Supplementary Methods

Free Energy Molecular Dynamics Simulations. Valence (bonds, angles, dihedral and improper torsions) and short range van der Waals interactions for the PEB, polysulfide, 1,3-dioxlane (DOL), 1,3-dioxlane (DOL) and TFSI molecules were described using the DREIDING\textsuperscript{1} forcefield. As in our previous work\textsuperscript{2}, the electrostatic interactions were treated as Gaussian charge distributions, dynamically evaluated by means of the QTPIE fluctuating charge model\textsuperscript{3}. Initially, we employed the original QEq parameters of Goddard and Rappe\textsuperscript{4}. Further optimizations of the lithium and sulfur electronegativity ($\chi$) and hardness ($\eta$) parameters were performed to reproduce the Bader charge distributions on the solvated lithium polysulfides given in our previous work\textsuperscript{5}. Here we applied a Newton-Rapson iterative approach, minimizing the residual function (i.e., the differences in the calculated QTPIE and Bader charges for the ensemble lithium polysulfide structures). Optimal $\chi$ and $\eta$ parameters for the DOL and DME molecules were obtained from equilibrium molecular dynamics simulations of the bulk liquids, matching the experimental density. Details of our optimization procedure and forcefield parameters will be published separately\textsuperscript{6}.

Various systems comprising 1 PEB-1 molecule (4 units), TFSI\textsuperscript{−} and Li$_2$S$_n$ were embedded in a box of pre-equilibrated 1:1 DOL:DME molecules. These systems were then subjected to molecular dynamics (MD) simulations using the LAMMPS simulation engine\textsuperscript{7}. The system was equilibrated according to our usual approach\textsuperscript{8-10}. Briefly, after initial conjugant gradient minimization at a force tolerance of $10^{-4}$ kcal mol$^{-1}$ Å$^{-2}$, the system was slowly heated from 0 K to 298 K with a Langevin thermostat in the constant temperature, constant volume microcanonical (NVT) ensemble. The temperature coupling constant was 0.1 ps and the simulation time step was 1.0 fs.
This equilibration was followed by 10 ns of constant-pressure (iso-baric), constant-temperature (NPT) dynamics at the required temperature and 1 atm. The temperature coupling constant was 0.1 ps while the pressure piston constant was 2.0 ps. The equations of motion used are those of Shinoda et al.\textsuperscript{11}, which combine the hydrostatic equations of Martyna et al.\textsuperscript{12} with the strain energy proposed by Parrinello and Rahman\textsuperscript{13}. The time integration schemes closely follow the time-reversible measure-preserving Verlet integrators derived by Tuckerman et al.\textsuperscript{14}

After equilibration, the binding free energy of the polysulfide or TFSI\textsuperscript{−} were obtained separately from well-tempered Metadynamics simulations\textsuperscript{15,16}, employing the center of mass distances as the collective variable. Here, the Metadynamics step was 0.5 ps, at which time, Gaussian functions of with 0.5 kcal mol\textsuperscript{−1} were added to the biasing function of the system. Metadynamics simulations of at least 100 ns were run, with the collective variable monitored to ensure ballistic behavior and that the residual functional of the free energy calculated every 10 ps converged to zero. Usually, we found convergence after 50 ps.

**Simulated X-ray Absorption Spectroscopy Calculations.** Systems comprising a PEB-1/LiTFSI/Li\textsubscript{2}S\textsubscript{n} complex was equilibrated in a box of 60 1:1 DOL:DME solvent molecules and subjected to 20 ns of equilibration NPT MD simulations followed by 20 ns of NVT MD simulations. During the last 10 ns of NVT MD simulation, snapshots of the system (atomic positions) were saved every 0.5 ns (a total of 20 snapshots for each system) and used as input into an in-house code employing constrained-occupancy DFT calculations within the XCH approximation\textsuperscript{17–19} to calculate the XAS spectra (80 individual calculations). Plane–wave pseudopotential calculations using ultrasoft pseudopotentials\textsuperscript{20} were performed using the PWSCF code within the Quantum-ESPRESSO package\textsuperscript{21}. We used a kinetic energy cut-off for electronic wave functions of 25 Ry and a density cut-off of 200 Ry. The core-excited Kohn–
Sham eigenspectrum was generated using the XCH approach\textsuperscript{18}. Based on a numerically converged self-consistent charge density, we generated the unoccupied states for our XAS calculations non-self-consistently, sufficiently sampling the first Brillouin zone at the gamma point, employing an efficient implementation of the Shirley interpolation scheme\textsuperscript{22} generalized to handle ultrasoft pseudopotentials\textsuperscript{23}. Matrix elements were evaluated within the PAW frozen-core approximation\textsuperscript{24}. Core-excited ultrasoft pseudopotentials and corresponding atomic orbitals were generated with the Vanderbilt code\textsuperscript{20}. Each computed transition was convoluted with a 0.2 eV Gaussian function to produce continuous spectra.

Due to the use of pseudopotentials in our calculations (which means that we can only reliably compare the relative calculated excitation energies), we have developed an alignment scheme based on formation energy differences between the ground and core-excited states of the system and those of an isolated atom in the same simulation cell\textsuperscript{19,25}. Direct comparison to experiment is accomplished by first calibrating an unambiguous reference system. In the case of the sulfur compounds considered in this study, we rigidly shifted the first major peak in the sulfur K-edge XAS of an isolated S\textsubscript{2} molecule by $+2467.5$ eV to match the same in a gas phase experiment\textsuperscript{26}. This empirical shift, is unique to the pseudopotentials employed in this study, and is applied to all subsequent calculated spectra. Previous experience has shown that this alignment scheme predicts XAS peak positions to within $\sim0.1$ eV\textsuperscript{17,19}, which is typical of the experimental uncertainty in this energy range. It is well known that Kohn-Sham DFT within the PBE approximation underestimates band gaps\textsuperscript{27,28} and concomitantly band-widths due to inaccurate quasiparticle (excitation) energies\textsuperscript{20,30}. As a result, the calculated XAS spectrum is usually too narrow compared to experiments. Thus we dilated the computed XAS spectrum by 25%, as in our previous works\textsuperscript{2,31}.
Supplementary Figure 1 | CV curves of PEB-1/carbon black and PVDF/carbon black at a scan rate of 0.1 mV s\(^{-1}\).
Supplementary Figure 2 | Qualitative understanding of the polysulfide adsorbing character of PEB-1. a, Electrolyte composition: 1.0 M LiTFSI + 0.2 M LiNO₃. b, Electrolyte obviates use of both LiTFSI and LiNO₃. From left to right: Lithium polysulfides dissolved in electrolyte (10 mM, prepared nominally as Li₂S₆), the filtrate after PEB-1 had been introduced (and isolated) to sequester polysulfides from solution, the PEB-1/S₆ composite after PEB-1 underwent anion metathesis with Li₂S₆, pristine PEB-1 powder.
Supplementary Figure 3 | Quantitative determination of residual polysulfides in electrolyte after PEB-1 introduced as a chemisorbing species. a, UV-vis spectrum of the filtrate after anion metathesis. b, UV-vis spectra of standard Li$_2$S$_6$ solutions with concentrations of 0.20, 0.40, 0.60, 0.80, and 1.00 mM. c, Calibration curve linking optical absorbance at 280 nm to Li$_2$S$_6$ concentration.
Supplementary Figure 4 | DFT calculations of the valence electron charge density of N atoms in TFSI$^-$ (left hand side) and the pyrrolidinium moieties of a tetramer model of PEB-1.
Supplementary Figure 5 | Free energy curves highlighting the selective nature of Li$_2$S$_n$ and LiTFSI binding to PEB-1/S$_n$/LiTFSI ion clusters as it depends on oligomer length, $n$. a, The interaction of PEB-1 and Li$_2$S$_n$ when LiTFSI is present. b, The interaction of PEB-1 and LiTFSI when Li$_2$S$_n$ is present.
Supplementary Figure 6 | Simulated sulfur K-edge X-ray absorption near edge structure spectra of PEB-1/Li$_2$S$_8$ with closed and open polysulfide complexes, with respect to Li$^+$ coordination. These calculations support the assessment of features in the experimentally observed S K-edge XAS as arising from a ring-opened polysulfide configuration.
Supplementary Figure 7 | Characterization of N-Doped Mesoporous Carbon (N-MC) and N-MC/S. a, SEM of N-MC. b, TEM of N-MC. c, Nitrogen adsorption isotherms of N-MC and N-MC/S. d, BJH pore size distribution of N-MC and N-MC/S.
**Supplementary Figure 8 | XPS analysis of N-MC hosts for sulfur active materials.** a, Survey scan noting the presence of N, C, and O elements in the material. b, Analysis of the N 1s signal, noting the presence of un-oxidized and oxidized $sp^2$ motifs, and quaternized $sp^3$ motifs.
Supplementary Figure 9 | TGA analysis of N-MC/S composite.
Supplementary Figure 10 | SEM images of sulfur cathodes with different binders. a-b, PEB-1. c-d, PVDF.
Supplementary Figure 11 | Discharge-Charge voltage profiles of PVDF and PEB-1 cells with a sulfur loading of 1.2 mg cm$^{-2}$ deposited onto an aluminum current collector. a, 1$^{st}$ and b, 200$^{th}$ cycles.
Supplementary Figure 12 | 500 MHz $^1$H NMR spectra of PEB-1.

Supplementary Figure 13 | FT-IR spectrum of PEB-1.
Supplementary Figure 14 | TGA analysis of PEB-1.
**Supplementary Table 1 | Comparison of recently reported binders for Li–S batteries.**

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This Work
### Supplementary Table 2 | Elemental analysis of PEB-1.

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Supplementary References


