A Robust and Biocompatible Bismuth Ellagate MOF Synthesized Under Green Ambient Conditions

Supplemental Information

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6. **Supplemental References**
1. Chemicals and Synthesis

Chemical Reagents
The reagents were obtained as follows: reagent-grade ellagic acid (97%, isolated from chestnut tree bark) was purchased from Acros Organics, bismuth acetate (99%) was purchased from Alfa Aesar, glacial acetic acid (EMSURE glacial acetic acid, 100%) was purchased from Merck, supplemental ellagic acid (90%, isolated from pomegranate hulls) was purchased from PureBulk (PureBulk Inc., Roseburg, Oregon, USA), white vinegar was bought in a Swedish convenience store (‘Perstorp Ättika’, 24% acetic acid in water). All chemicals were used as-received without further purification. Acetic acid solutions were prepared with deionized water along with the acetic acid source.

Synthesis of SU-101
In a typical synthesis, 0.15 g reagent-grade ellagic acid (Acros Organics, 97% ellagic acid, isolated from chestnut tree bark, 0.5 mmol) and 0.38 g bismuth acetate (Alfa Aesar, 99%, 1 mmol) were added to 30 mL of a water and acetic acid mixture (6 vol.% acetic acid, made from glacial acetic acid, with the possibility of replacing with store-bought white vinegar) in common borosilicate glass beakers with PTFE stir bars. The resulting suspension (pH ≈ 2.3) was stirred at room temperature for 48 h, after which it was centrifuged at 8000 rpm for 10 min and placed in an oven (60 °C) to dry overnight. It was found that successively higher surface areas could be obtained after washing the as-synthesized material with water or with both water and ethanol. Yield (after washing with water and ethanol, then drying overnight at 60 °C): 0.28 g (76% of theoretical yield).

Larger batches of SU-101 were synthesized using 3.3 g of ellagic acid (90 wt. %, isolated from pomegranate hulls, 10 mmol), sold as a dietary supplement (PureBulk Inc.), and 7.6 g bismuth acetate (20 mmol) which was added to a beaker containing 600 mL of a water and acetic acid mixture (6 vol.% acetic acid, made from glacial acetic acid, with the possibility of replacing with store-bought white vinegar). The solution was allowed to stir for 48 h before being centrifuged at 8000 rpm for 10 min, after which it was placed in an oven at 60 °C overnight. Yield after washing with water and ethanol, then drying overnight at 60 °C: 5.6 g (74% of theoretical yield).

The phase purity of both materials was confirmed by PXRD and elemental analysis. Calculated (%) for Bi$_2$O(H$_2$O)$_2$$_{(C_{14}H_{26}O_8)}$·2H$_2$O using reagent-grade ellagic acid: C 20.91 H 1.25; measured (%): C 22.49 H 1.80. Calculated (%) for Bi$_2$O(H$_2$O)$_2$$_{(C_{14}H_{26}O_8)}$·2H$_2$O using supplement-grade ellagic acid: C 20.91 H 1.25; measured (%): C 22.35 H 1.65.

Larger crystals of SU-101 (> 2 µm) could be synthesized as a phase-mixture under hydrothermal conditions by adding 10 mg of reagent-grade ellagic acid (Acros Organics, 97% ellagic acid, isolated from chestnut tree bark, 0.03 mmol) and 24 mg bismuth acetate (Alfa Aesar, 99%, 0.06 mmol) to a 5 mL borosilicate 3.3 glass tube (Duran 12 x 100 mm, DWK Life Sciences) containing 3 mL of deionized water. The tube was then sealed with a polybutylene terephthalate (PBT) cap containing a PTFE seal, whereafter it was heated to 120 °C for 16 h. The contents were then filtered off and left to dry at ambient conditions.
2. Structure Determination and Characterization

Scanning electron microscopy
Scanning electron microscopy (SEM) images were collected on a JEOL JSM7401F SEM.

![SEM images](image)

Fig. S1. SEM images of SU-101 made using reagent-grade ellagic acid (a), as well as SU-101 made from supplement-grade ellagic acid (b), showing aggregates of columnar crystals (≤ 100 nm in width).

Transmission electron microscopy
Transmission electron microscopy (TEM) images were collected on a JEOL JEM 2100-LaB₆ operating at 200 kV using a Gatan ORIUS 200 D detector.

![TEM images](image)

Fig. S2. TEM images of SU-101 made using reagent-grade ellagic acid (a), as well as SU-101 made from supplement-grade ellagic acid (b).

3D electron diffraction (3DED)
Three-dimensional electron diffraction data were collected using a JEOL JEM2100-LaB₆ TEM, equipped with a Timepix detector from Amsterdam Scientific Instruments, while continuously rotating the crystal at 0.45° s⁻¹. The experiment was carried out using Instamatic,¹ with data reduction being performed in XDS.² The acquired intensities were then used to solve the structure of SU-101 with SHELXT,³ and refined using SHELXL⁴ with electron scattering factors extracted from SIR2014.⁵ From the 3DED data, all non-hydrogen atoms could be located in the initial structure solution from SHELXT. A data completeness of 99% could be obtained due to the high symmetry of the crystals, belonging to the tetragonal space group $P4_2/n$ (No. 86). Upon refinement against the acquired 3DED data, dynamical scattering, which is common to 3DED, led to an $R_1$ value considered high in comparison to acceptable refinement statistics for SCXRD data. Therefore, the structure was subsequently refined against high-resolution synchrotron X-ray powder diffraction data (Figure S4), despite confidence in the 3DED model.
Fig. S3. Reciprocal space projections of 3DED data acquired from a crystal of SU-101 (bottom right).

Table S1. Crystallographic table for 3DED data of SU-101.

| Specimen       | SU-101                      |
|----------------|-----------------------------|
| Crystal system | Tetragonal                  |
| Space group    | $P4_{2}/n$ (No. 86)         |
| Unit cell dimensions | $a = 18.44 \text{ Å}$  |
|                | $c = 5.82 \text{ Å}$        |
| Volume ($\text{Å}^3$) | 1979 $\text{Å}^3$         |
| $Z$            | 4                           |
| Rotation range | $102.40^\circ$ (-27.38 to 75.02$^\circ$) |
| Index ranges   | $-22 \leq h \leq 22$       |
|                | $-22 \leq k \leq 22$       |
|                | $-7 \leq l \leq 7$         |
| Reflections collected | 4172                       |
| Independent reflections | 1980                       |
| $[R(\text{int}) = 0.1711]$ |
| Completeness (to 0.8 Å resolution) | 99.0%                     |
| $R_1$ (ED model) [$I > 2\sigma(I)$] | 0.3343                     |
High-resolution PXRD

High-resolution PXRD data for the structure refinement of SU-101 were collected at 11BM at the Advanced Photon Source (APS), Argonne National Laboratory, USA, using the dedicated mail-in system, for which the sample was loaded in a Kapton capillary and measured with an X-ray wavelength of 0.457863 Å (stepsize of 0.000998 Å) using a multi-analyzer detector assembly. The refinement of the electron-diffraction model against high-resolution PXRD data was carried out in TOPAS-Academic V6. The refinement of the electron-diffraction model against high-resolution PXRD data was carried out in TOPAS-Academic V6. Topological analysis of the SU-101 framework was carried out using the software package ToposPro, as well as Systre and 3dt (both part of the GAVROG package).

Fig. S4. Plot for the structure refinement of SU-101. High-resolution PXRD data were collected at 11BM at the APS, Argonne National Laboratory, USA. λ = 0.457863 Å.

Table S2. Crystallographic table for the structure refinement of SU-101 against PXRD data.

| Identification code | SU-101 |
|---------------------|--------|
| Crystal system      | Tetragonal |
| Space group         | P42/n (No. 86) |
| Unit cell dimensions| a = 18.6217(3) Å  |
|                     | c = 5.5466(1) Å  |
| Volume (Å³)         | 1923.38(7) Å³ |
| Wavelength          | 0.457863 Å |
| Refinement method   | Profile method |
| Refinement statistics| \( R_{wp} = 8.08\% \) |
|                     | \( R_{Bragg} = 3.76\% \) |
|                     | GOF = 2.50 |
Asymmetric unit of SU-101

Fig. S5. Asymmetric unit of SU-101, containing half of an elligate linker, a coordinated oxygen (O5), and a coordinated water molecule (O6), as well a water molecule (O7) occupying the one-dimensional channels inside the material. Displacement spheres are drawn at the 50% probability level.

Hydrogen-bonding distances

Fig. S6. Hydrogen-bonding distances observed between the water molecules occupying the one-dimensional channels in SU-101, as well as between the carbonyl oxygen of the elligate linker and a coordinated water molecule.
Thermogravimetric analysis (TGA)
Thermogravimetric analysis data were gathered on a sample of SU-101 using a TA Instruments Discovery TGA. The sample was put into a platinum crucible and heated in air from 28 °C to 600 °C with a heating rate of 10 °C min\(^{-1}\). The sum formula best matching the observed data was determined as Bi\(_2\)O(H\(_2\)O)\(_2\)C\(_{14}\)H\(_{22}\)O\(_8\)·nH\(_2\)O (n = 1, i.e. one rather than two non-coordinated water molecules, as was determined from the refinement against HR-PXRD data).

![Thermogravimetric measurement of SU-101 in air. The dashed lines indicated expected relative mass remaining, assuming an initial formula of Bi\(_2\)O(H\(_2\)O)\(_2\)C\(_{14}\)H\(_{22}\)O\(_8\)·nH\(_2\)O, which is then converted into Bi\(_2\)O\(_3\) when heated beyond 350 °C.](image)

**Fig. S7.** Thermogravimetric measurement of SU-101 in air. The dashed lines indicated expected relative mass remaining, assuming an initial formula of Bi\(_2\)O(H\(_2\)O)\(_2\)C\(_{14}\)H\(_{22}\)O\(_8\)·nH\(_2\)O, which is then converted into Bi\(_2\)O\(_3\) when heated beyond 350 °C.
3. Stability and Porosity of SU-101

Variable temperature powder X-ray diffraction (VT-PXRD)
In-house PXRD measurements were carried out using a Panalytical X’pert Pro diffractometer (Cu Kα1,2, λ₁ = 1.5406 Å, λ₂ = 1.5444 Å) using a Bragg–Brentano geometry. Thermodiffraction measurements were carried out using the aforementioned in-house diffractometer, equipped with an Anton Paar XRK 900 high-temperature chamber.

![Variable temperature diffraction data for SU-101 under vacuum](image-url)

**Fig. S8.** Variable temperature diffraction data for SU-101 under vacuum. The dashed lines mark expected reflections from Si (used as internal standard).
Fig. S9. Variable temperature diffraction data for SU-101 in N₂ atmosphere. The dashed lines mark expected reflections from Si (used as internal standard).
**Fig. S10.** Variable temperature diffraction data for SU-101 in air. The dashed lines mark expected reflections from Si (used as internal standard).
**Sorption properties**

Gas adsorption/desorption isotherms were recorded on a Micromeritics ASAP2020 surface area and porosity analyzer. Prior to the experiments, the samples were pretreated at 150 °C under vacuum for 10h. Nitrogen adsorption/desorption isotherms were recorded at liquid nitrogen temperature (-196 °C). A liquid nitrogen bath was used as temperature control. The Brunauer–Emmett–Teller (BET) specific surface area of SU-101 was calculated using the N₂ adsorption points recorded at a relative pressure range $p/p_0 = 0.02 - 0.10$. Nitrogen (N₂), carbon dioxide (CO₂), and methane (CH₄) adsorption-desorption isotherms were recorded at 0°C. An ice slurry bath was used as the temperature control for these experiments.

**Fig. S11.** N₂ adsorption/desorption isotherms of SU-101 (made using reagent-grade ellagic acid, 97%, isolated from chestnut tree bark) hulls) and the same material washed with water (dark-green circles) as well as water and ethanol (green circles), all recorded at liquid N₂ temperature. The adsorption points are shown as solid symbols and the desorption points as hollow symbols. BET surface areas (as synthesized, water wash, water and ethanol washed): 304, 406, 412 m² g⁻¹.

**Fig. S12.** N₂ adsorption-desorption isotherm of as-synthesized SU-101 (black circles, made using supplement-grade ellagic acid, 90%, isolated from pomegranate hulls), and the same material washed with water (dark-green circles) as well as water and ethanol (green circles), all recorded at liquid N₂ temperature (77 K). The adsorption points are shown as solid symbols and the desorption points as hollow symbols. BET surface areas (as synthesized, water wash, water and ethanol washed): 208, 318 and 354 m² g⁻¹.

S10
Fig. S13. DFT pore size distribution as determined for reagent-grade SU-101, using a N₂ slit pore model. The dashed line is drawn at a pore-size value of 6.8 Å.

Fig. S14. CO₂ (red), CH₄ (green) and N₂ (blue) adsorption/desorption isotherms of SU-101 recorded at 0 °C. The adsorption points are shown as solid symbols and the desorption points are shown as hollow symbols.
Stability in solvents and solutions
For the stability tests, 10 mg of SU-101 was added to a 5 mL glass vial fitted with a screw-cap. For every trial, 1 mL of each respective solvent or solution was added and the resulting dispersion was stirred at room temperature or 80 °C for 24 h unless otherwise specified.

Fig. S15. Powder X-ray diffraction patterns of SU-101 after being immersed in various solvents or solutions for 24 h (stirring at 800 rpm, 21 °C unless specified).
Fig. S16. Powder X-ray diffraction patterns of SU-101 after being immersed in various solvents or solutions for 24 h at 80 °C (unless specified) while stirring at 800 rpm.
Stability in the presence of L-cysteine and L-cystine

The integrity of SU-101 in the presence of L-cysteine and L-cystine at 37 °C was evaluated by preparing solutions with 1 mg mL$^{-1}$ of the material and each respective compound in water. The SU-101 dispersions were then allowed to stir at 37 °C for 24 h before the MOF was retrieved by centrifugation (8000 rpm, 10 min). PXRD patterns were acquired after the powders were allowed to dry under ambient conditions. Residual crystalline L-cystine can be observed in the sample previously immersed in a solution of L-cystine.

![PXRD patterns](image)

**Fig. S17.** Powder X-ray diffraction patterns acquired of SU-101 after being stirred in aqueous solutions of L-cysteine and L-cystine, as well as patterns of the as-synthesized material and L-cystine for comparison.
**pH-dependent stability**

For the pH-dependent stability tests, 20 mg of as-synthesized SU-101 was immersed in 3 mL of stock solution, prepared from either NaOH or concentrated HCl, as to obtain the desired pH.

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**Fig. S18.** Powder X-ray diffraction patterns acquired of SU-101 after being stirred in aqueous solutions at various pH levels, at room temperature. The phase acquired at pH < 2 is tetragonal BiOCl. When exposed to 20 M NaOH the material is dissolved, forming a clear yellow solution.
SU-101 stability in biorelevant media (colloidal and structural)
SU-101 in PBS solution was prepared by dispersing the material in PBS solution (10 mg mL⁻¹ of SU-101 in 0.01 M phosphate buffer, 0.0027 M KCl, 0.137 M NaCl, pH = 7.4) or cell culture medium (1 mg mL⁻¹ of SU-101 in RPMI: 0.09 M Na₂HPO₄, 0.044 M NaHCO₃, 0.002 M CaCl₂, 0.0008 M MgSO₄, 0.0053 M KCl, 0.11 M NaCl, pH = 7.4). The remaining solid were kept in order to collect cell culture media (30 µL medium) in 96 well plates. The cytotoxic activity of SU-101 was analyzed by the colorimetric MTT assay. The cytotoxicity was determined by adding the MTT reactant (0.5 mg mL⁻¹ in PBS, incubated at 37 °C under continuous stirring. After different incubation times (1, 2, 4, 6 and 24 h), the colloidal stability was evaluated by dynamic light scattering (DLS; Zetasizer Nano, Malvern Instruments). Subsequently, in each incubation time and in each type of media, SU-101 samples were centrifugated (14,500 rpm, 10 min). The remaining solid were kept in order to collect the XRPD patterns. Profiles were generally collected in the 3° < 2θ < 30° range with a typical step size of 0.02° in continuous mode using a D8 Advance Bruker diffractometer (Cu Ka1 radiation, λ = 1.5406 Å).

![SU101 stability in biorelevant media](image)

**Fig. S19.** Colloidal stability of SU-101 (reagent grade) in: water (red) and RPMI (green), representing a) the NP size and b) \( \zeta \)-potential evolution vs. time.

4. Biocompatibility of SU-101

Cells and culture
HL-60 cell lines (ATCC®CCL-240™) were cultured in RPMI 1640 medium supplemented with glutamax-1 with 10% of heated-inactivated FBS and 1% penicillin/streptomycin at 37 °C in a humidified 5% CO₂ atmosphere and passaged twice a week (at 80% of confluence) at a density of 5 × 10⁴ cells cm⁻².

Cytotoxicity studies
The cytotoxic activity of SU-101 as well as its precursors (57% of Bi(AOC)₃ and 43% of ellagic acid) was analyzed by the colorimetric MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay. The promyelocytic cell line HL-60 (cells in suspension) was seeded 24h prior to the assay in 96-well plates at a density of 1 × 10⁵ cells per well in RPMI (Roswell Park Memorial Institute medium) supplemented with 10% FBS. The particle suspensions were prepared as a dilution series with cell culture media (30 µL of the sample in aqueous solution were added to a final volume of 300 µL per well), yielding different concentrations (from 1000 to 8 µg mL⁻¹). Subsequently, all these treatments were added into the cells for 24 h, while being kept at 37 °C with a 5% CO₂ atmosphere. The cytotoxicity was determined by adding the MTT reactant (0.5 mg mL⁻¹ in PBS, incubated at 37 °C for 24 h).
°C for 2 h) followed by a PBS washing with 100 µL, ending with 100 µL of dimethylsulfoxide (DMSO) added to each well. Absorbance was determined at λ= 539 nm under stirring. The percentage of cell viability was calculated by the absorbance measurements of control growth and test growth in the presence of the formulations at various concentration levels.

![Graph](image)

Fig. S20. Cell viability of HL-60 cell line after 24 h incubation with SU-101 (blue), ellagic acid (green) and bismuth acetate (red). Note that the shown data corresponds to the average of triplicates for each concentration, obtained in two independent experiments (a total of n=6). The vertical error bars drawn in the diagram indicate the range of fluctuations (0.06 - 0.8) from which the standard deviations were calculated.

5. SO₂ and H₂S capture

SO₂ capture
The adsorption-desorption SO₂ isotherms were carried out at 298, 303 and 308 K up to 1 bar in a Dynamic Gravimetric Gas/Vapour Sorption Analyser, DVS vacuum (Surface Measurement Systems Ltd). Before each experiment, as-synthesized SU-101 was activated at 120 °C and 1.7 × 10⁻⁶ Torr for 6 h.

![Graph](image)

Fig. S21. SO₂ adsorption-desorption isotherm for SU-101 at 298 K. Closed symbols = adsorption, open symbols = desorption.
SO\textsubscript{2} isosteric heat of adsorption

The acquired SO\textsubscript{2} adsorption isotherms were used to estimate the isosteric heat of adsorption (Fig. S18). The isosteric heat of adsorption was determined by fitting a virial-type equation (Eq. S1) to 303 and 308 K SO\textsubscript{2} adsorption isotherms. Where \( p \) is the pressure, \( n \) is the amount adsorbed and \( A_0, A_1, \ldots \) are the virial coefficients (\( A_2 \) and higher terms can be neglected at lower coverage values). A plot of \( \ln(n/p) \) vs. \( n \) should give a straight line at low surface coverage (Fig. S19). The heat of adsorption was estimated to be -29.60 kJ mol\(^{-1}\).

\[
\ln\left(\frac{n}{p}\right) = A_0 + A_1 n + A_2 n^2 + \ldots \quad \text{Eq. S1}
\]

![Graph showing SO\textsubscript{2} adsorption isotherms at 298, 303, and 308 K.](image)

**Fig. S22.** SO\textsubscript{2} adsorption isotherms of SU-101 (solid points) with the corresponding Dual Site Langmuir Freundlich fits (dashed lines).

![Graph showing fitting plots for SO\textsubscript{2} adsorption at 303 and 308 K.](image)

**Fig. S23.** Fitting plots for adsorption of SO\textsubscript{2} on SU-101 at 303 and 308 K.
Adsorption-desorption cycles for SO\textsubscript{2} in SU-101 at 1 bar and 298 K. The re-activation of this sample was conducted only by applying vacuum (1.7 x 10\textsuperscript{-6} Torr) for 15 min at 298 K.

**PXRD after SO\textsubscript{2} adsorption-desorption experiments**

Patterns were collected in Bragg-Brentano geometry with Cu-K\textalpha\textsubscript{1} radiation (\(\lambda = 1.5406 \text{ Å}\)) on a Rigaku ULTIMA IV. The powder patterns were recorded from 5 to 40\textdegree\ (2\theta) in 0.02\textdegree\ steps and a scan rate of 0.2\textdegree\ min\textsuperscript{-1}.

**Fig. S25.** SU-101 PXRD patterns after SO\textsubscript{2} adsorption experiments (\(\lambda = 1.5406 \text{ Å}\)).
PXRD after humid SO$_2$ adsorption experiments
Humid SO$_2$ adsorption studies were carried out in a previously reported lab-made system.$^{12}$ The system contains two principal parts (Fig. S26): SO$_2$ gas generator (left), a dropping funnel with conc. H$_2$SO$_4$ [1] connected to a schlenk flask with Na$_2$SO$_3$ (s) under stirring [2]; and a saturation chamber (right), constructed from a round-bottom flask with distilled water [3], connected to a sintered glass filter adapter [4] and a vacuum line [5]. The activated sample is placed on the glass filter adapter. The PXRD results indicated structural retention after exposure to humid SO$_2$ (Fig. S27).

Fig. S26. Lab-made system for humid SO$_2$ adsorption experiment.

Fig. S27. PXRD patterns of SU-101 after exposure to humid SO$_2$ ($\lambda$=1.5406 Å).
**H₂S breakthrough experiments**

H₂S experiments were carried out using a HP 5890 GC, where the exhausted gas was continuously injected to the gas chromatograph, acquiring a chromatogram for each injection. From the corresponding chromatogram the H₂S signal was integrated to obtain its quantity. Knowing the H₂S concentration from the feed, the H₂S concentration can be calculated for each injection, as the saturation concentration is the original feed concentration. Dynamic breakthrough experiments were carried out in a lab-made system (Scheme S1).

![Scheme S1](image)

**Scheme S1.** Representation of breakthrough dynamic system for H₂S uptake experiments.

The H₂S adsorption capacity for each cycle was calculated using Eq. S2, where \( V_{H₂S} \) represents the H₂S volumetric capacity (cm³ g⁻¹), \( m \) the adsorbent mass (g), \( F \) the input flow rate (cm³ min⁻¹), \( C_f \) and \( C_t \) the influent and downstream H₂S concentrations respectively (% vol), and \( t \) the time (min).¹³

\[
V_{H₂S} = \frac{F}{c_m} \cdot \int_0^t (C_f - C_t) \, dt 
\]

Eq. S2

As mentioned before, the adsorption column has a porous glass bed and a blank run was performed before each experiment to eliminate the adsorption contribution of the column. In Fig. S21 the black circles represent the adsorption of the column, and the others circles represent the MOF adsorption for each cycle. Then the corrected volumetric capacity \( V_{H₂S,corr} \) for SU-101 was estimated using Eq. S3 for each cycle.

\[
V_{H₂S,corr} = V_{H₂S,blank} - V_{H₂S, sample} \quad \text{Eq. S3}
\]

The H₂S adsorption capacity is often reported as \( q_{H₂S} \) (mol g⁻¹), this value was roughly estimated with the volumetric adsorption capacity \( V_{H₂S,corr} \) (cm³ g⁻¹) and the ideal gas law Eq. S4, where \( p \) is the system pressure (77.3 kPa), \( T \) the measurement temperature (298 K), and \( R \) the ideal gas constant (8314.4598 cm³ kPa K⁻¹ mol⁻¹).

\[
q_{H₂S} = \frac{V_{H₂S,corr} \cdot p}{R \cdot T} \quad \text{Eq. S4}
\]

The H₂S uptake for SU-101 was measured in this home-made system using the following conditions: average temperature of 298 K, a gas concentration of 4.3% vol H₂S/N₂ and a gas flow of 25 mL min⁻¹, \( p = 0.78 \) atm and 50 mg of SU-101 material were used for each adsorption cycle. Before carrying out the experiments the material was activated at 120 °C for 6 h under a flow of N₂ (25 mL min⁻¹). For each experiment, three independent measurements were performed.
**Fig. S28.** Adsorption breakthrough curve for H$_2$S with SU-101.

**PXRD after H$_2$S experiments**
Patterns were collected in Bragg-Brentano geometry with Cu Kα1 radiation (λ = 1.5406 Å) on a Rigaku ULTIMA IV. The powder patterns were recorded from 5 to 40° (2θ) in 0.02° steps and a scan rate of 0.2° min$^{-1}$.

**Fig. S29.** PXRD of SU-101 before and after H$_2$S experiments.
Raman spectroscopy
The Raman experiments were measured on a DXR2 Thermo Scientific instrument with a lamp of 780 nm and 10X microscope objective for samples of SU-101 before and after H₂S experiments.

Fig. S30. Raman spectra of SU-101. SU-101 As: as synthesized (black line) and SU-101 H₂S C1: after H₂S adsorption experiment (first cycle, C1) (blue line).

FTIR Spectroscopy
FTIR spectra were measured (in-situ and at 25 °C) using an FTIR Nicolet 6700 spectrophotometer (DTGS detector) with a 4 cm⁻¹ resolution equipped with a diffuse reflectance vacuum chamber with CaF₂ windows.

Fig. S31. DRIFT spectra of SU-101. SU-101 As: as-synthesized (black line) and SU-101 H₂S C1: after H₂S adsorption experiment (first cycle, C1, blue line).
**Proposed mechanism for polysulfide formation**

The formation of polysulfides from adsorbed H₂S can proceed through a sequence of steps: in the first part, H₂S is adsorbed within the SU-101 material (inside the pores) modifying the redox properties of H₂S. The mechanism can be explained as below, which is adapted from previous studies.¹⁴,¹⁵

I. \( H₂S \) adsorption at the surface of the MOF: \( H₂S(g) \rightarrow H₂S(ads) \)

II. \( 2H₂S(ads) \) is dissociated: \( 2H₂S(g) \rightarrow 2HS(ads) + 2H(ads) \)

III. \( 2HS(ads) + 2H(ads) \rightarrow S₂(ads) + 2H₂(g) \)

IV. Formation of linear or cyclic sulfur polymers (sulfur recombination): \( XS-S(ads) \rightarrow XS_x(ads) \)
Supplemental References

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