Electronic Supplementary Information

Understanding and Controlling the Chemical Evolution and Polysulfide-Blocking Ability of Lithium–Sulfur Battery Membranes Cast from Polymers of Intrinsic Microporosity

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Materials and methods

Materials

Diethylene glycol dimethyl ether (diglyme, anhydrous, 99.5%), 1,2-dimethoxyethane (glyme, anhydrous, 99.5%), 4-*tert*-butylcatechol (98%), potassium carbonate, tetrafluoroterephthalonitrile (99%), tetrahydrofuran-d_8 (99.5% atom D) and 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetraol (96%) were obtained from Sigma-Aldrich. Lithium foil (99.9%, 1.5 mm thick and 0.75 mm thick), lithium nitrate, lithium sulfide (99.9% metals basis), and sulfur (99.9995% metals basis) were obtained from Alfa Aesar. Lithium bis(trifluoromethanesulfonimide) (LiTFSI) was obtained from 3M. 2,6-Bis(4-azidobenzylidene)cyclohexanone (**3**, wetted with ca. 30% water, >90% purity) was obtained from TCI. KetjenblackEC-600JD was obtained from AzkoNobel. Celgard® 2400 was obtained from Celgard (Charlotte, NC). Glassy carbon electrodes with 1 mm diameter were purchased from BAS Inc. (West Lafayette, IN) and polished before each experiment with 3-µm diamond paste. *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were taken from a JC Meyer solvent system. Chloroform (HPLC grade) was obtained from EMD Millipore. All chemicals were used as received unless otherwise specified. Lithium nitrate and LiTFSI were dried under vacuum for 16 h at 110 and 150 ˚C, respectively. Diglyme was dried over 3 Å molecular sieves to < 20 ppm water. Electrolyte refers to 0.50 M LiTFSI and 0.15 M $LiNO_3$ in diglyme unless otherwise specified. A stock solution of 2.50 M S as Li_2S_8 was prepared by adding sulfur (701 mg, 21.9 mmol S) and lithium sulfide (144 mg, 3.1 mmol) to electrolyte (10 mL) at 60 ˚C. The stock solution was stored at 60 ˚C to prevent precipitation of polysulfides and was diluted as necessary.

Instrumentation

Unless otherwise mentioned, all manipulations were performed in an argon glovebox with oxygen and water levels below 5 and 1 ppm, respectively. NMR spectra were acquired on a Bruker Avance II 500 MHz NMR spectrometer at 500 MHz for [1]H. [1]H chemical shifts were referenced with respect to residual solvent peaks ([1]H (δ) chloroform-d_3 7.26, [1]H (δ) THF-d_8 1.72 ppm). Polymer molecular weight was measured using size-exclusion chromatography with a Malvern Viscotek TDA 302 system calibrated with a 99 kDa monodisperse polystyrene standard. Electrochemical experiments were performed on a Bio-Logic VMP3 potentiostat. Cyclic voltammograms were acquired with iR drop compensation by measuring the uncompensated resistance with a 100 kHz impedance measurement and correcting for 85% of the expected drop. Battery cycling was performed on an Arbin 2043 battery cycler. Water content measurements were performed on a Mettler Toledo C20 Coulometric KF Titrator Karl-Fischer apparatus. Nitrogen adsorption measurements were performed at liquid nitrogen temperature (~77 K) with a Micromeritics Tristar II 3020 adsorption system. In situ FT-IR spectroscopy of PIM-1 in the presence of lithium polysulfides was performed with a Mettler Toledo ReactIR 15 spectrometer. All other FT-IR spectra were acquired in transmission mode on a Varian 3100 FT-IR spectrometer. ESI-MS spectra were acquired with a Bruker microTOF-Q high-resolution mass-spectrometer.

Synthesis of PIM-1

PIM-1 with molecular weight 200 kg mol^{-1} was synthesized as described elsewhere.[1] Briefly, a mixture of anhydrous potassium carbonate (8.3 g, 60 mmol), 3,3,3′,3′-tetramethyl-1,1'-spirobisindane-5,5′,6,6′-tetrol (6.8 g, 20 mmol) and tetrafluoroterephthalonitrile (4.0 g, 20 mmol) in dry DMF was stirred at 65 °C for 4 d. On cooling, the mixture was added to water and the crude product collected by filtration. Repeated precipitations from a concentrated solution of polymer in chloroform into methanol yielded 8.90 g (19.3 mmol, 97% yield) of the fluorescent yellow polymer (PIM-1).

Synthesis of model compound 1

Model compound **1** was synthesized as described elsewhere.[2] Briefly, an oven-dried 40 mL septum-capped vial was charged with a stir bar, 4-*tert*-butylcatechol (997 mg, 6 mmol), tetrafluoroterephthalonitrile (600 mg, 3 mmol), and dry DMF (13 mL). The mixture was stirred for several minutes to give a transparent orange solution. Next, potassium carbonate (871 mg, 6.3 mmol) was added, and the mixture was heated to 70 ˚C under nitrogen for 25 h. The resulting suspension was added to 100 mL water, filtered, and rinsed with water and acetone. Finally, the product was dried at reduced pressure overnight to yield 1.306 g (2.9 mmol, 96% yield) of **1** as a bright yellow powder. [1]H (CDCl$_3$, 500 MHz): δ 7.03 (dd, 2H, J_{HH} = 8.2, 2.2 Hz, Ar*H*), 7.02 (d, 2H, J_{HH} = 2.1 Hz, Ar*H*), 6.92 (d, 2H, J_{HH} = 8.2 Hz, Ar*H*), 1.29 (s, 18H, C*H*$_3$).

Crossover measurement and analysis

A PIM-1 membrane of known thickness (typically 8–12 μm) was placed between two halves of an H-cell with an aperture diameter of 1.6 cm and sealed in place with a chemically resistant O-ring. One half of the H-cell (the retentate) was charged with 12 mL of Li$_2$S$_8$ in electrolyte, while the other half (the permeate) was charged with the same volume of electrolyte with no Li$_2$S$_8$. Both compartments were stirred to ensure homogeneity. Every 20–30 min, the stirring was stopped and the concentration was measured electrochemically by acquiring a CV at 100 mV s^{-1} from 2.00 V to 3.00 V *vs.* Li/Li$^+$. The peak anodic current was related to polysulfide concentration with a calibration curve (Fig. S1).
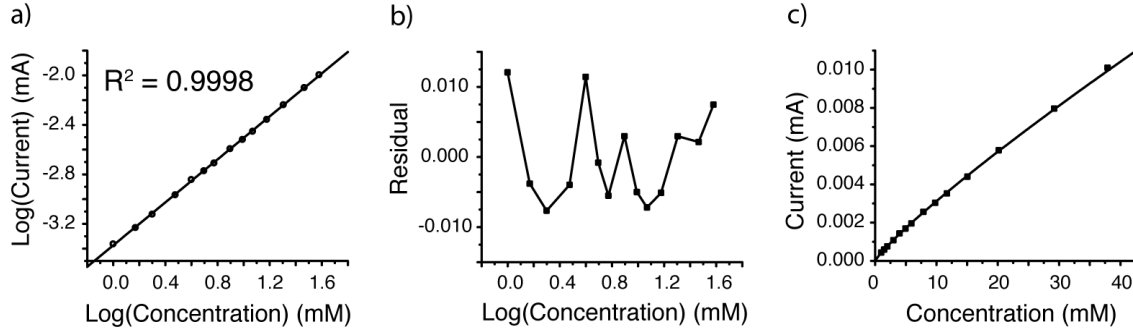
Figure S1. a) Calibration plot of log(current) *vs.* log(concentration) with the linear regression, b) residuals from (a), showing that the deviations from the fit are random, c) the calibration plot (a) on linear axes.

Table S1. Known concentration, calculated concentration from the calibration curve, and the percent difference for all points on the calibration curve.

Actual Conc. (mM)	Calc. Conc. (mM)	Difference (%)
0.998	1.030	*3.3*
1.478	1.463	*-1.0*
1.992	1.952	*-2.0*
2.982	2.951	*-1.0*
3.968	4.090	*3.1*
4.95	4.939	*-0.2*
5.929	5.843	*-1.5*
7.874	7.936	*0.8*
9.804	9.675	*-1.3*
11.719	11.498	*-1.9*
15.034	14.832	*-1.3*
20.154	20.313	*0.8*
29.19	29.357	*0.6*
37.893	38.651	*2.0*

Calculation of D_{eff} from crossover measurement

At any moment, the flux of active-species across the membrane (J, mmol cm^{-2} s^{-1} can be described with Fick's first law:

$$J = D_{eff} \frac{\partial C}{\partial x} = D_{eff} \frac{C_{retentate}(t) - C_{permeate}(t)}{l}$$

Where D_{eff} is the effective diffusion coefficient in cm^2 s^{-1}, C is the concentration in mmol cm^{-3} and l is the membrane thickness in cm. For short times, the difference $C_{retentate}(t) - C_{permeate}(t)$ does not change significantly from its initial value of $C_{retentate}(t_0) - C_{permeate}(t_0) = C_0$, and the flux is constant with time:

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$$J(t \approx 0) = D_{eff} \frac{C_0}{l}$$

The concentration of active species in the permeate compartment can be calculated by integrating the flux of active species over time from 0 to t, multiplying by the membrane area, A, and dividing by the volume of solution in the permeate compartment:

$$C_{permeate}(t) = \frac{A \int_0^t J(t)dt}{V_{permeate}} = \frac{D_{eff}C_0A}{lV_{permeate}}t$$

By measuring active-species concentration in the retentate compartment and plotting these values as a function of time, the effective diffusion coefficient of the active-species through the membrane can be quantified.

Characterization of chemically transformed model compound

Assignment of ^{1}H-NMR of reacted model compound

Solutions of lithium polysulfides are well known to consist of numerous species.[3,4] Therefore, a number of lithiated thioamides are expected to result from the reaction of model compound **1** with Li_2S_8. The aliphatic region of the ^{1}H NMR spectrum of **1** + 20 Li_2S_8 has one sharp singlet at 1.28 ppm and three broad singlets at 1.21, 1.13, and 0.97 ppm with relative integration of the sharp singlets to broad singlets of 1:1. The sharp singlet, which is within 0.02 ppm of the unreacted compound resonance, is attributable to *tert*-butyl groups on the opposite side of the molecule from the reacted nitrile group (Fig. S2a, proton 8). The broad peaks correspond to *tert*-butyl groups close to the reacted nitrile, and can be assigned to two separate species: one where the rotation around the C–CN bond is unhindered, and another where the rotation is hindered. We hypothesized that for lithiated thioamides containing more than 3 sulfur atoms (species B in Fig. S2), the unbound terminal sulfur atom can chelate lithium along with the neighboring oxygen, thus hindering rotation about the C-CN bond. As a result, the protons from the *tert*-butyl groups in the α and β conformers are chemically distinct, with peaks at 1.21 and 0.97 ppm. As temperature was increased to 55 ˚C (Fig. S3), these peaks broadened as is typical before coalescence, which supports this assignment. On the other hand, lithiated thioamides with fewer sulfur atoms cannot chelate lithium in the same way, and so they have less hindered rotation about the C–CN bond, leading to one broad peak at 1.13 ppm for the signal average between the α and β conformers. As expected, this peak did not broaden as temperature is increased. The multiplets from 7.1 to 6.9 ppm are similar in chemical shift to the multiplets in the unreacted model compound and can be assigned to protons 4, 5, and 6. This is further supported by the relative integration of the peaks, with the multiplets from 7.1 to 6.9 ppm having a relative integration of 3, equivalent to the total integral from 6.8 to 6.1 ppm. The remaining peaks were readily assigned on the basis of ^{1}H-COSY (Fig. S4) and integration data. H_3 protons were assigned based on the absence of *o*- coupling and the absence of ^{1}H-COSY cross-peaks, with the upfield peak assigned to the more shielded proton of species B. Pairs of multiplets corresponding to H_1 and H_2 were assigned based on ^{1}H-COSY cross-peaks, with the upfield pair assigned to species B and the more upfield of each pair of multiplets assigned to proton 2.
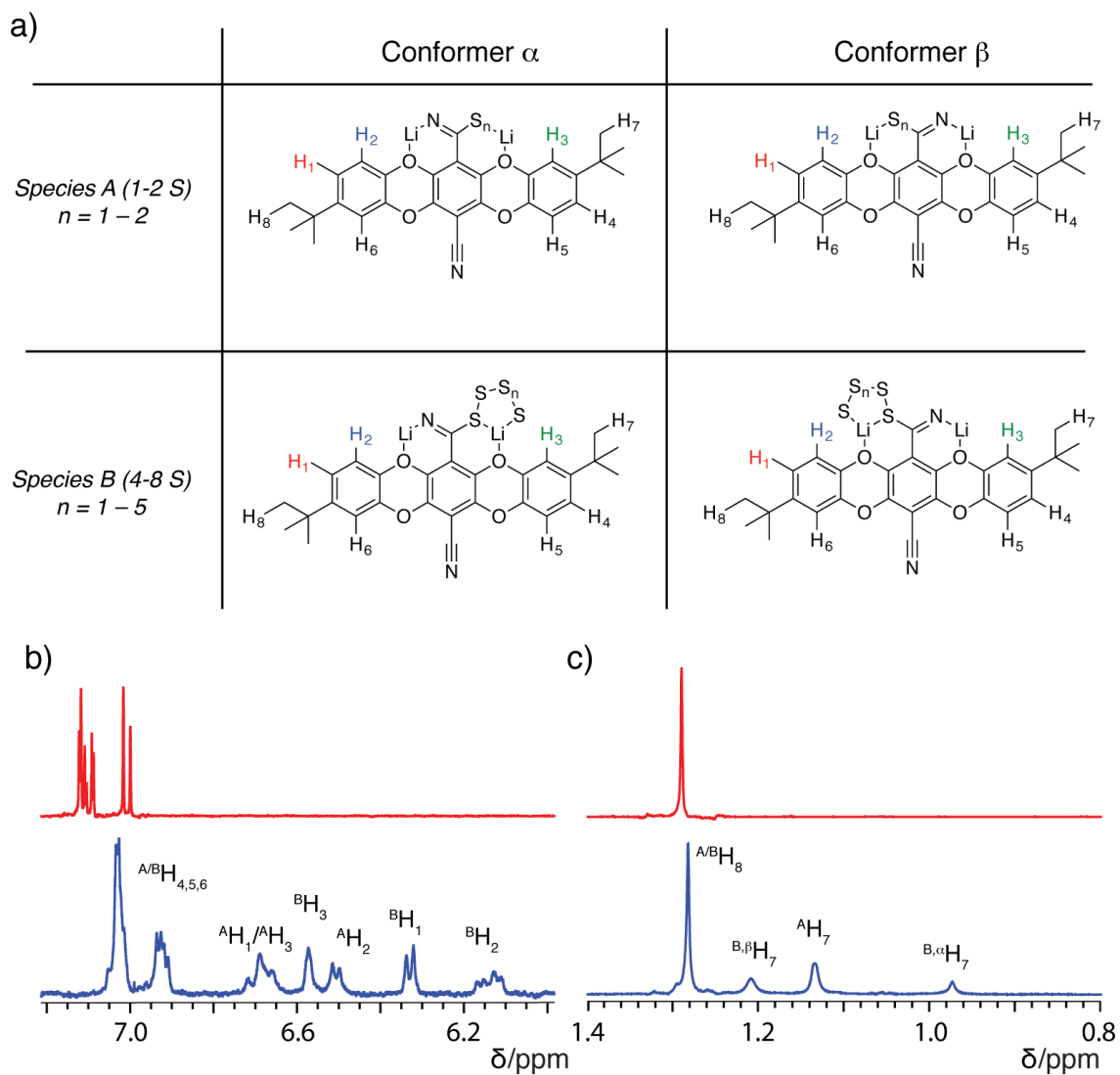
Figure S2. a) Proposed chemical structure of model compound **1** after reaction with lithium polysulfides, b) aromatic and c) aliphatic region of the ^{1}H-NMR of model compound **1** before (red, top) and after (blue, bottom) reaction with 20 equiv. Li$_2$S$_8$ with peak assignments.
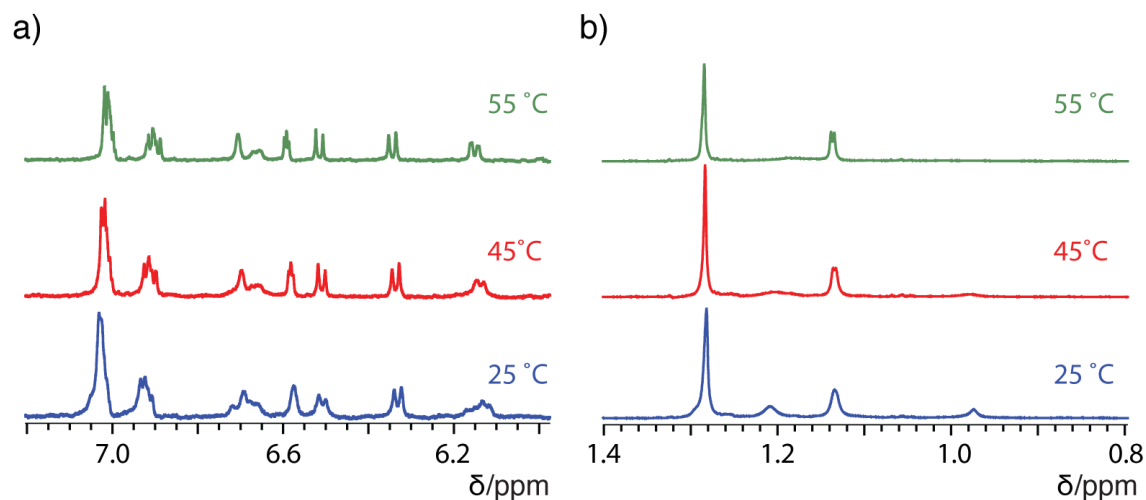
Figure S3. Variable temperature ^{1}H-NMR of model compound **1** + 20 equiv. Li_2S_8 at 25, 45, and 55 °C for the a) aromatic and b) aliphatic region of the spectrum.
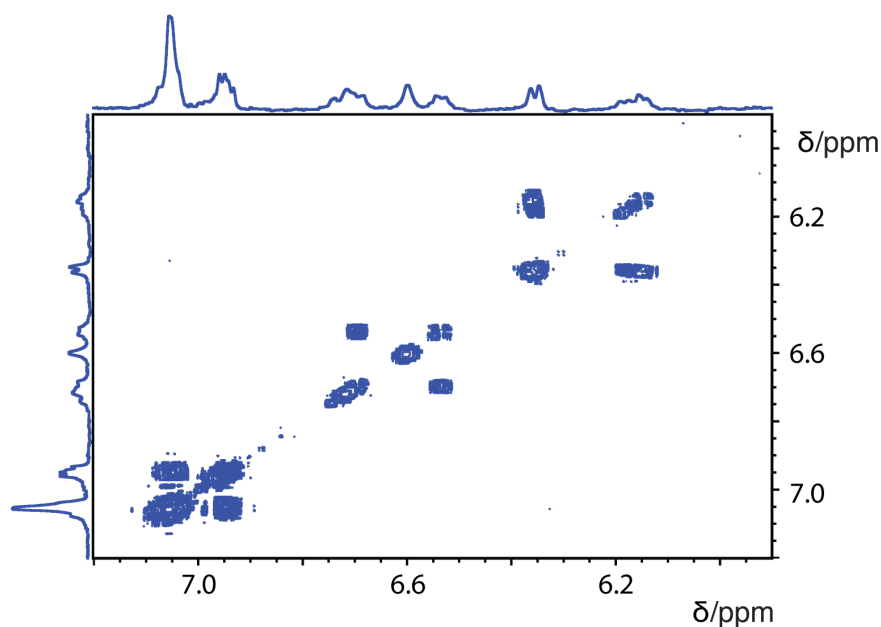

Figure S4. ^{1}H-COSY of model compound **1** + 20 equiv. Li_2S_8.

ESI-MS of reacted model compound

An 8 mM solution of **1** in 1:1 diglyme:THF-d_8 was treated with 20 equivalents of Li_2S_8 in the same solvent mixture. After 10 days mixing to ensure complete equilibration, the solution was diluted to 8×10^{-6} M in **1**. To avoid contamination/decomposition of the reacted model compound with water and oxygen, the syringe and capillary of the ESI-MS instrument were purged with dry, air-free THF immediately prior to analysis. The ESI-MS was operated in negative mode with an injection rate of 5 µL min^{-1}.

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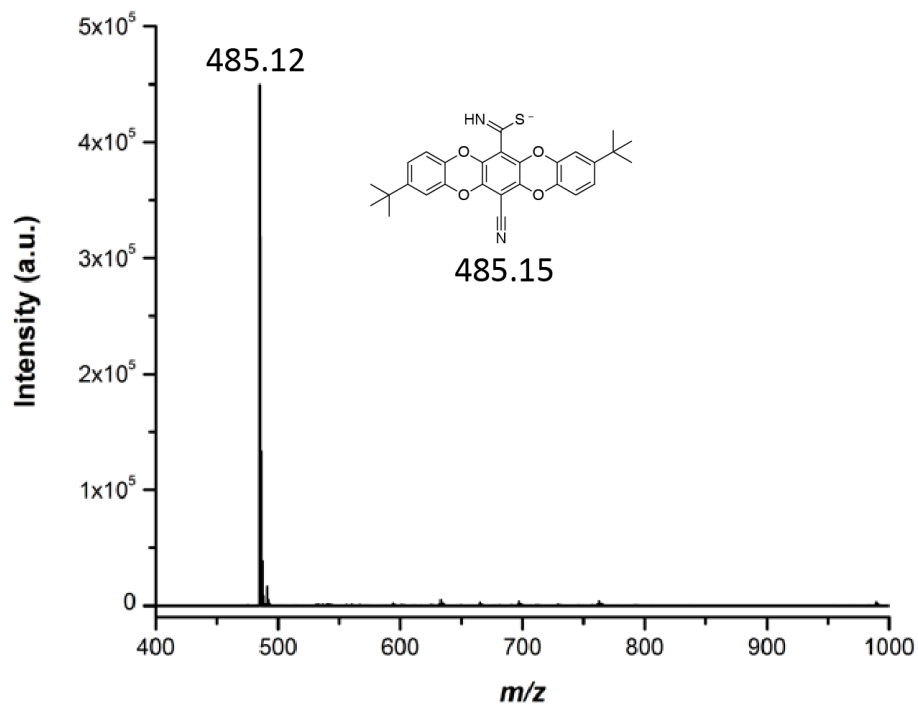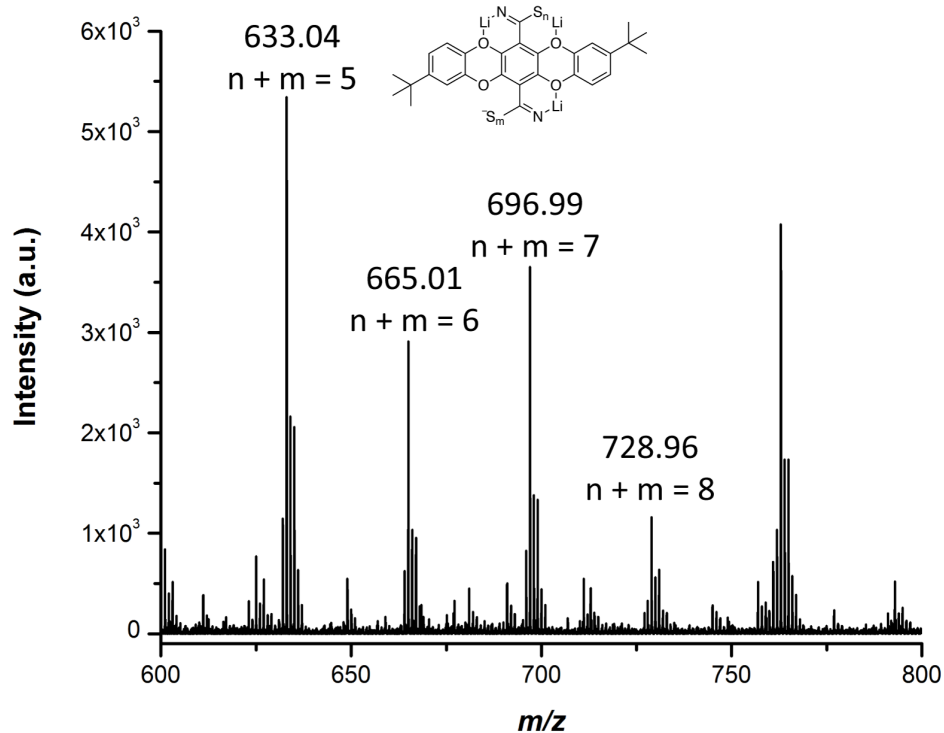**Figure S5.** ESI-MS showing the most intense peak assigned to [**M**+SH]⁻.

Figure S6. Lower intensity region from Figure S5 highlighting peaks attributed to both nitrile groups of the model compound reacting with polysulfide. Isotopic distributions for all assigned peaks are similarly well matched to those displayed in the main text.

Characterization of chemically transformed PIM-1

FT-IR of PIM-1 in the presence of lithium polysulfides
PIM-1 was drop-cast onto the polished silicon ATR probe of the spectrometer from a 12.5 mg mL^{-1} solution in chloroform, which was dipped into electrolyte blanketed under nitrogen. A stock solution of Li_2S_8 in electrolyte was injected to yield a sulfur concentration of 1.0 M or 0.2 M, as appropriate. The resulting solution was stirred under nitrogen and spectra were acquired every 5 min. Peak heights as shown in Fig. 4b were measured from a 2-point baseline.
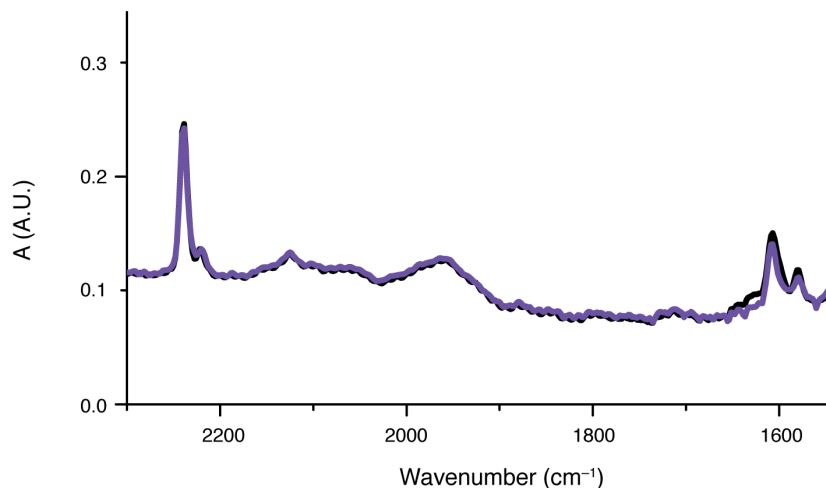

Figure S7. FT-IR of PIM-1 after soaking in 1.0 M S as Li_2S_8 in electrolyte for 22.5 h (black) and after replacing the Li_2S_8 solution with fresh electrolyte and soaking for an additional 8.5 h (violet).
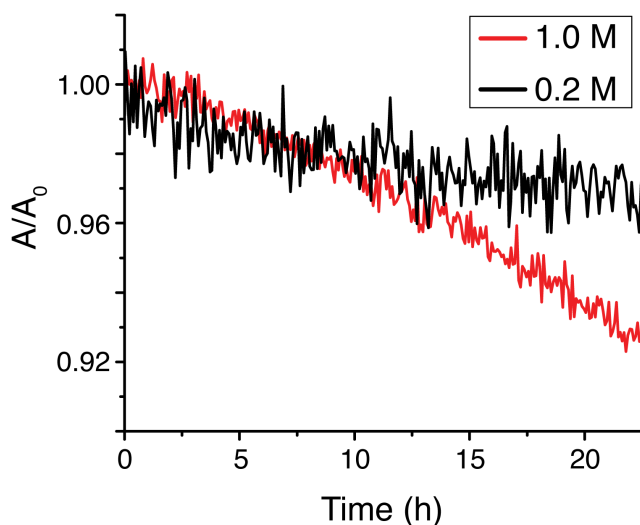

Figure S8. Normalized intensity of the nitrile stretch at 2239 cm^{-1} of PIM-1 in the presence of 0.2 M (black) and 1.0 M (red) S as Li_2S_8.

Gas adsorption measurements of PIM-1

PIM-1 was soaked in electrolyte or electrolyte containing 1.0 M S as Li_2S_8 for 24 h, followed by washing with and soaking in diglyme for a total of 26 h. Finally, the membranes were washed with glyme, dried under vacuum at room temperature for 70 h, and dried under vacuum at 120 ˚C for 19 h before measurement.
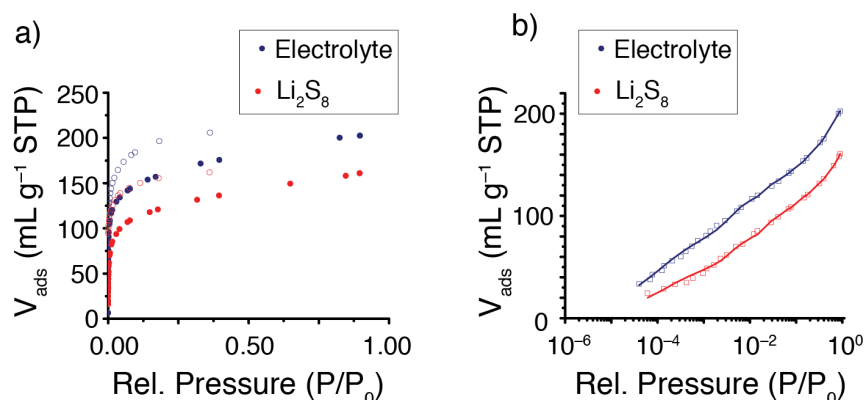

Figure S9. a) Adsorption (filled circles) and desorption (hollow circles) isotherms and b) simulated NLDFT adsorption isotherms (lines) with experimental isotherms (points) for PIM-1 soaked in electrolyte (blue) and electrolyte containing 1.0 M S as Li_2S_8 (red).
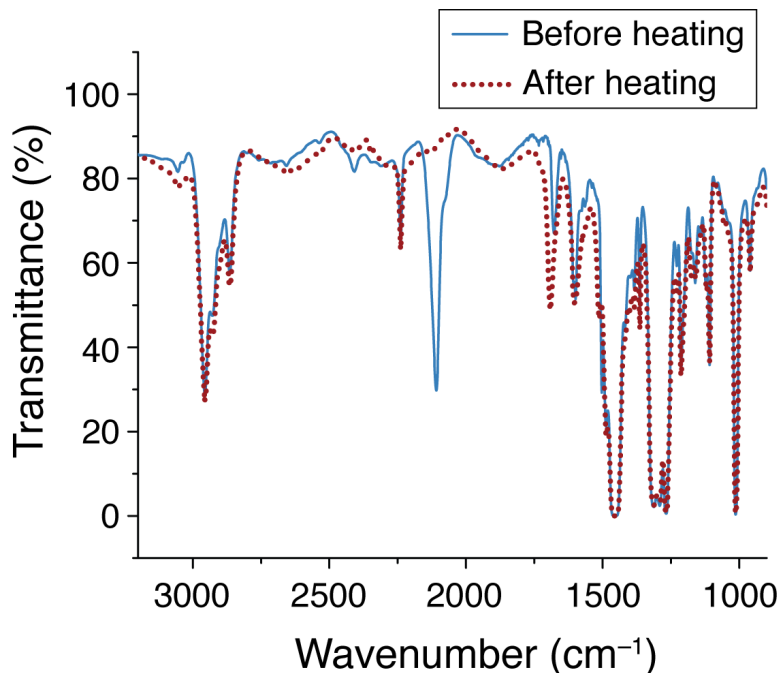

Figure S10. FT-IR spectra of membranes cast from PIM-1 with 0.1 molar equivalents of cross-linker **3** before (blue, solid) and after (red, dotted) heating at 175 ˚C for 7.5 h. Complete disappearance of the azide peak at 2110 cm^{-1} indicates complete reaction of the cross-linker.
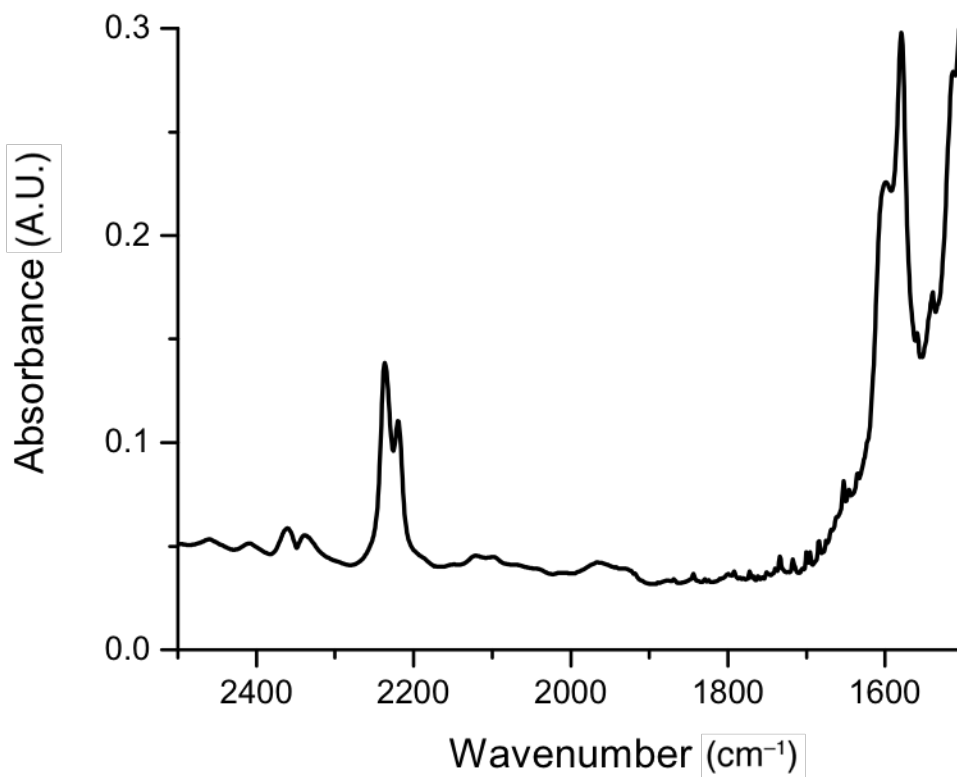
Figure S11. FT-IR spectrum of cross-linked PIM-1 membrane soaked in 1.0 M S as Li$_2$S$_8$ in electrolyte for 24 h. The appearance of new peaks at 2221 and 1579 cm^{-1} indicates conversion of nitrile groups to lithiated thioamides.

Ionic conductivity of PIM-1 membranes

Membranes with a diameter of 14 mm were soaked in electrolyte and sandwiched between two 12 mm diameter stainless steel electrodes in a Swagelok cell, with the excess membrane folded around one of the electrodes. Electrochemical impedance spectra were acquired on a Biologic VMP3 at a 0 V DC bias and 10 mV AC bias from 200 kHz to 1 kHz. The data were fitted to an equivalent circuit (Fig. S12) with the EC-Lab software by minimizing the fitting error, χ^2 given by $\chi^2 = \sum_i \frac{\left(z_{meas}(f_i) - z_{fit}(f_i)\right)^2}{|z_{meas}(f_i)|}$. The equivalent circuit accounts for the resistance and inductance of the wiring connecting the potentiostat and the conductivity cell, which were measured to be 0.34 Ω and 2.7 × 10^{-6} H, respectively. All capacitors were modeled as constant phase elements, which have an impedance given by $Z(f) = [Q(j2\pi f)^{\alpha}]^{-1}$. When α is 0, the CPE acts as a perfect resistor, and when α is 1, it acts as a perfect capacitor. For intermediate values of α, the CPE acts as a "leaky capacitor." The membrane conductivity was calculated from the membrane resistance using the relation $\sigma = l(AR_M)^{-1}$, where σ is the membrane

conductivity in S cm^{-1}, l is the membrane thickness in cm, A is the electrode area in cm^2, and R_M is the membrane resistance in Ω.
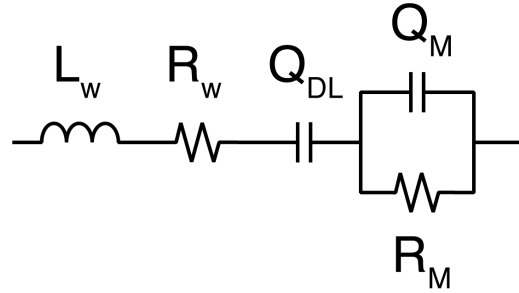

Figure S12. Equivalent circuit used to model electrochemical impedance spectra of membranes soaked in electrolyte. R_W and L_W correspond to the resistance and inductance of the wiring leading from the potentiostat to the conductivity cell, respectively. Q_{DL} and Q_M correspond to the double layer and membrane capacitances, respectively, and R_M corresponds to the ionic resistance of the membrane.
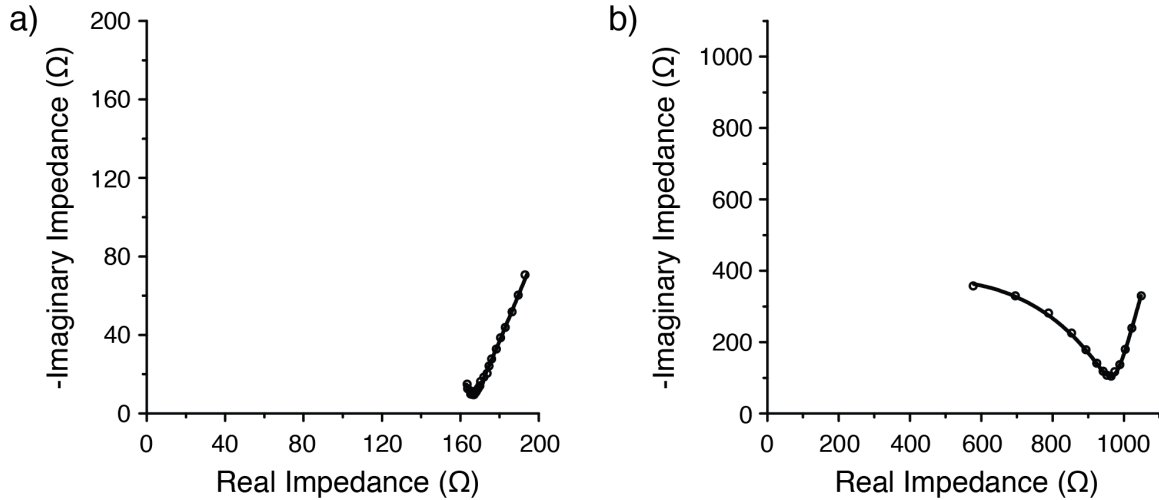

Figure S13. Electrochemical impedance spectra (points) and fits (lines) for a) native PIM-1 and b) 10% cross-linked PIM-1 soaked in electrolyte

Table S2. Fitting parameters from Fig. S13

Sample	Membrane Thickness (μm)	Q_{DL} (Fs$^{\alpha-1}$) [α]	Q_M (Fs$^{\alpha-1}$) [α]	R_M (Ω)	χ^2
Native PIM-1	11	$(18 \pm 2) \times 10^{-6}$ [0.75]	$(2 \pm 1) \times 10^{-9}$ [0.93]	165 ± 1	0.130×10^{-3}
Cross-linked PIM-1	20	$(2 \pm 1) \times 10^{-6}$ [0.84]	$(7 \pm 1) \times 10^{-9}$ [0.83]	967 ± 1	0.171×10^{-3}

Li–S battery assembly and testing

Preparation of the cathode

All battery electrolyte was 0.5 M LiTFSI in diglyme (with no added $LiNO_3$). A slurry of Ketjen-black/Li_2S_8 was prepared by adding 30.8 mg Ketjen-black to 500 µL 1.0 M S as Li_2S_8 in electrolyte and sonicating for 30 min. Approximately 20 mg of the resulting slurry, which contained 5% *w*/*w* conductive Ketjenblack, was then added to a carbon nanofiber paper disk[5] (1.13 cm^2, ~ 2mg), which served as the sulfur cathode.

Cell assembly

CR2032 coin cells were used for all battery tests. The anode was a lithium disk with a diameter of 15 mm and thickness of 750 µm. The anode was covered with one layer of Celgard® 2400 followed by a 10 µm native or cross-linked PIM-1 membrane. Finally, the cathode was added to the top of this stack and the cell was sealed. All membranes were soaked in electrolyte overnight before use.

Battery cycling

The cells were galvanostatically cycled at a C/16 rate with voltage cut-offs of 1.8 and 2.8 V. The discharge capacity of the cell with cross-linked PIM-1 dropped to 833 mA h g^{-1} after 7 cycles, which is about 72.2% of the initial capacity (Fig. S14a). At the same time, the discharge capacity of the cell with native PIM-1 decreased to 734 mA h g^{-1}, which is only 67.3% of the initial capacity. Thus, cross-linked PIM-1 achieves better capacity retention when applied in Li-S batteries. Furthermore, the Coulombic efficiency of the cells containing cross-linked PIM-1 membranes was higher than the cells with native PIM-1 membranes (100.4 *vs.* 93.7 % after 7 cycles, Fig. S14b). These improvements in Coulombic efficiency and cycle-life are a direct consequence of the improved polysulfide-blocking ability of cross-linked PIM-1.
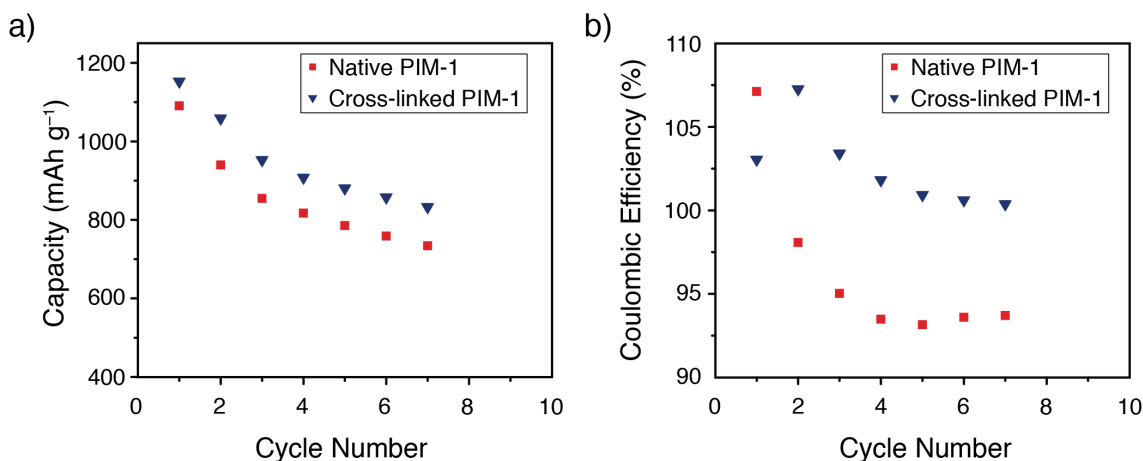

Figure S14. a) Discharge capacity and b) Coulombic efficiency of Li–S cells equipped with native (red squares) and cross-linked (blue triangles) PIM-1 membranes as a function of cycle number.

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