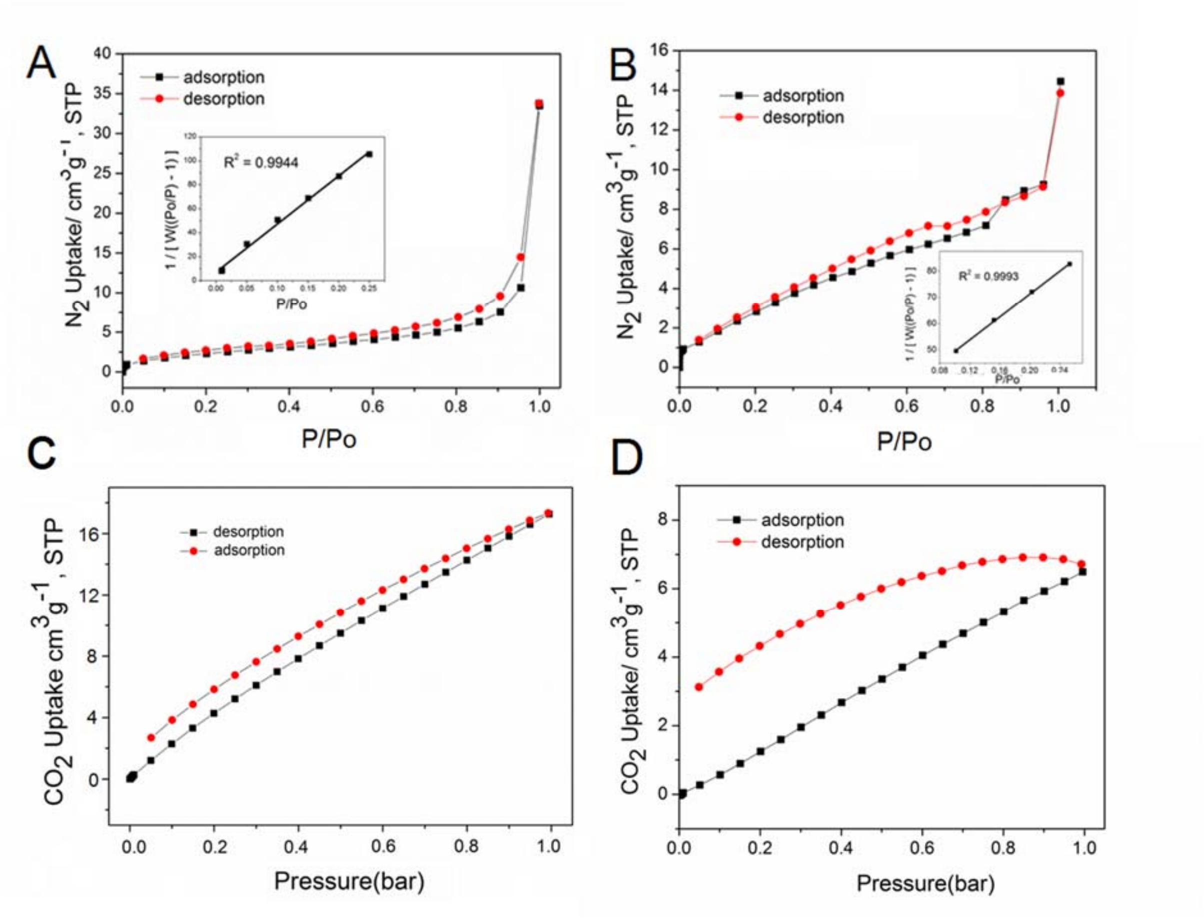


Figure S11 N_2 sorption isotherms at 77 K for an activated sample of Zr-**L1** (panel a) and Zr-**L3** (panel b), CO_2 sorption isotherms at 273 K for an activated sample of Zr-**L1** (panel c) and Zr-**L3** (panel d). The MOF samples were first solvent-exchanged with acetonitrile and then evacuating at 100 °C for activation. Insets: the corresponding BET plots.

For this, the samples were solvent-exchanged with acetonitrile and degassed in vacuo at 100 °C for 10 hours. CO_2 sorption experiments at 273 K (pressure range: from 8×10^{-3} to 780 mmHg) on the Zr-**L1** crystals (solvent-exchanged with CH_3CN) revealed a typical type-I gas adsorption isotherm (CO_2 gas, 273 K, Fig. S11) with a significant CO_2 uptake of 17.2 cm^3g^{-1} at 1 bar. The N_2 sorption (e.g., at the much lower temperature of 77K), however, shows little uptake at the micropore domain (i.e., at very low relative pressure), indicating access difficulty likely caused by the bulky side chains. Such a marked difference from the typical adsorption observed of CO_2 is also often observed of microporous polymeric materials, and has been well rationalized, e.g., by the stronger thermal motion at 273K, the quadrupole moment and smaller kinetic diameter of CO_2.

Significant hysteresis, however, was observed in the CO_2 sorption by the Zr-**L3** crystals (Fig. S11; like Zr-**L1**, N_2 sorption was minimal). Such hysteresis points to difficulty in exiting the pores in the degassing stage, and can be ascribed to the partial collapse of the host framework (thus trapping the guests). The sample degradation is also confirmed by the weaker and broader PXRD pattern collected on the sample after gas sorption measurements (see Figure S12 below). Such observations thus further unveil the lesser stability of Zr-**L3** as compared with Zr-**L1**, in addition to the PXRD monitoring described above.

The broadened peaks after gas sorption measurements point to degradation of the crystalline frameworks, which also likely resulted in the poor gas sorption performances observed (as in Figure S11).

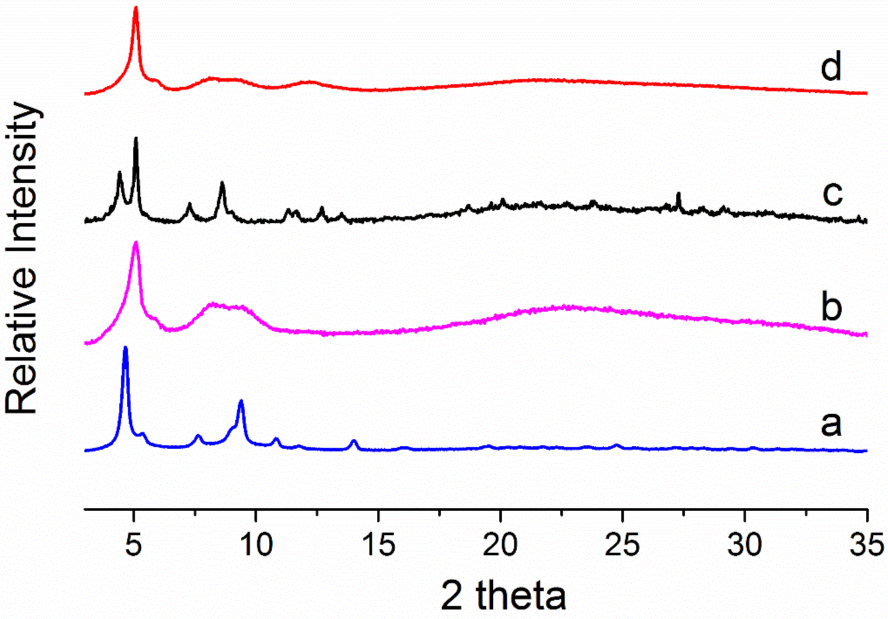


Figure S12. PXRD patterns (Cu Kα, $\lambda = 1.5418$ Å): a) an as-made sample of Zr-**L1**; b) an activated sample of Zr-**L1** after gas sorption measurements (e.g., degassed in vacuo at 100 °C for 10 hours) ; c) an as-made sample of Zr-**L3**; d) an activated sample of Zr-**L3** after gas sorption measurements (e.g., degassed in vacuo at 100 °C for 10 hours). The broadened peaks after gas sorption measurements point to degradation of the crystalline frameworks, which also likely resulted in the poor gas sorption performances observed (as in Figure S11).

Refinement details of PXRD of $HgCl_2$-Zr-**L1**, as-made Zr-**L3** and as-made Zr-**L4**:

(a) $HgCl_2$-Zr-**L1** (Fig. 3 pattern d):

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Initial values     : (Refinement keys on 2nd line)
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  Zero    Lambda      a        b        c       alpha  beta   gamma   volume
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   0      0         1        0        0        0      0      0

    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    0    0    2     5.3840       5.3840     5.4050    -0.0210
    0    2    2     7.6540       7.6540     7.6466     0.0074
    3    1    1     8.9830       8.9830     8.9690     0.0140
    3    1    3    11.8150      11.8150    11.7963     0.0187
    3    3    3    14.0870      14.0870    14.0727     0.0143
    2    4    4    16.2700      16.2700    16.2635     0.0065
    5    5    5    23.5590      23.5590    23.5612    -0.0022
    7    3    5    24.8220      24.8220    24.8050     0.0170

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0150
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0141

Final values       : (Standard errors on 2nd line)
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  Zero    Lambda      a        b        c       alpha  beta   gamma   volume
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  0.0000 0.00000   0.0207   0.0000   0.0000   0.000  0.000  0.000   22.070


    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    0    0    2     5.3840       5.3840     5.4079    -0.0239
    0    2    2     7.6540       7.6540     7.6508     0.0032
    3    1    1     8.9830       8.9830     8.9739     0.0091
    3    1    3    11.8150      11.8150    11.8028     0.0122
    3    3    3    14.0870      14.0870    14.0805     0.0065
    2    4    4    16.2700      16.2700    16.2725    -0.0025
    5    5    5    23.5590      23.5590    23.5743    -0.0153
    7    3    5    24.8220      24.8220    24.8188     0.0032

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0126
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.011
```

(b) as-made Zr-**L3** (Fig. 4 pattern d):

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yl2b.dif

Initial values    : (Refinement keys on 2nd line)
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   0      0         1        0        0        0      0      0

    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    1    1    1     4.4220       4.4220     4.4907    -0.0687
    0    0    2     5.0990       5.0990     5.1859    -0.0869
    2    0    2     7.2890       7.2890     7.3364    -0.0474
    1    1    3     8.6260       8.6260     8.6049     0.0211
    2    2    2     8.9900       8.9900     8.9883     0.0017
    3    1    3    11.3460      11.3460    11.3168     0.0292
    2    0    4    11.6300      11.6300    11.6118     0.0182
    2    2    4    12.7050      12.7050    12.7245    -0.0195
    1    1    5    13.5080      13.5080    13.4999     0.0081
    8    3    6    27.3000      27.3000    27.3198    -0.0198

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0434
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0412

Final values      : (Standard errors on 2nd line)
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  0.0000 0.00000   0.0798   0.0000   0.0000   0.000  0.000  0.000   92.821


    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    1    1    1     4.4220       4.4220     4.4872    -0.0652
    0    0    2     5.0990       5.0990     5.1819    -0.0829
    2    0    2     7.2890       7.2890     7.3308    -0.0418
    1    1    3     8.6260       8.6260     8.5983     0.0277
    2    2    2     8.9900       8.9900     8.9814     0.0086
    3    1    3    11.3460      11.3460    11.3081     0.0379
    2    0    4    11.6300      11.6300    11.6029     0.0271
    2    2    4    12.7050      12.7050    12.7147    -0.0097
    1    1    5    13.5080      13.5080    13.4894     0.0186
    8    3    6    27.3000      27.3000    27.2984     0.0016

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0426
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0404
```

(c) as-made Zr-**L4** (Fig. 3 pattern d):

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ylZrL4a.lst

Initial values    : (Refinement keys on 2nd line)
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   0      0         1        0        0        0      0      0

    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    0    0    2     3.8040       3.8040     3.9182    -0.1142
    2    0    2     5.4580       5.4580     5.5423    -0.0843
    2    2    2     6.7600       6.7600     6.7892    -0.0292
    0    0    4     7.8570       7.8570     7.8410     0.0160
    0    2    4     8.8060       8.8060     8.7683     0.0377
    2    2    4     9.6940       9.6940     9.6070     0.0870
    4    0    4    11.2030      11.2030    11.0976     0.1054

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0830
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0769

Final values      : (Standard errors on 2nd line)
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  0.0000 0.00000   0.5201   0.0000   0.0000   0.000  0.000  0.000 1049.772


    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    0    0    2     3.8040       3.8040     3.9334    -0.1294
    2    0    2     5.4580       5.4580     5.5638    -0.1058
    2    2    2     6.7600       6.7600     6.8156    -0.0556
    0    0    4     7.8570       7.8570     7.8715    -0.0145
    0    2    4     8.8060       8.8060     8.8024     0.0036
    2    2    4     9.6940       9.6940     9.6444     0.0496
    4    0    4    11.2030      11.2030    11.1408     0.0622

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0792
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0733
```

Table S2. Comparison of the adsorption capacity for Hg(II) of Zr-**L1**, Zr-**L2**, Zr-**L3** and Zr-**L4** with other zirconium-based MOFs.

Zr-MOFs	Capacity (mg g^{-1})	K_d (ml g^{-1})	S : Hg ratio	Regeneration method	Reference
UiO-66-NHC(S)NHMe	769	–	–	–	4
SH-Fe_3O_4@ SiO_2@UiO-66	282	–	2.94	0.01 M HCl + 0.1% thiourea (pH 1.8)	5
Zr-DMBD	197, 236.4	9.99×10^5	2.22	1 M HCl + 0.66 M thiourea (pH 0.2) at 70°C	6
Zr-**L1**	193	1.95×10^3	7.92	2-mercaptoethanol aqueous solution (10%)	This work
Zr-**L2**	275	1.47×10^4	4.13		
Zr-**L3**	245	4.47×10^3	4.21		
Zr-**L4**	322	2.40×10^4	3.47		

4. H. Saleem, U. Rafique and R. P. Davies, *Microporous Mesoporous Mater.*, 2016, 221, 238.

5. L. Huang, M. He, B. Chen and B. Hu, *J. Mater. Chem. A*, 2016, 4, 5159.

6. K.-K. Yee, N. Reimer, J. Liu, S.-Y. Cheng, S.-M. Yiu, J. Weber, N. Stock, Z. Xu, *J. Am. Chem. Soc.*, 2013, 135, 7795; K. Leus, J. P. H. Perez, K. Folens, M. Meledina, G. Van Tendeloo, G. D. Laingb and P. V. D. Voort, *Faraday Discuss.*, 2017, 201, 145.

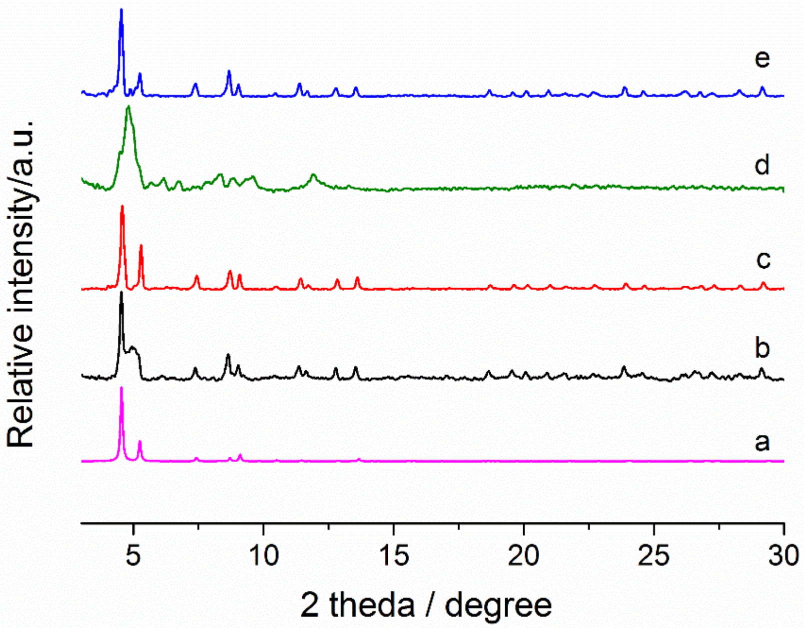

Figure S13. PXRD patterns (Cu Kα, $\lambda = 1.5418$ Å) from: (a) calculation from a reported UiO-type structural model of Zr-**L2**; (b) an as-made sample of Zr-**L3** after being immersed for 24 hours in an aqueous HCl solution of pH=1; (c) an as-made sample of Zr-**L3** after being immersed for 24 hours in an aqueous NaOH solution of pH=11; (d) an as-made sample of Zr-**L3** after being immersed for 24 hours in an aqueous NaOH solution of pH=12; (e) The sample after three cycles of the capture-release treatment.

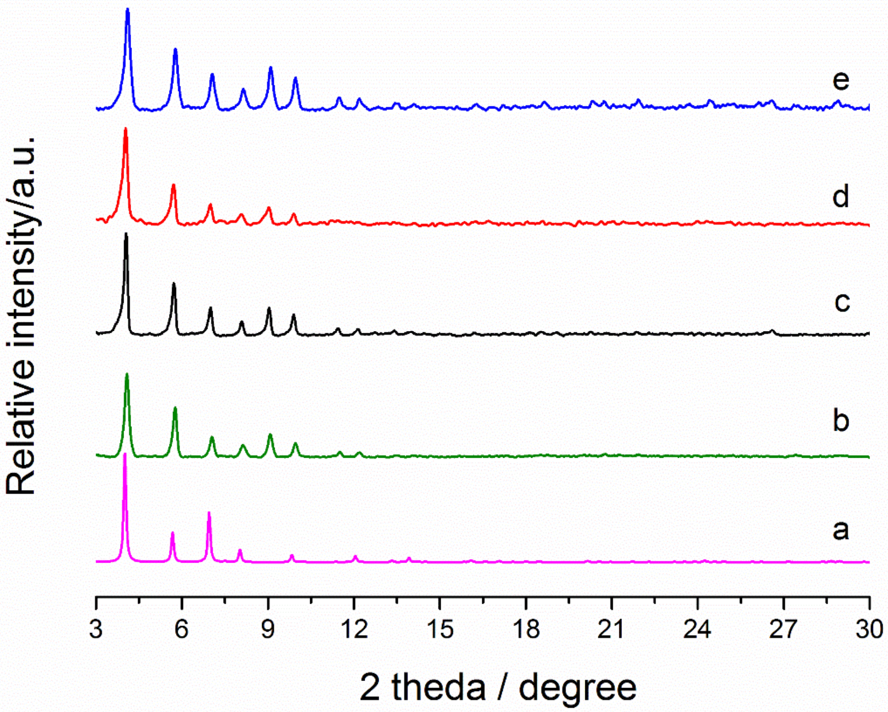

Figure S14. PXRD patterns (Cu K*α*, *λ* = 1.5418 Å) from: (a) calculation from a reported NU1100 structural model; (b) an as-made sample of Zr-**L4** after being immersed for 24 hours in an aqueous HCl solution of pH=1; (c) an as-made sample of Zr-**L4** after being immersed for 24 hours in an aqueous NaOH solution of pH=10; (d) an as-made sample of Zr-**L4** after being immersed for 24 hours in an aqueous NaOH solution of pH=11; (e) The sample after three cycles of the capture-release treatment.

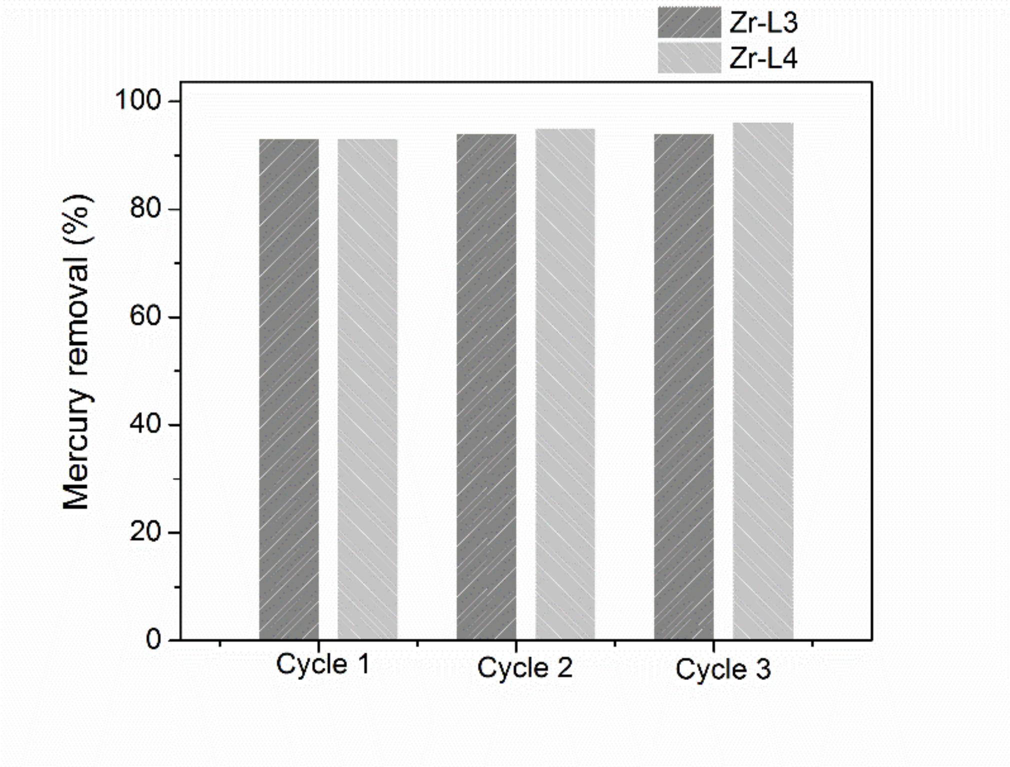

Figure S15. Sorption capacities (plotted as a column chart) of Hg(II) in the three cycles of loading and stripping for Zr-**L3** and Zr-**L4**.