
A circular oligo(disulfide) anolyte enables practical aqueous redox flow batteries

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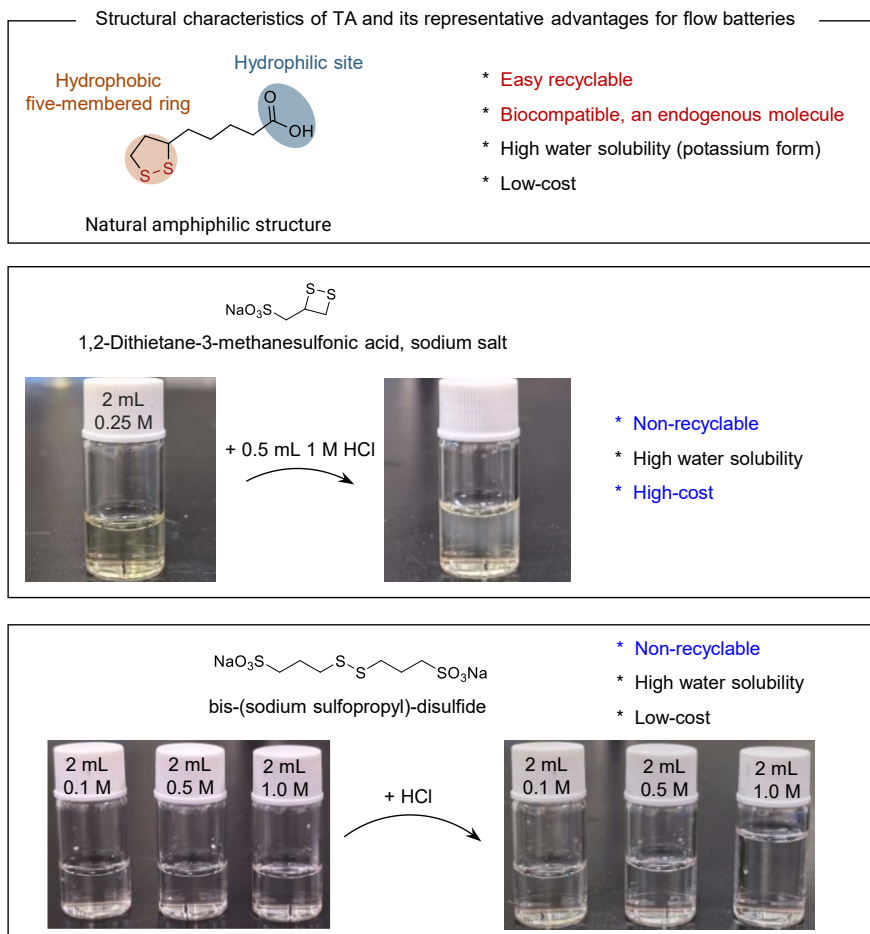
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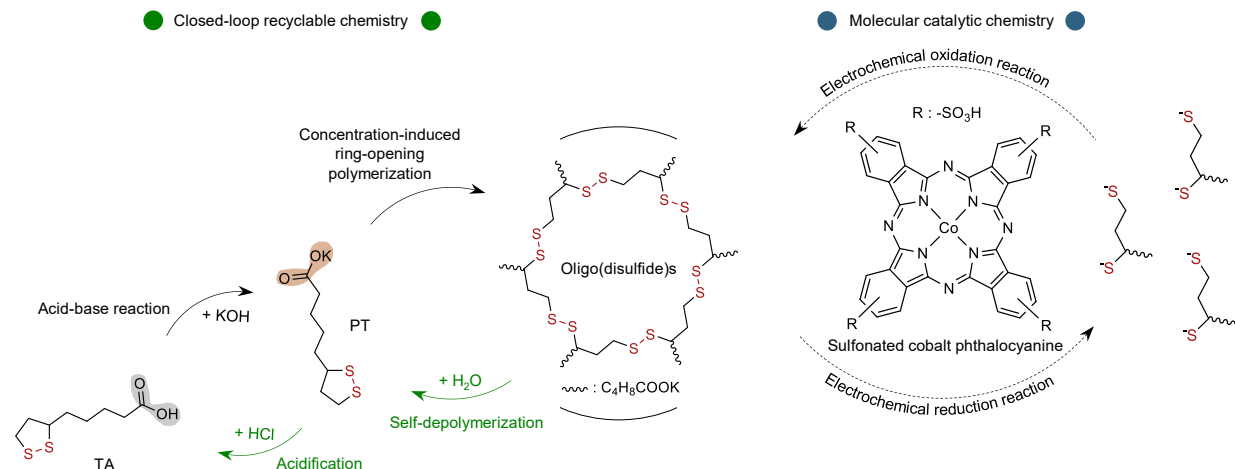
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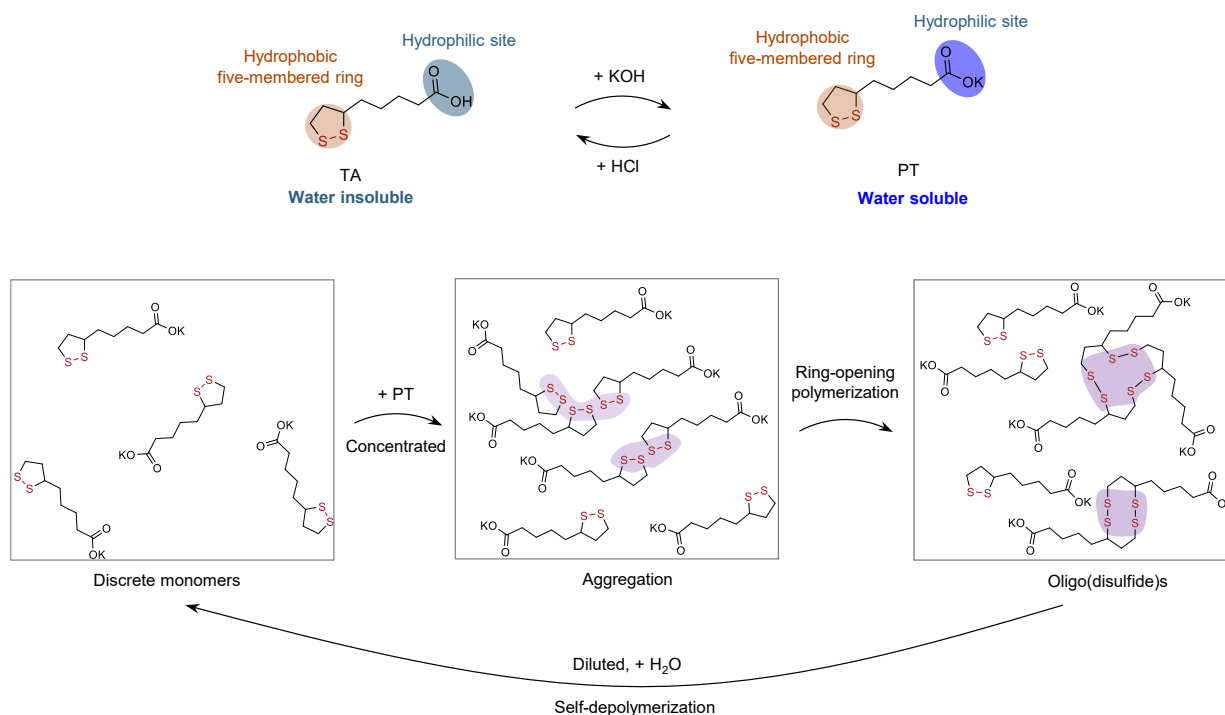
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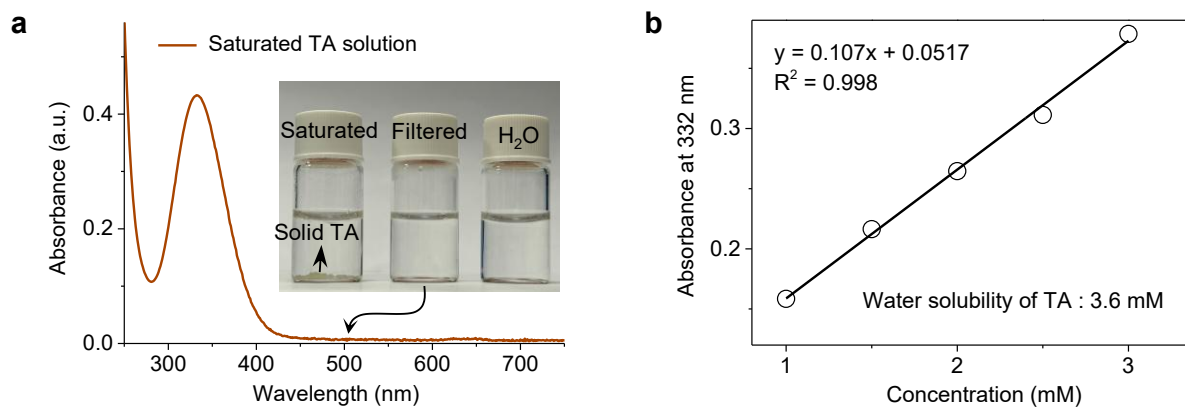
Supplementary Fig. 1. Molecular properties of three water-soluble organosulfur materials for aqueous RFBs.



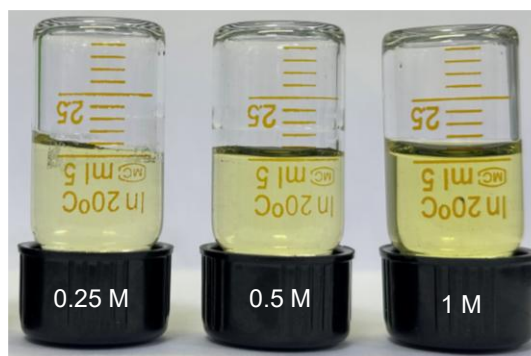
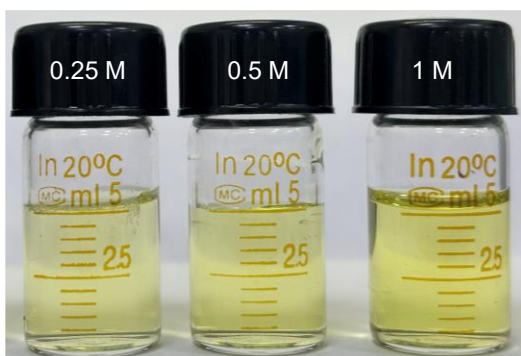
Supplementary Fig. 2. Design concept of the recyclable oligo(disulfide)s-based anolyte and catalyst. Left: formation and recycling process of oligo(disulfide)s. Right: in the presence of the sulfonated cobalt phthalocyanine catalyst, the redox reaction process of a representative oligo(disulfide) and representative features of the oligo(disulfide)s-based anolyte.



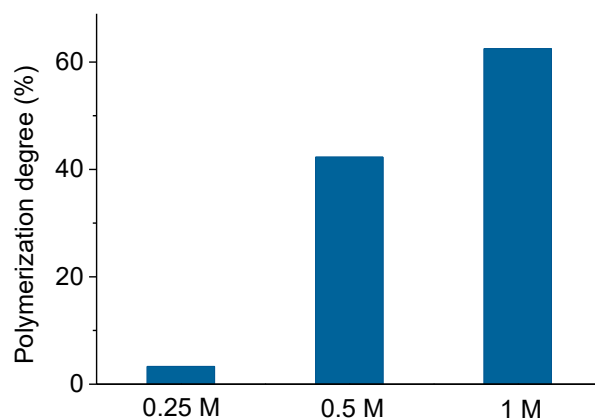
Supplementary Fig. 3. Diagram of the detailed recycling process. The formation and recycling of oligo(disulfide)s are achieved by regulating ion types and electrolyte concentrations. First, PT disperses in solution as disordered molecular monomers at low concentration. Second, after increasing the PT concentration, the hydrophobic five-membered rings tend to aggregate to minimize interactions with surrounding high-energy water molecules and to form oligo(disulfide)s via ring-opening polymerization. Accordingly, a relatively high concentration is required for the formation and stabilization of oligo(disulfide)s. After the oligo(disulfide)s solution is diluted with water, the stable environment for oligo(disulfide)s is disrupted, driving self-depolymerization into disordered molecular monomers. Finally, adding acid to the discrete monomer solution completes the conversion from highly soluble oligo(disulfide)s to TA monomers.



Supplementary Fig. 4. (a) UV-vis spectrum of saturated TA solution. Inset: a photograph of saturated TA solution, the corresponding filtrated solution, and deionized water. (b) The standard curve of TA. The solubility of TA was confirmed via absorbance at 332 nm and the standard curve.



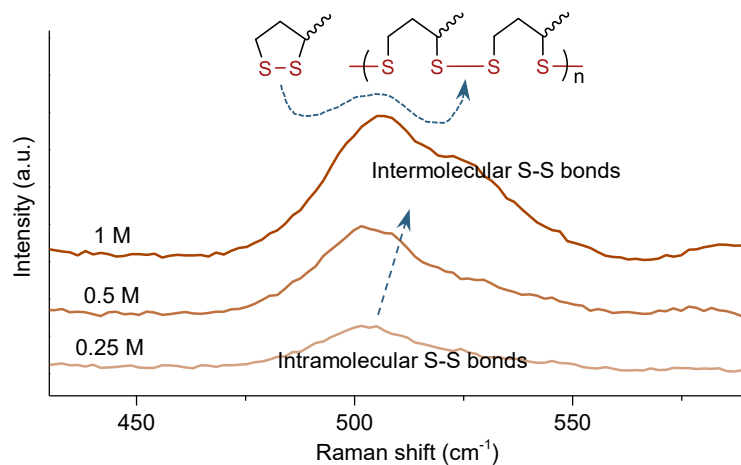
Supplementary Fig. 5. Photographs of three homogeneous analytes with the S-S bond concentrations ranging from 0.25 to 1 M at room temperature.



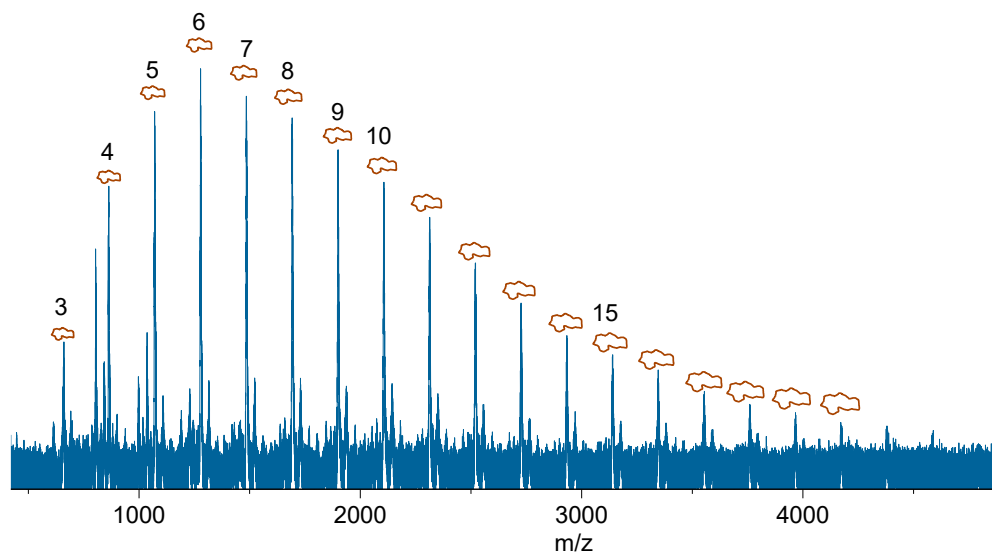
Supplementary Fig. 6. Polymerization degrees of three homogeneous anolytes with S-S bond concentrations ranging from 0.25 to 1 M. Based on the ^1H NMR spectra in Fig. 1c, the polymerization degrees (Dp) were determined according to the following equation:

$$Dp = A_{2.8}/3 / (A_{2.8}/3 + A_m/2) \times 100\%$$

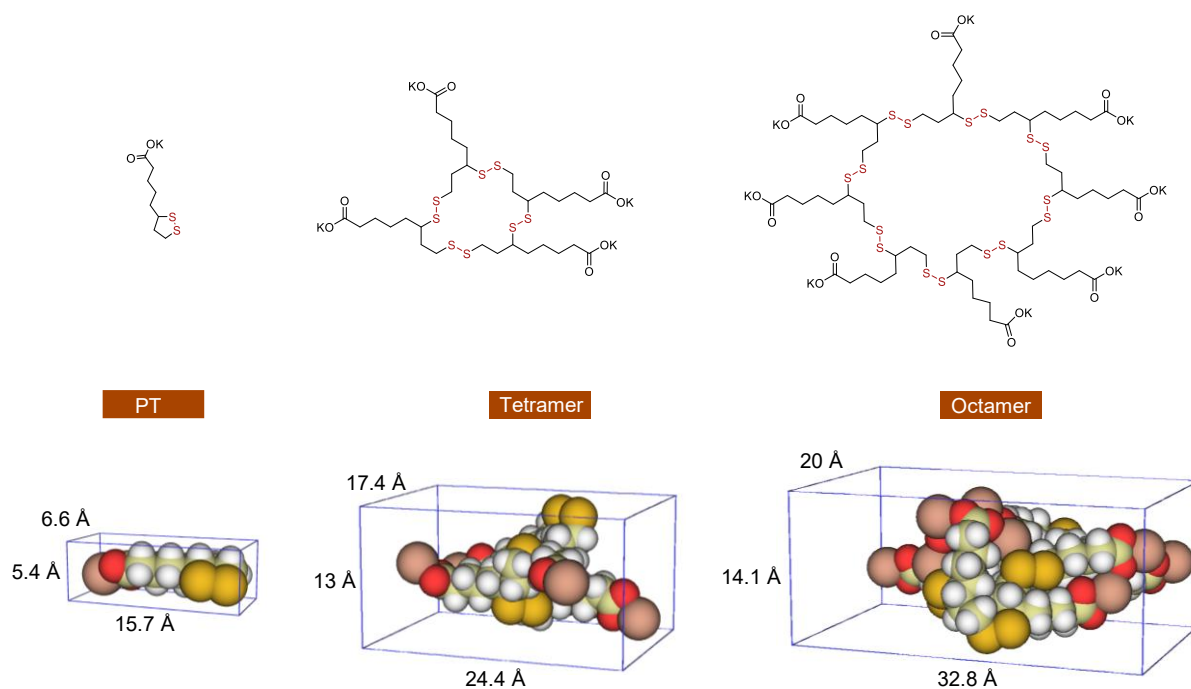
Where $A_{2.8}$ is the sum of the values of a' and c' ($\delta = 2.8$ ppm) in polymers, and A_m is the peak area value of a ($\delta = 3.1\text{-}3.2$ ppm) in PT monomers.



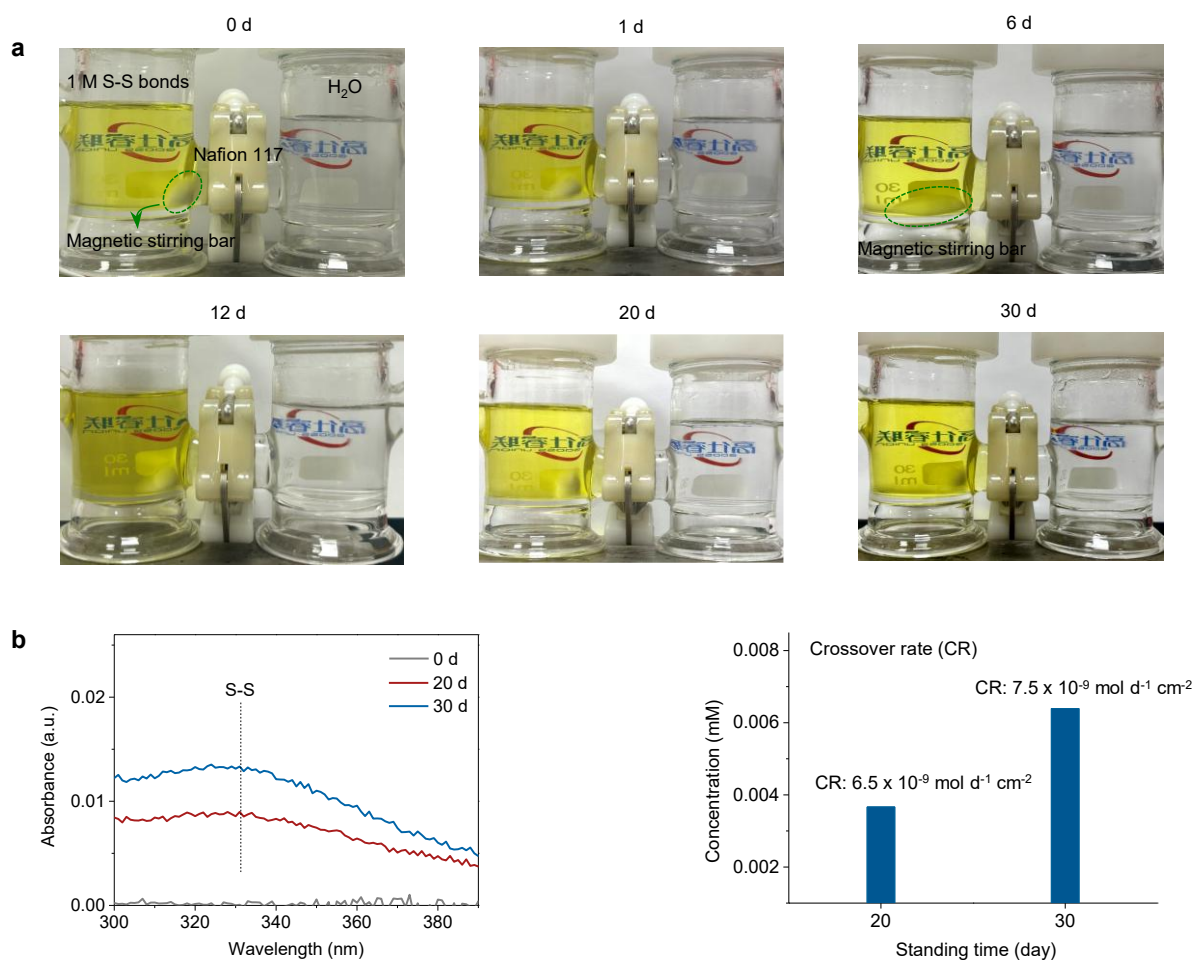
Supplementary Fig. 7. Raman spectra of three homogeneous analytes with S-S bond concentrations ranging from 0.25 to 1 M. The peak of S-S bonds splits into two, confirming the formation of intermolecular S-S bonds.



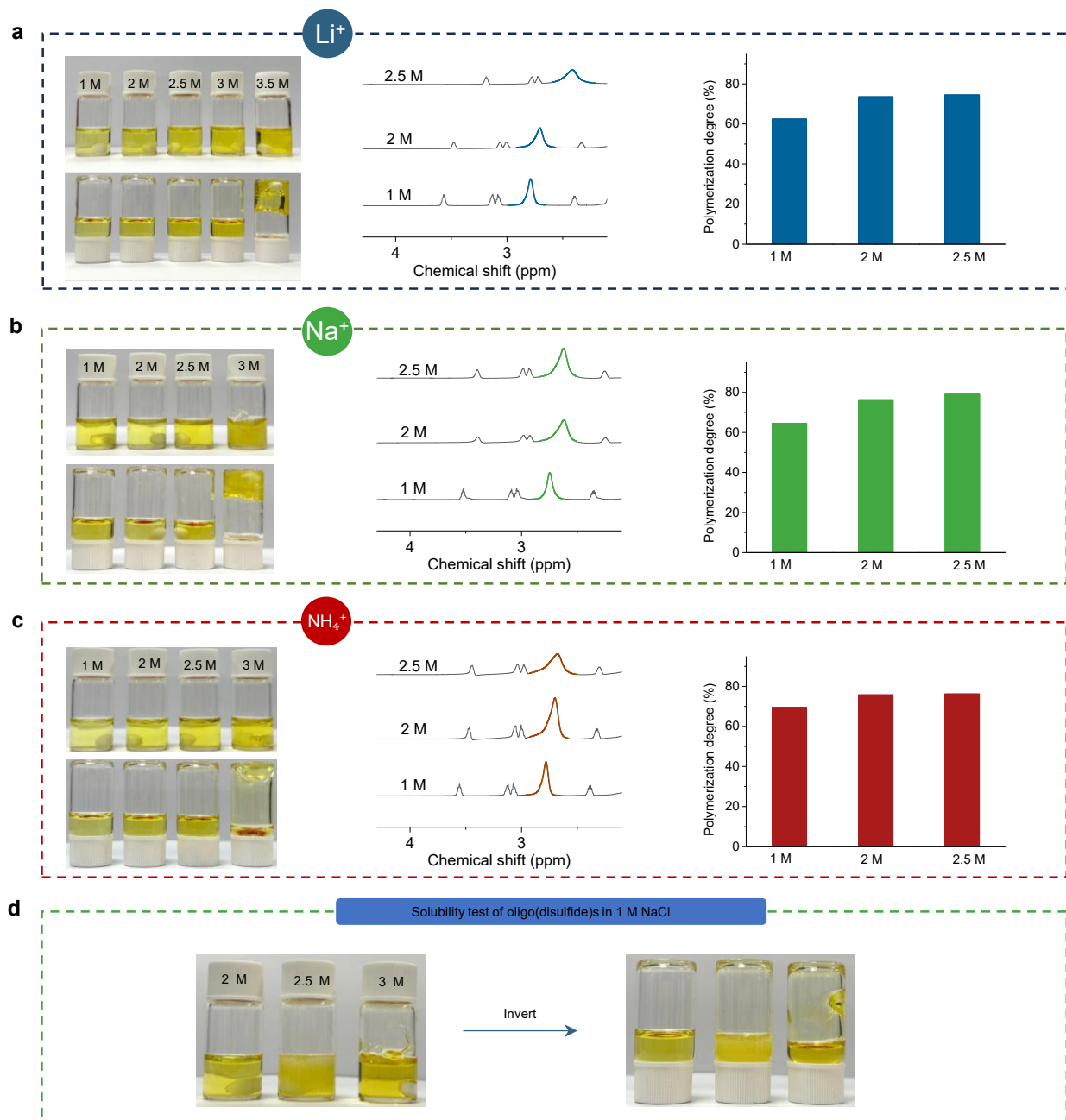
Supplementary Fig. 8. MALDI-TOF-MS spectrum of an analyte with 0.25 M S-S bonds.



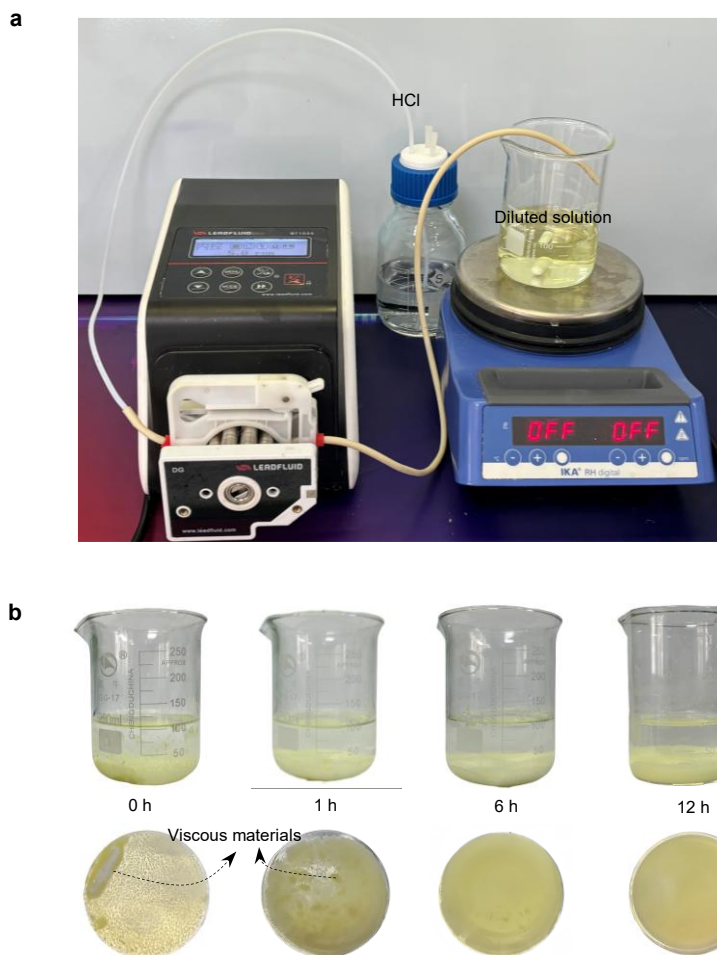
Supplementary Fig. 9. Molecular structures and theoretical molecular sizes of PT, tetramer, and octamer. Light yellow, white, golden yellow, red, and brown represent C, H, S, O, and K atoms, respectively.



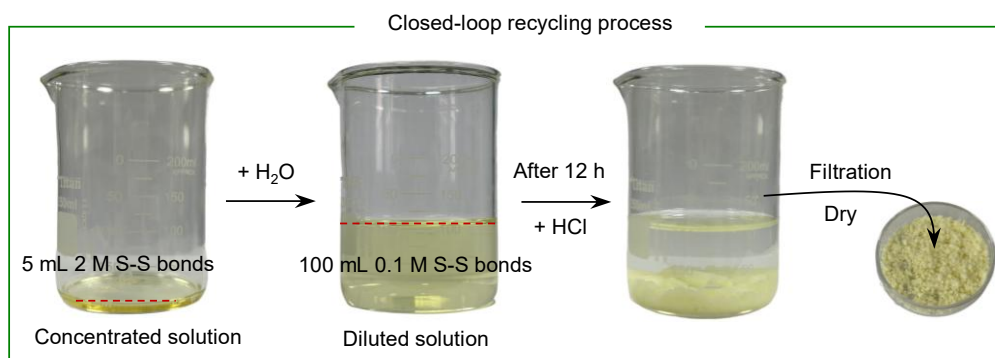
Supplementary Fig. 10. (a) Static diffusion of an oligo(disulfide)s-based anolyte with 1 M S-S bonds through Nafion 117 membrane in a two-compartment cell. 40 mL of 1 M S-S bonds on the left side, while the opposite is 40 mL of water. Continuous magnetic stirring (600 rpm) was applied to the left side. UV-vis spectroscopy measurements were performed on the water side at different times. 3 mL of the solution was withdrawn for UV-vis characterization each time, followed immediately by the addition of the same volume of water. The S-S bond exhibits a characteristic absorption peak at approximately 330 nm. **(b)** UV-vis spectroscopy analysis on the pure water side at different standing days and the corresponding concentration of S-S bonds and crossover rate.



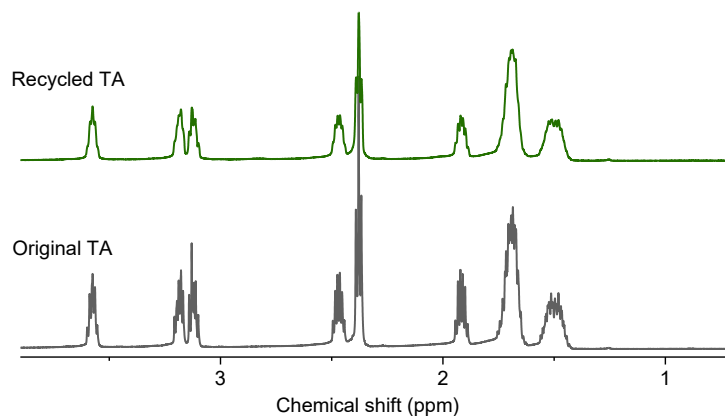
Supplementary Fig. 11. (a) Photographs of mixing TA with an equivalent amount of LiOH in H_2O , and the corresponding ^1H NMR spectra and polymerization degrees. (b) Photographs of mixing TA with an equivalent amount of NaOH in H_2O , and the corresponding ^1H NMR spectra and polymerization degrees. (c) Photographs of mixing TA with an equivalent amount of $\text{NH}_3\cdot\text{H}_2\text{O}$ in H_2O , and the corresponding ^1H NMR spectra and polymerization degrees. (d) Solubility test of oligo(disulfide)s in 1 M NaCl. This results in a solubility of up to 2.5 M in 1 M NaCl.



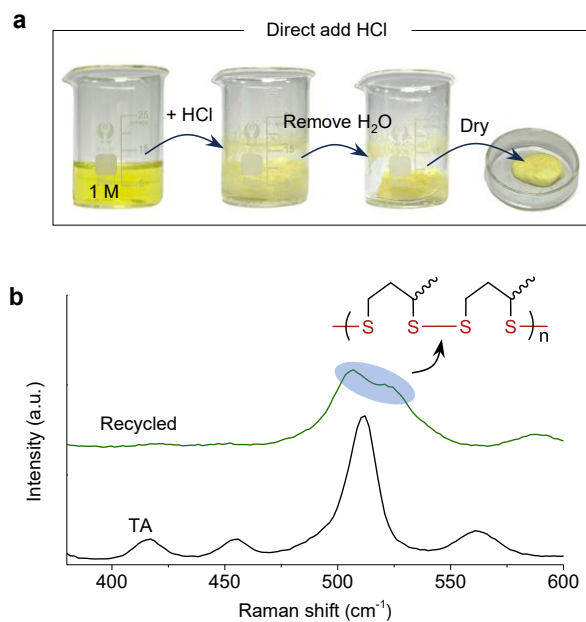
Supplementary Fig. 12. (a) Photograph of the recycling device. 1.0 M HCl solution was pumped at a constant speed of 5 rpm via a peristaltic pump into the diluted solution (0.1 M S-S bonds) under continuous magnetic stirring at 500 rpm. (b) Photographs of four acidified solutions with various resting times from 0 to 12 h (solutions were diluted from a solution with 2 M S-S bonds). No viscous materials are observed in the recycled product after 12 h of resting, followed by acidification.



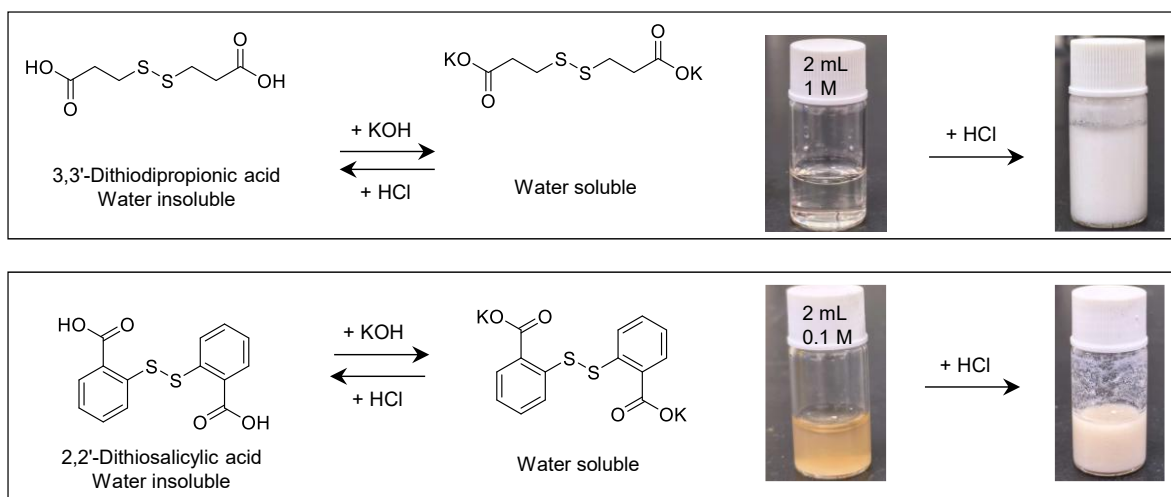
Supplementary Fig. 13. Photographs of a closed-loop recycling process.



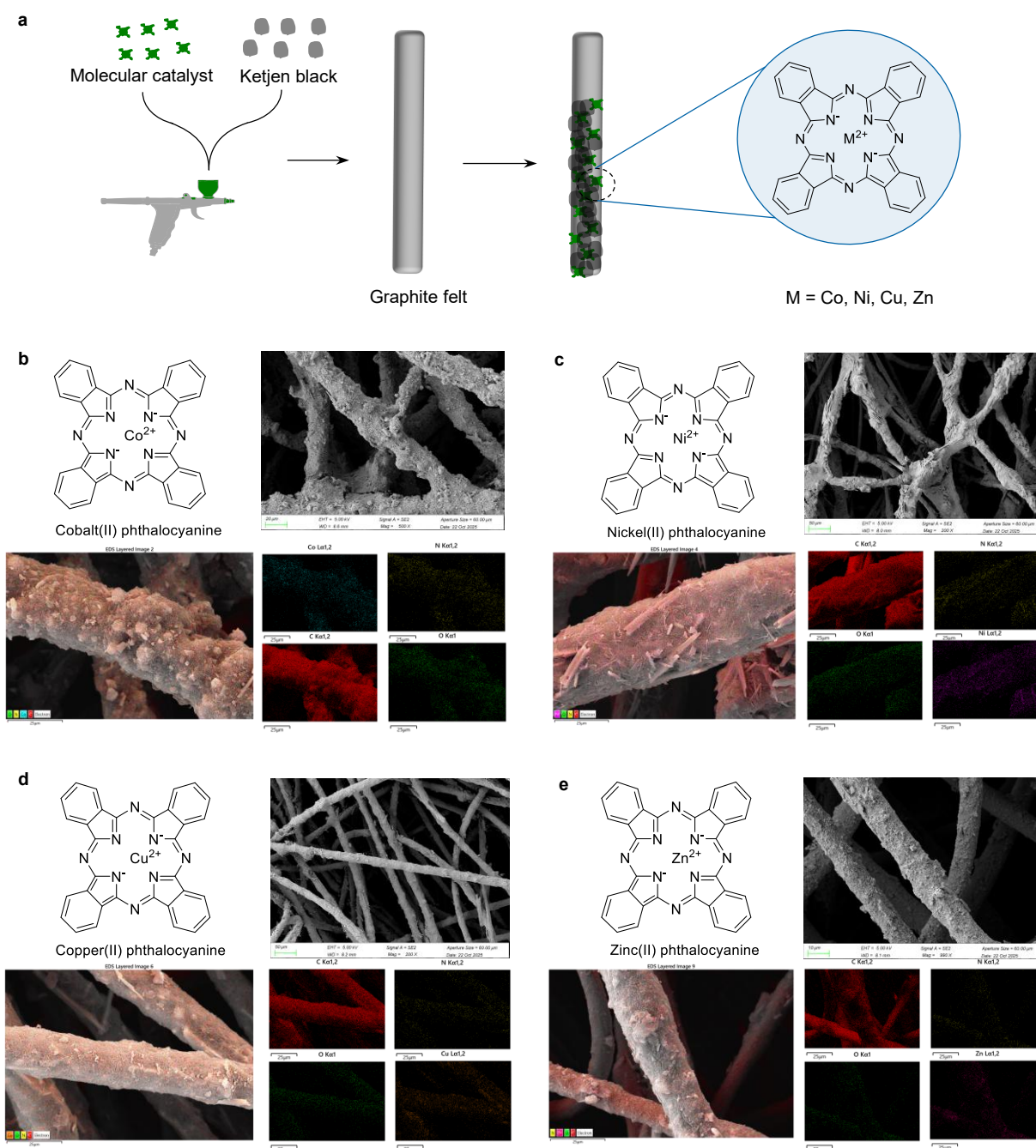
Supplementary Fig. 14. ¹H NMR spectra of the recycled TA and original TA (600 MHz, CDCl₃). The NMR peaks of the recycled TA remain consistent with those of the original TA, confirming the transformation from oligo(disulfide)s to monomers.



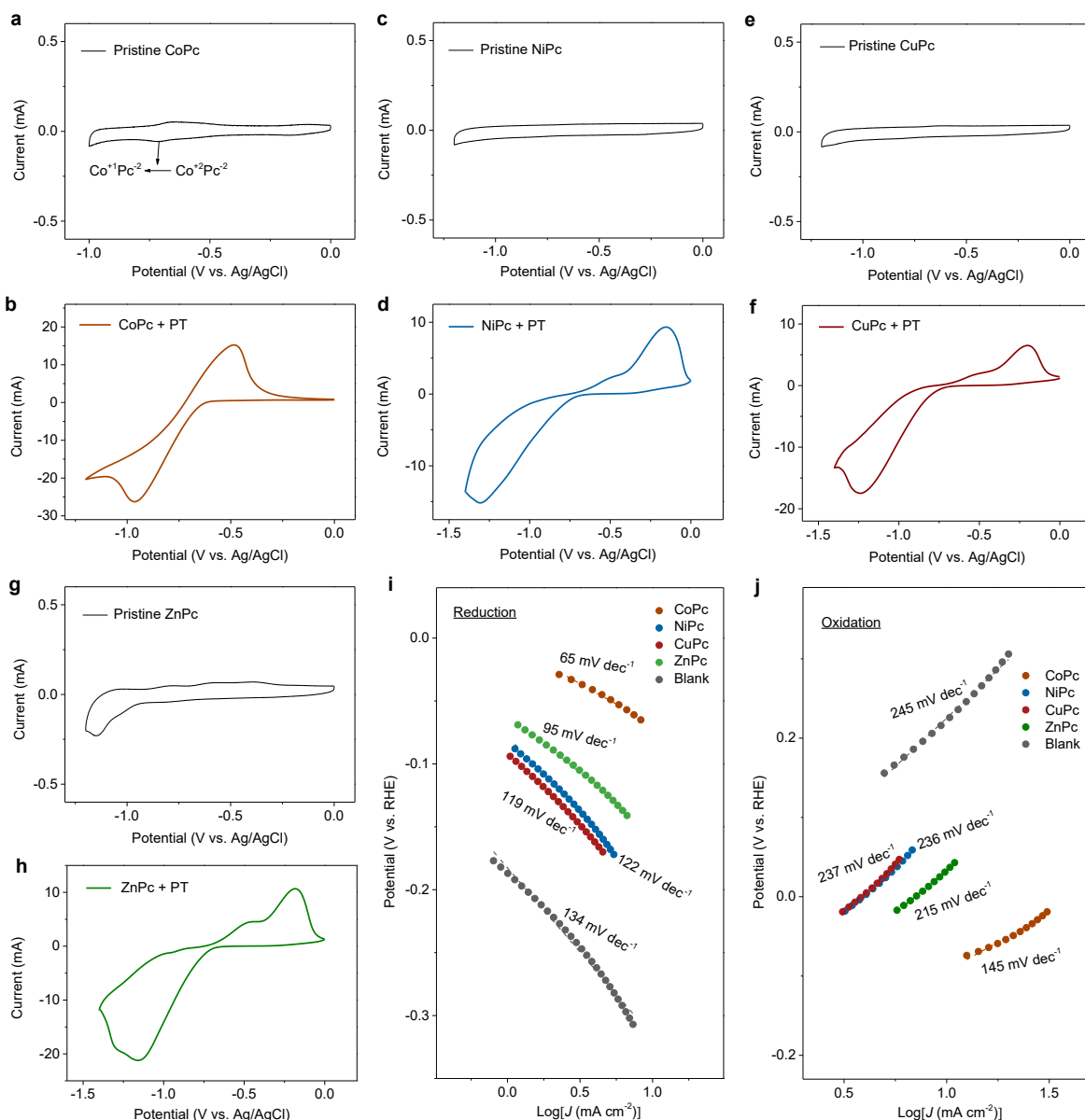
Supplementary Fig. 15. (a) Photographs of a recycling process in the absence of dilution (the solution contains 1 M S-S bonds). Viscous materials were obtained after recycling. (b) Raman spectra of the recycled TA and original TA. The S-S bond peak splits into two, confirming that the recycled materials are polymers.



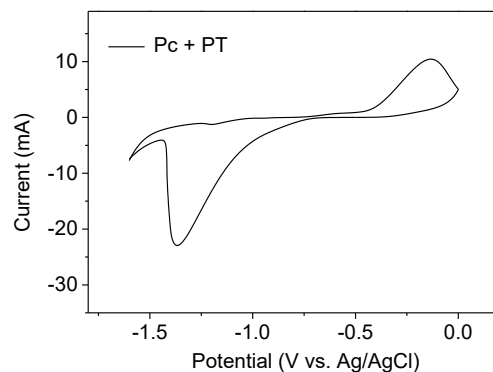
Supplementary Fig. 16. Recycling processes of the other two disulfides with carboxyl groups.



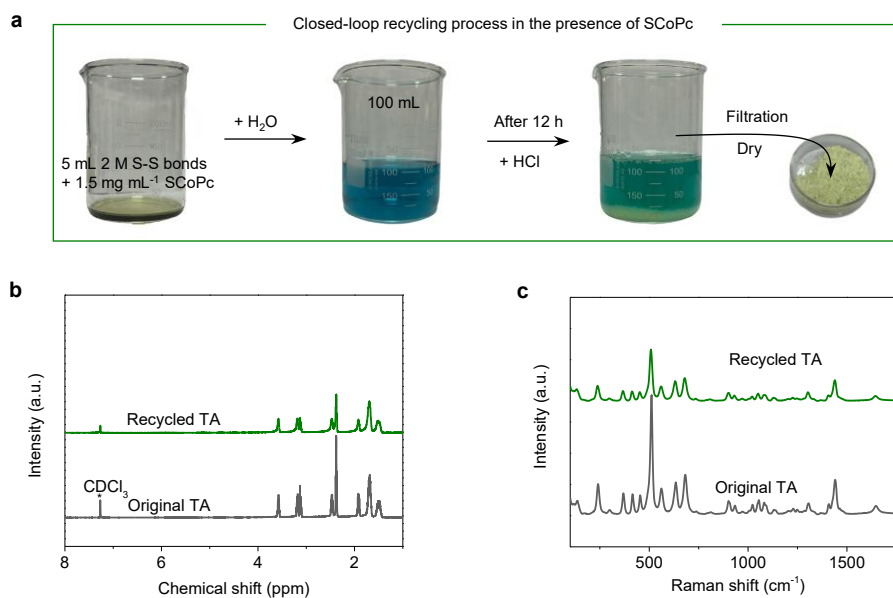
Supplementary Fig. 17. (a) Schematic diagram of the preparation of MPc (M = Co, Ni, Cu, and Zn) modified graphite felts. (b-e) Scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) elemental mapping images of MPc-modified graphite felts. The SEM characterization demonstrates that MPc are uniformly dispersed on graphite felts with an aggregated morphology. Corresponding EDS elemental mapping verifies the presence of metal elements originating from the MPC. The morphological and compositional results confirm the formation of these MPC-modified graphite felts.



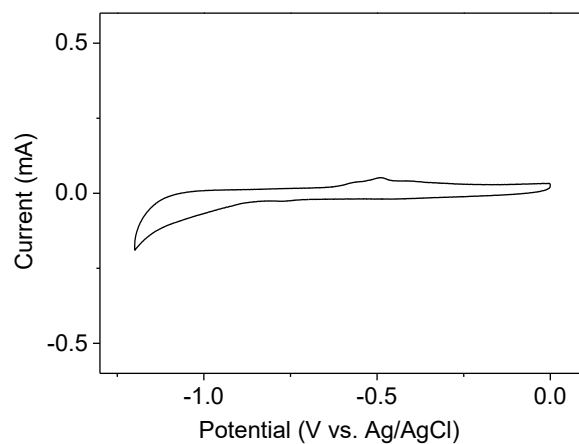
Supplementary Fig. 18. (a-h) Cyclic voltammograms of an anolyte with 0.25 M S-S bonds, using MPc modified-graphite felts (0.25 cm^2) as the working electrodes at a scan rate of 5 mV s^{-1} (supporting electrolyte: 1 M KCl), with platinum (Pt) as the counter electrode, and an Ag/AgCl as the reference electrode (cyclic voltammograms of various metal phthalocyanines were obtained via testing MPc modified-graphite felts in 1 M KCl solution). (i-j) The corresponding Tafel plots. The potential differences between the anodic and cathodic peaks of the tested anolyte in the presence of CoPc, NiPc, CuPc, and ZnPc are 0.48 V, 1.15 V, 1.04 V, and 0.98 V, respectively. In sharp contrast to NiPc, CuPc, and ZnPc, CoPc delivers the lowest Tafel slopes in both the reductive and oxidative directions, with values of 65 and 145 mV dec^{-1} . These results evidence that CoPc shows superior catalytic ability for the rapid electrochemical cleavage and formation of S-S bonds.



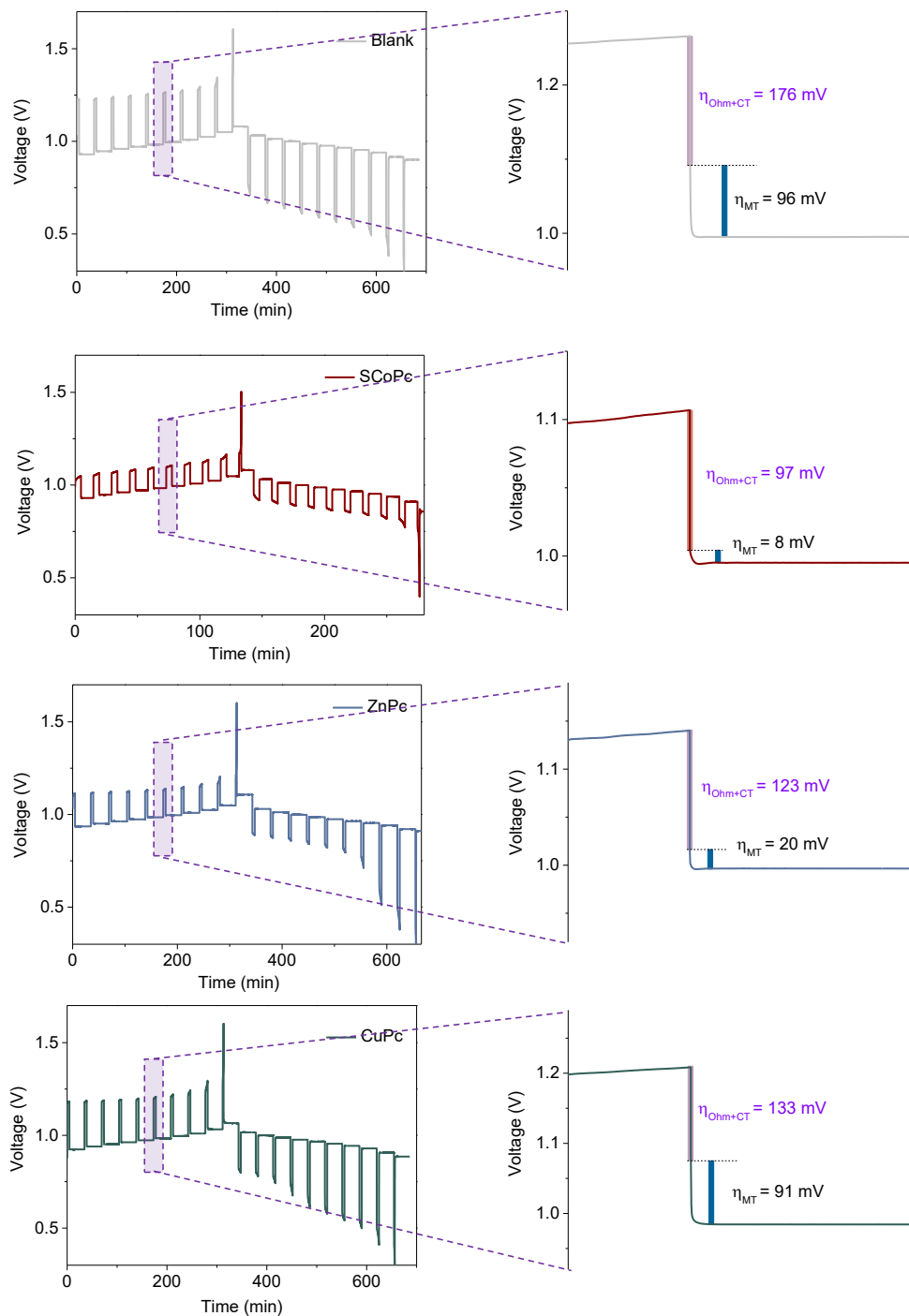
Supplementary Fig. 19. Cyclic voltammogram of an anolyte with 0.25 M S-S bonds, using a pristine phthalocyanine (Pc)-modified graphite felt (0.25 cm^2) as the working electrode at a scan rate of 5 mV s^{-1} (supporting electrolyte: 1 M KCl), with platinum (Pt) as the counter electrode, and an Ag/AgCl as the reference electrode.



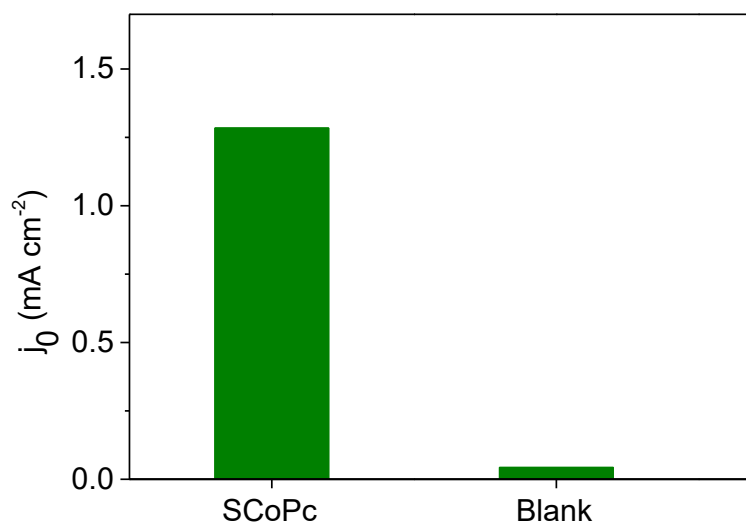
Supplementary Fig. 20. (a) Photographs of a recycling process in the presence of SCoPc. (b) ¹H NMR spectra and (c) Raman spectra of the recycled product, showing no polymers and confirming that the SCoPc does not affect the recycling process of TA monomers from oligo(disulfide)s-based analytes.



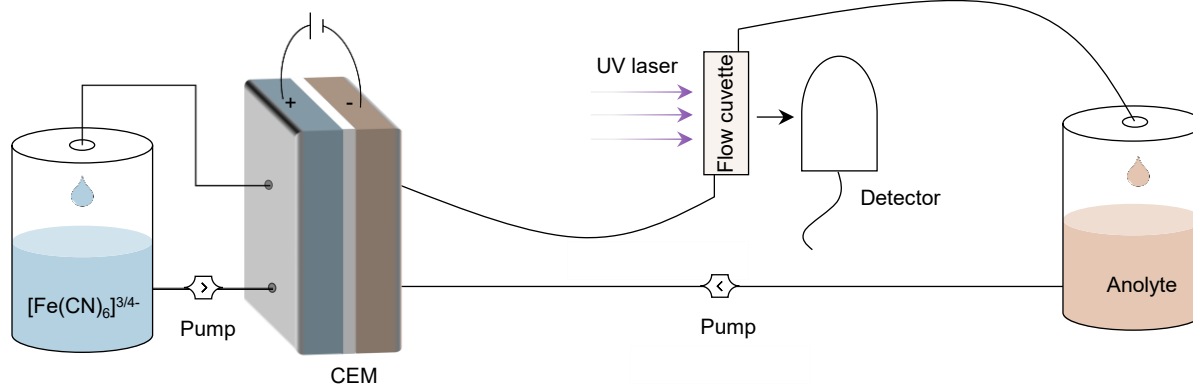
Supplementary Fig. 21. Cyclic voltammogram of pristine SCoPc (1.5 mg mL^{-1}), using a graphite felt (0.25 cm^2) as the working electrode at a scan rate of 5 mV s^{-1} (supporting electrolyte: 1 M KCl), with platinum (Pt) as the counter electrode, and an Ag/AgCl as the reference electrode.



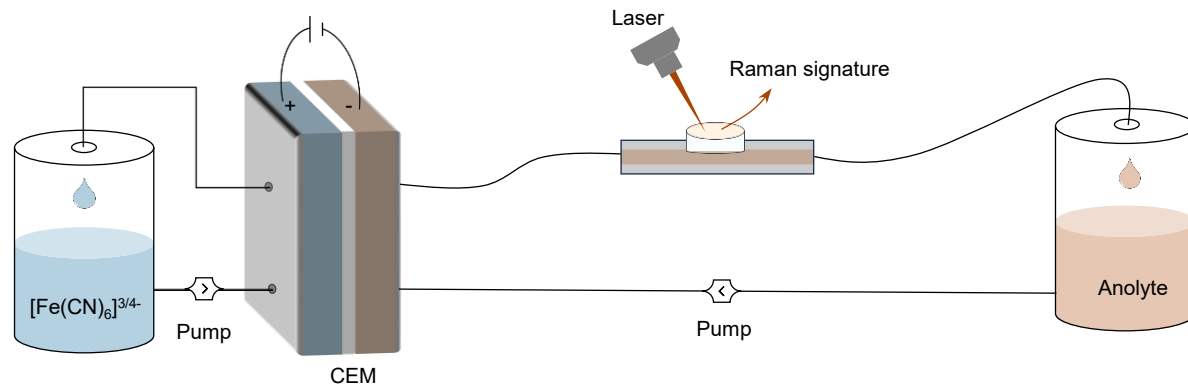
Supplementary Fig. 22. Galvanostatic intermittent titration technique analysis results. η_{MT} : mass transportation overpotential; η_{CT} : charge-transfer overpotential; η_{Ohm} : ohmic overpotential. These flow cells consisted of 10 mL of 0.25 M S-S bonds as the anolyte (supporting electrolyte: 1 M KCl) and 33 mL of 0.3 M $\text{K}_4[\text{Fe}(\text{CN})_6]$ as the catholyte (supporting electrolyte: 1 M KCl), separated by a Nafion 117 membrane. Both electrolytes flowed at approximately 15 mL min^{-1} through a peristaltic pump.



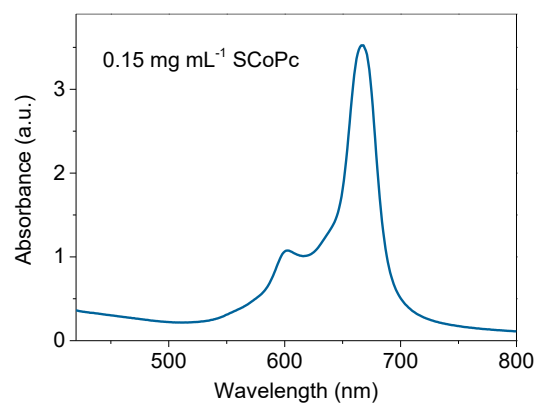
Supplementary Fig. 23. Exchange current density results of carbon felt in the reduction of S-S bonds with and without 1.5 mg mL^{-1} SCoPc.



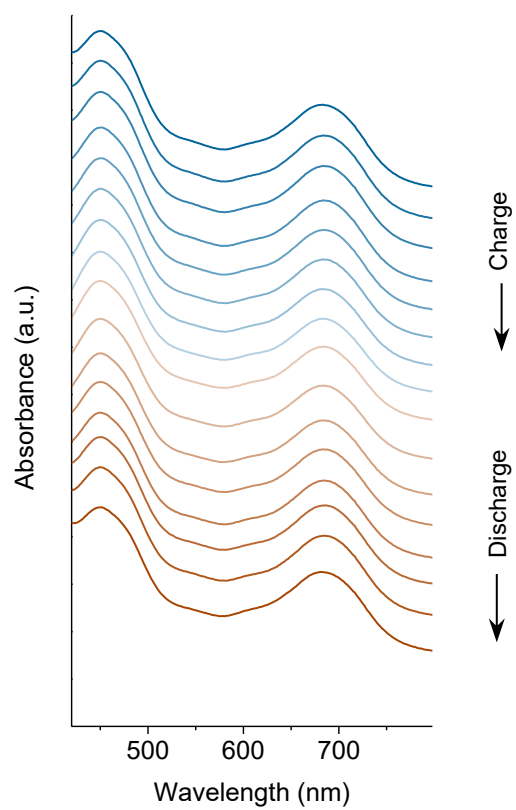
Supplementary Fig. 24. Diagram of an *in situ* UV-vis spectroscopy measurement device.



Supplementary Fig. 25. Diagram of an *in situ* Raman spectroscopy measurement device.



Supplementary Fig. 26. UV-vis spectrum of 0.15 mg mL⁻¹ SCoPc.



Supplementary Fig. 27. *In situ* UV-vis spectra of the anolyte side during the 2nd charge and discharge process.



Before cycling

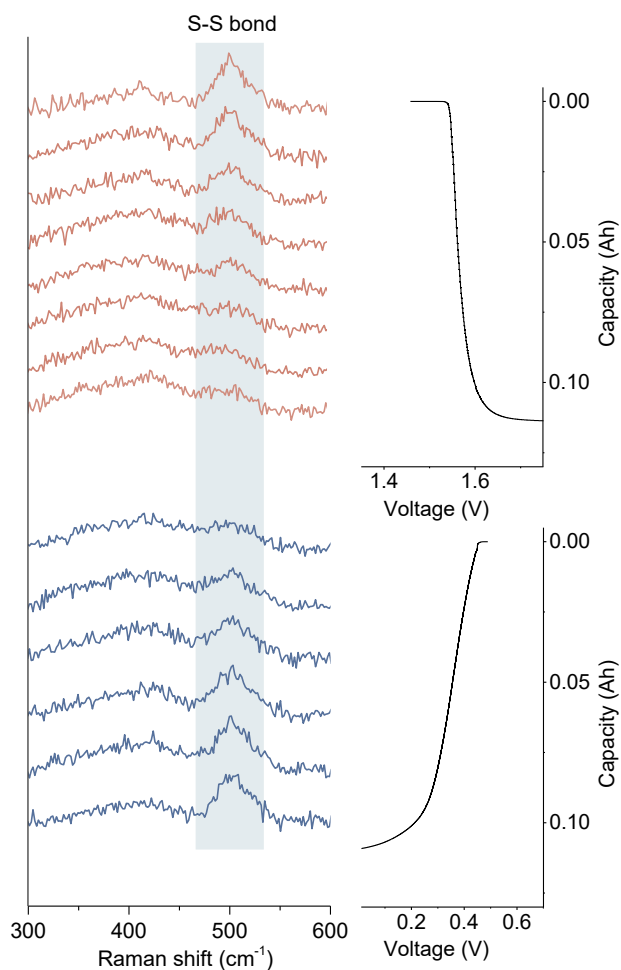


After charging

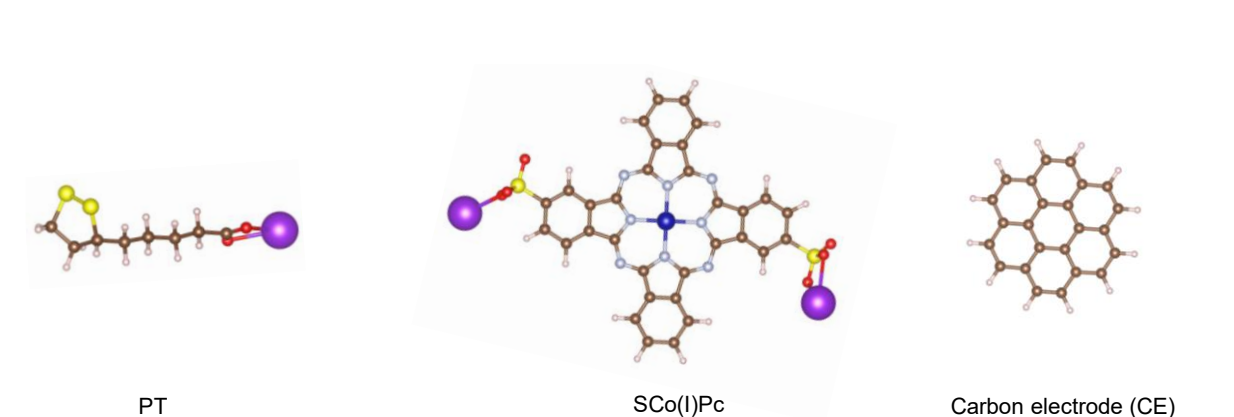


After discharging

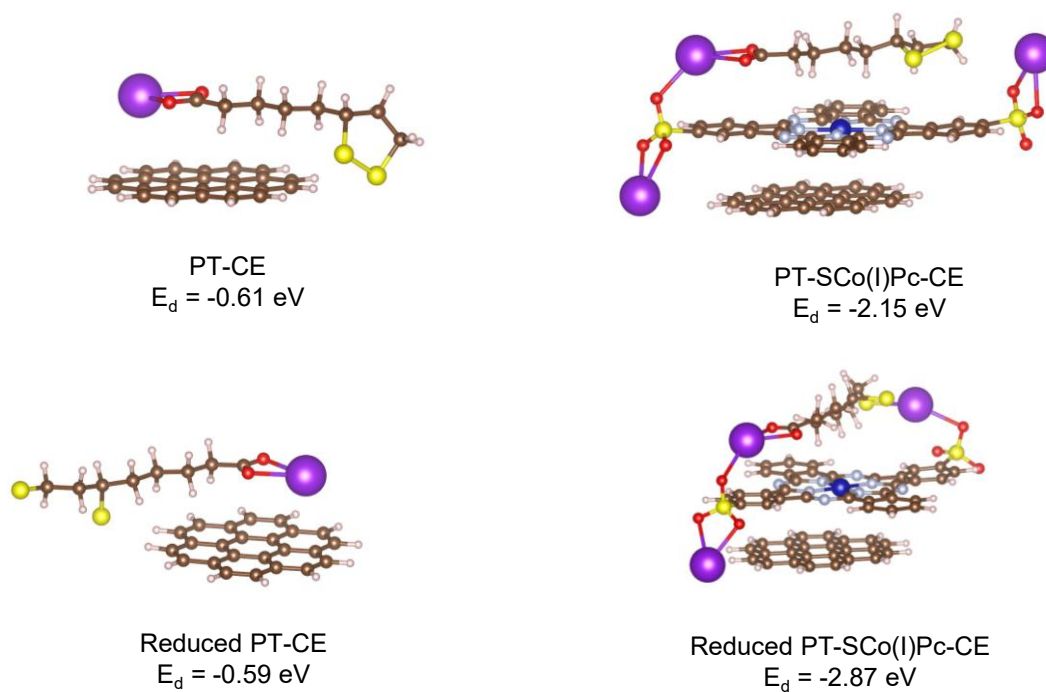
Supplementary Fig. 28. Photographs of an anolyte with 0.25 M S-S bonds and 3 mg mL⁻¹ SCoPc after charging or discharging. The color changes of the anolyte intuitively indicate the transformation from SCoPc to SCo(I)Pc; correspondingly, the anolyte appears blue with SCoPc, and becomes dark yellow after charging or discharging.



Supplementary Fig. 29. *In situ* Raman spectra of the anolyte with 0.25 M S-S bonds. The flow cell consisted of 10 mL of 0.25 M S-S bonds as the anolyte (supporting electrolyte: 1 M KCl) and 33 mL of 0.3 M $\text{K}_4[\text{Fe}(\text{CN})_6]$ as the catholyte (supporting electrolyte: 1 M KCl), with a Nafion 117 membrane. The flow rate of both electrolytes was approximately 15 mL min^{-1} through a peristaltic pump.



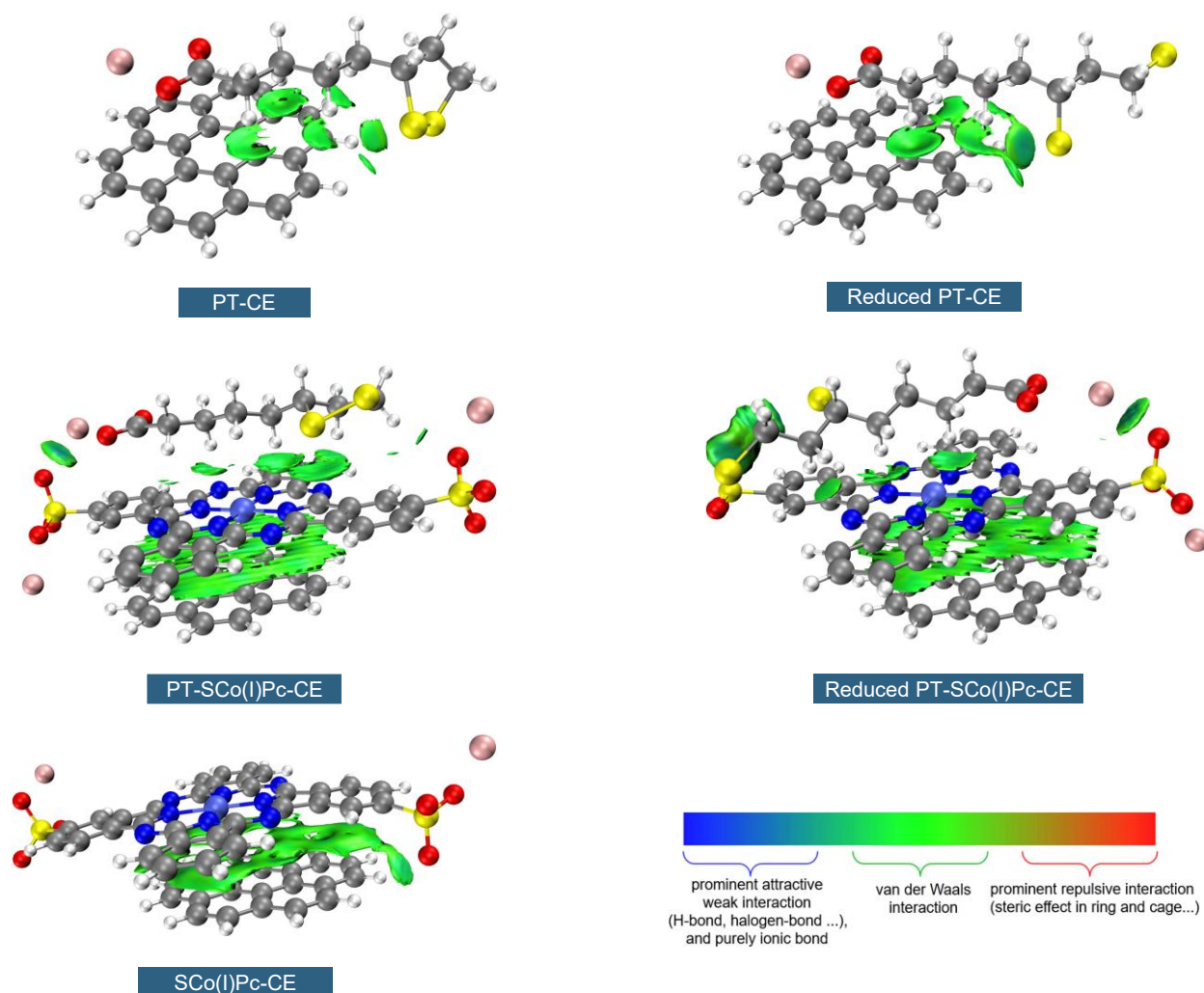
Supplementary Fig. 30. Molecular structures of PT, SCo(I)Pc, and the carbon electrode (CE) for density functional calculations. The density functional calculations for adsorption energy were completed with the PBE0¹ functional in combination with the D3BJ² dispersion correction as implemented in the Gaussian 16 software¹⁻³. The def2-SVP basis set and PCM solvent model were adopted for the geometry optimization and frequency calculations⁴⁻⁵. The geometries were fully optimized without any structural constraints. The final and solvation energies were calculated by employing the SMD continuum solvation model⁶ with the larger def2-TZVP basis set⁶.



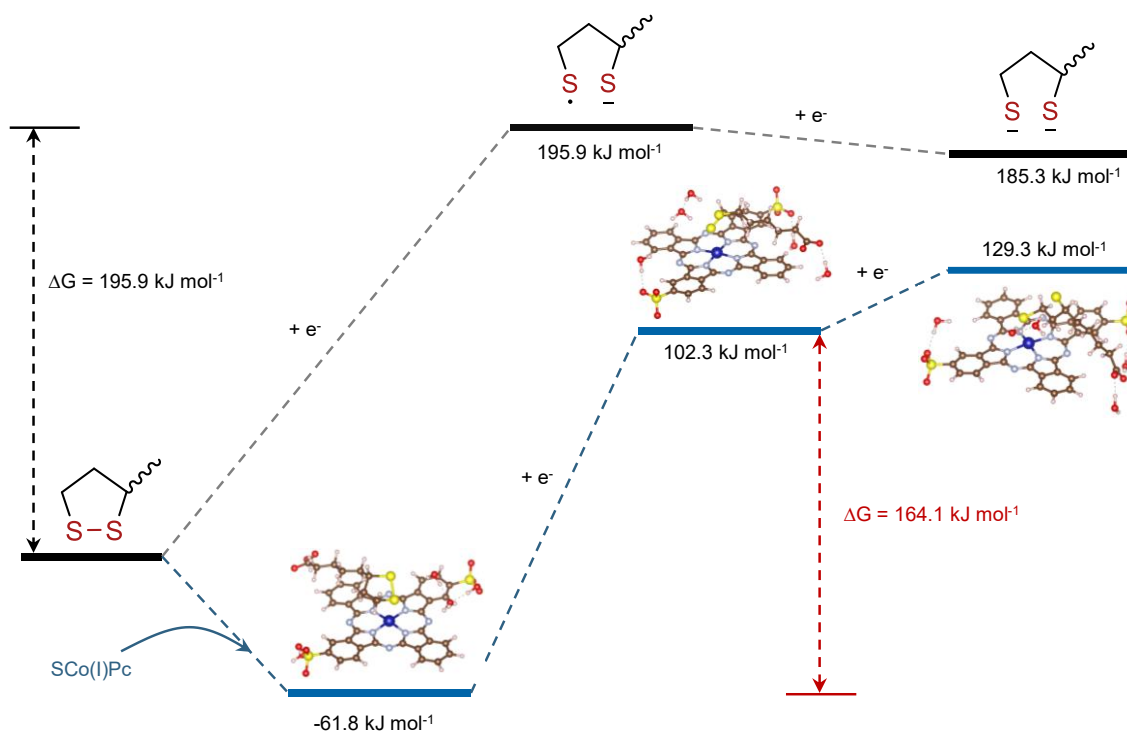
Supplementary Fig. 31. Adsorption energy (E_d) of PT and reduced PT on the carbon electrode (CE) with/without SCo(I)Pc. The E_d was calculated by the following equation:

$$E_d = E_{\text{Complex}} - (E_{M1} + E_{M2})$$

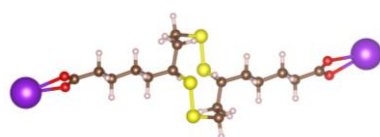
where E_{Complex} , E_{M1} , and E_{M2} represent the energies of the complex and the energies of the interacting molecules, respectively.



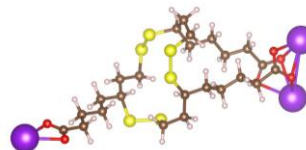
Supplementary Fig. 32. Visualization of weak interactions between active materials and carbon electrode with/without SCo(I)Pc. The red plate represents repulsive interactions, the blue plate represents electrostatic interactions, and the green plate represents dispersion attraction (mainly van der Waals interactions).



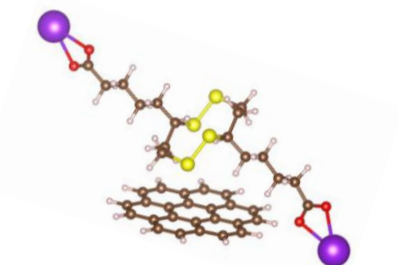
Supplementary Fig. 33. Gibbs free energy (kJ mol⁻¹, 298.15K) changes for the electroconversion of PT with and without SCo(I)Pc.



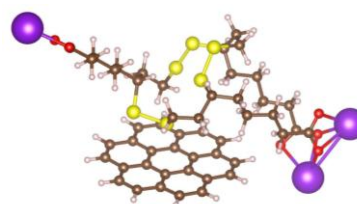
Dimer



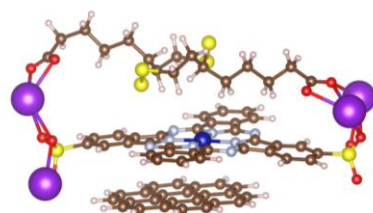
Trimer



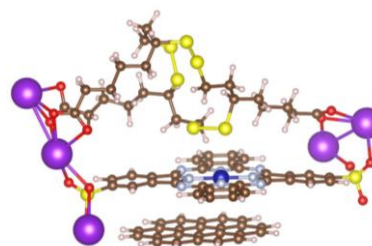
Dimer-CE
 $E_d = -0.54$ eV



Trimer-CE
 $E_d = -0.59$ eV

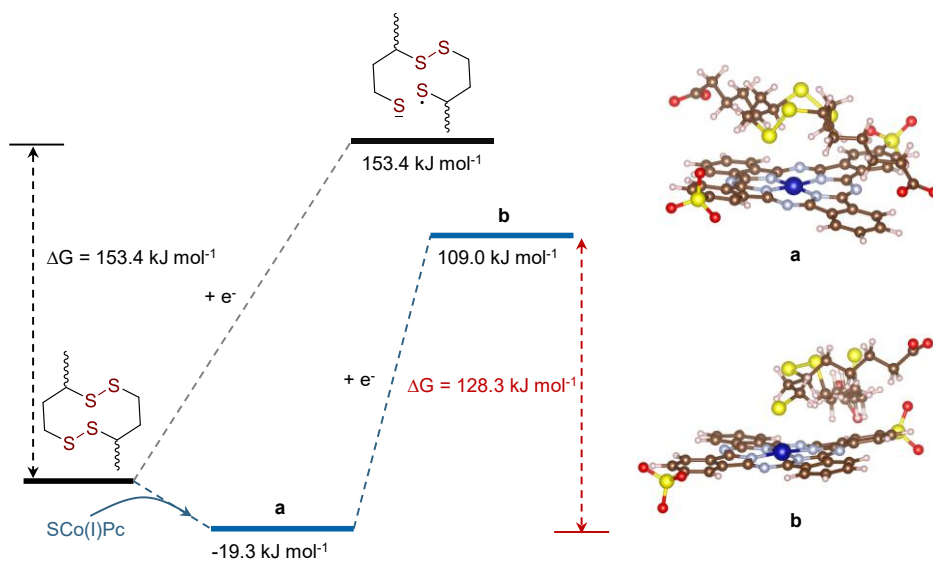


Dimer-SCo(I)Pc-CE
 $E_d = -2.92$ eV

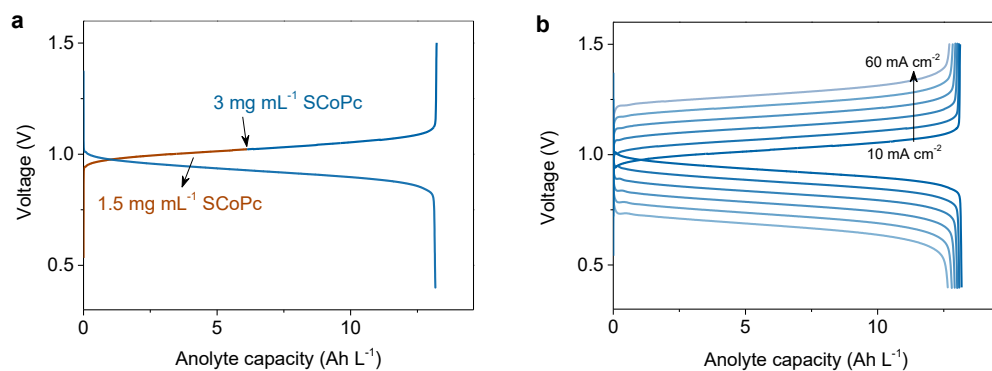


Trimer-SCo(I)Pc-CE
 $E_d = -2.73$ eV

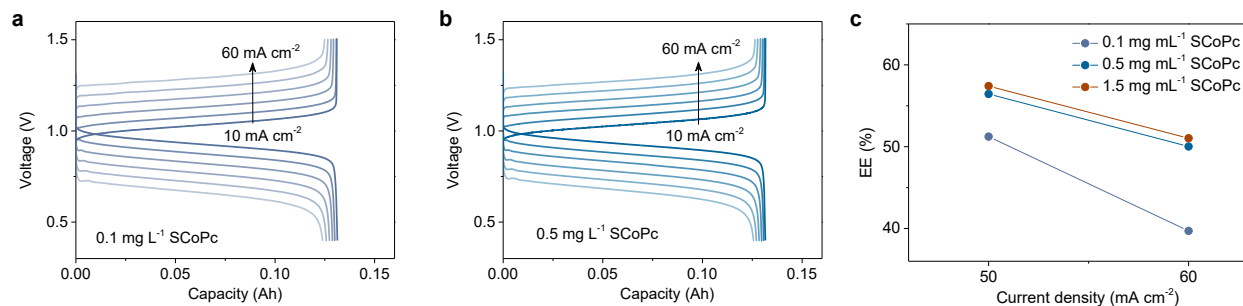
Supplementary Fig. 34. Molecular structures of dimer and trimer for DFT calculations, and the corresponding adsorption energy (E_d) of dimer and trimer on the carbon electrode (CE) with and without SCo(I)Pc.



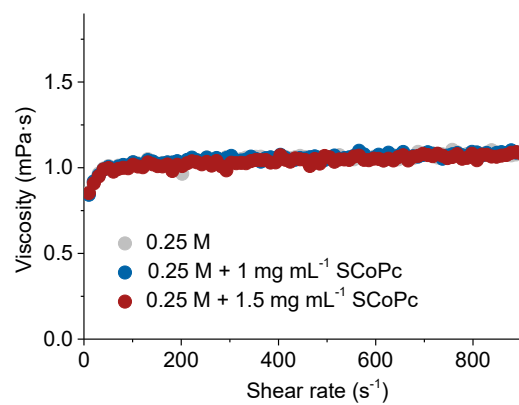
Supplementary Fig. 35. Gibbs free energy (kJ mol^{-1} , 298.15K) changes for the electroconversion of dimer with and without SCo(I)Pc.



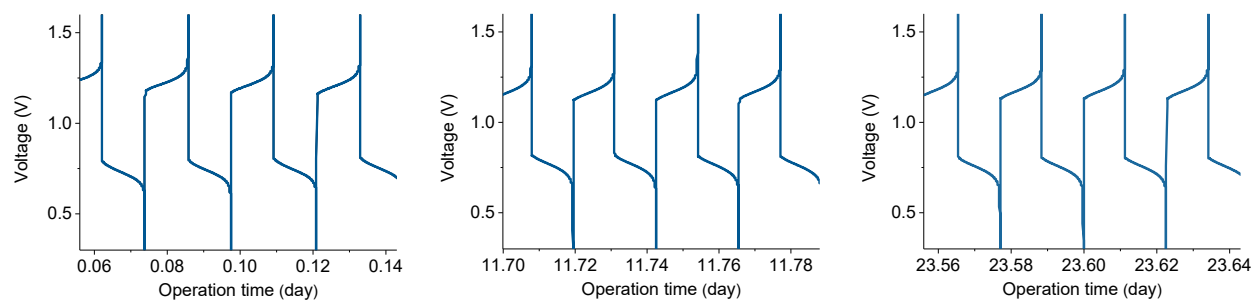
Supplementary Fig. 36. (a) Voltage profile of an oligo(disulfide)s-based RFB after increasing the SCoPc concentration to 3 mg mL⁻¹ at 10 mA cm⁻². (b) Voltage profiles of an oligo(disulfide)s-based RFB with 3 mg mL⁻¹ SCoPc at various current densities ranging from 10 to 60 mA cm⁻². Detailed RFB assembly parameters are given in Supplementary Table 1.



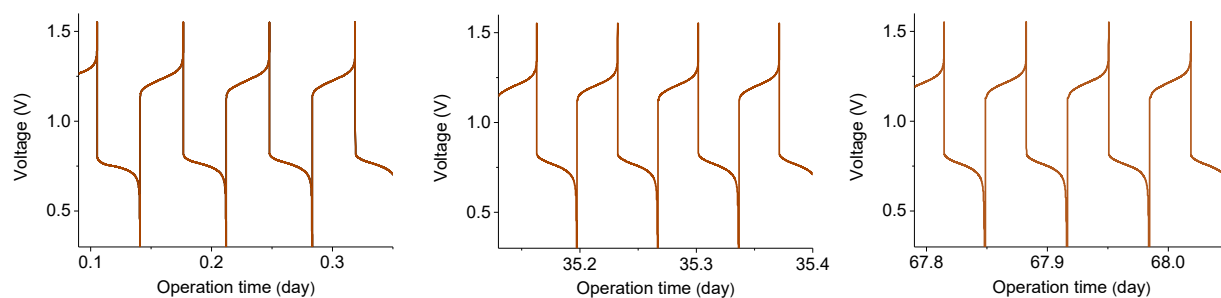
Supplementary Fig. 37. Voltage profiles of an oligo(disulfide)s-based RFB with 0.1 (a) and 0.5 mg mL⁻¹ (b) SCoPc at current densities varied from 10 to 60 mA cm⁻². c, EE vs. current density of oligo(disulfide)s-based RFBs with various SCoPc. Detailed RFB assembly parameters are given in Supplementary Table 1.



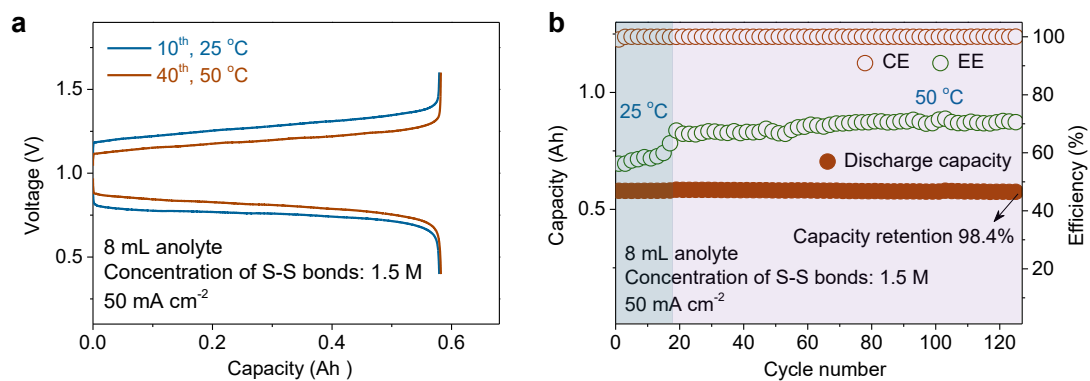
Supplementary Fig. 38. Viscosity analysis of an oligo(disulfide)s-based anolyte with 1 and 1.5 mg mL⁻¹ SCoPc.



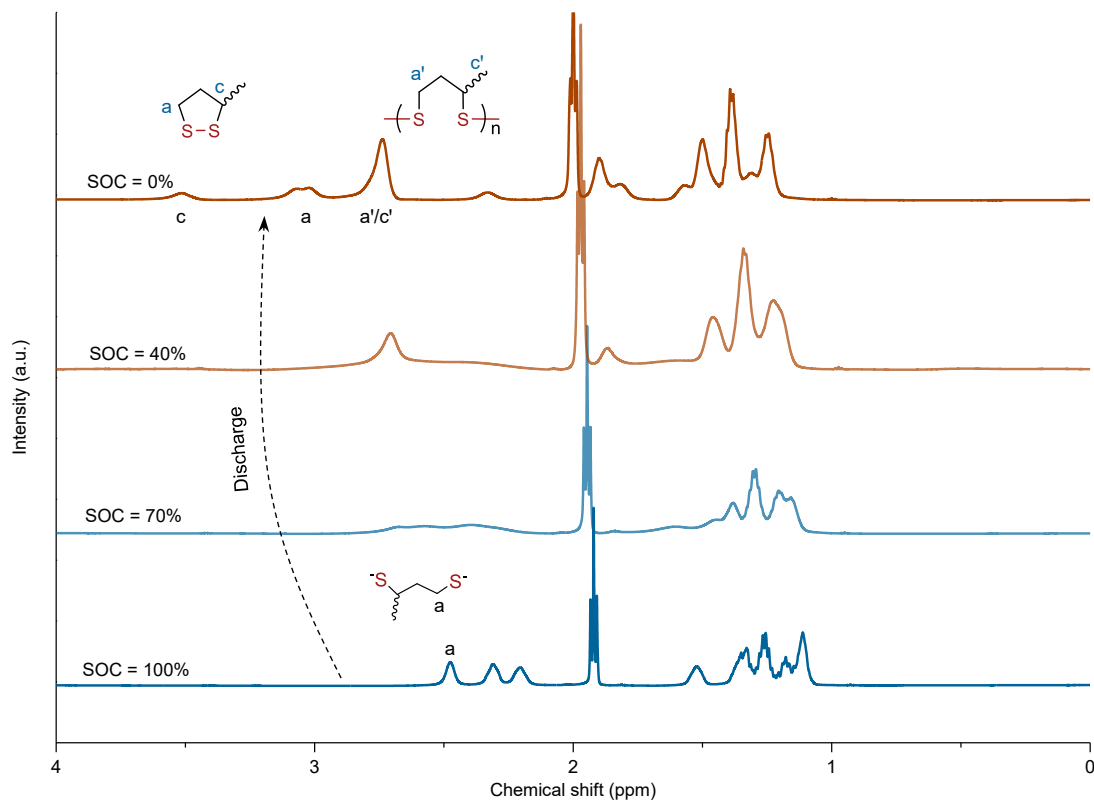
Supplementary Fig. 39. Voltage profiles of an oligo(disulfide)s-based RFB with 0.25 M S-S bonds at various cycling stages. Cycling performance is shown in Fig. 3d. Detailed RFB assembly parameters are given in Supplementary Table 1.



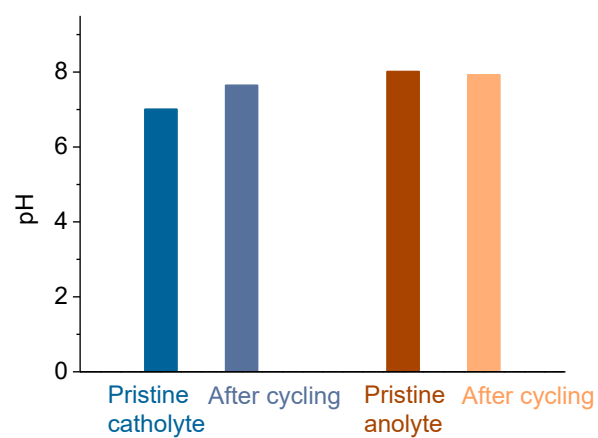
Supplementary Fig. 40. Voltage profiles of an oligo(disulfide)s-based RFB with 1 M S-S bonds at various cycling stages. Cycling performance is shown in Fig. 3e. Detailed RFB assembly parameters are given in Supplementary Table 1.



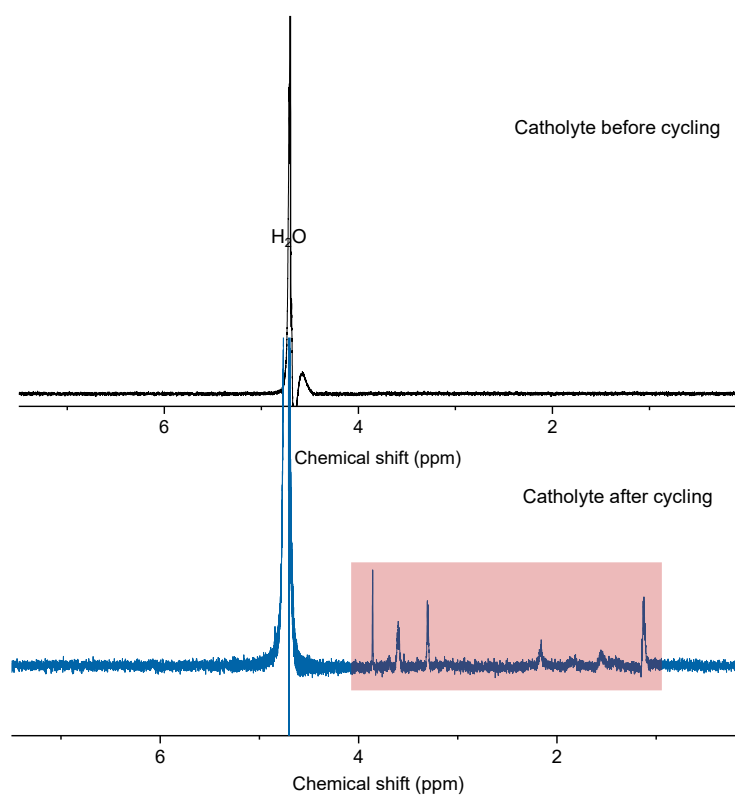
Supplementary Fig. 41. Electrochemical performance of the oligo(disulfide)s RFB with an S-S concentration of 1.5 M at 50 °C. The capacity retention is calculated as the ratio of the discharge capacity in the last cycle at 50 °C to the discharge capacity in the first cycle at 50 °C.



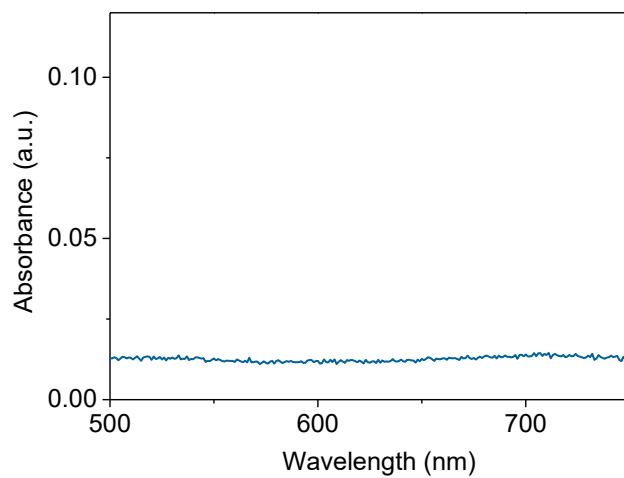
Supplementary Fig. 42. ^1H NMR spectra of an analyte with 1 M S-S bonds (without catalyst) at different discharge states, showing the reversible electrochemical conversion from the reduced PT to oligo(disulfide)s.



Supplementary Fig. 43. pH values of the catholyte and anolyte before and after 1000 cycles. The corresponding battery performance is shown in Fig. 3e.



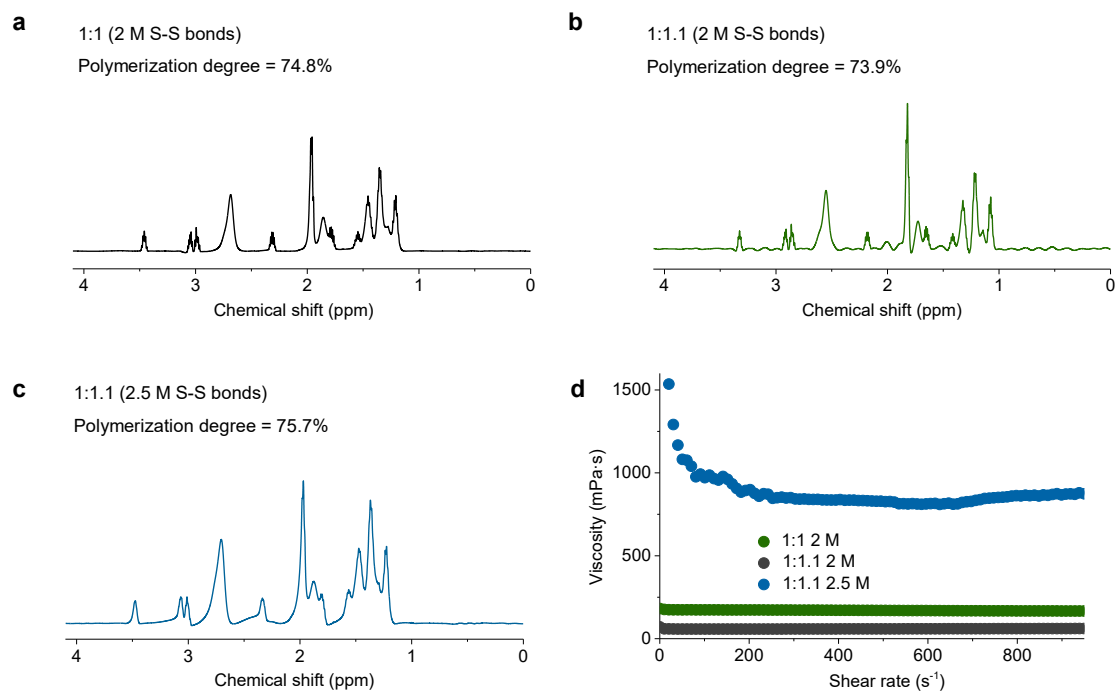
Supplementary Fig. 44. ^1H NMR spectra of the catholyte before and after over 1000 cycles (600 MHz, D_2O). The corresponding battery performance is shown in Fig. 3e. The observed peaks in the catholyte are attributed to organics, confirming the material crossover issue during battery cycling.



Supplementary Fig. 45. UV-vis spectra of the catholyte after over 1000 cycles. The corresponding battery performance is shown in Fig. 3e.



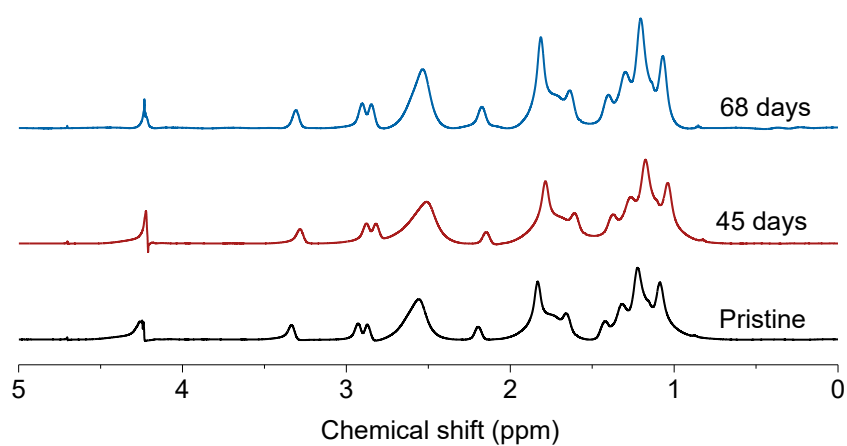
Supplementary Fig. 46. (a) Photographs of mixing TA with an equivalent amount of KOH. This results in a solubility of up to 2 M. (b) Photographs of mixing TA with an excess amount of KOH. This results in a solubility of up to 2.5 M.



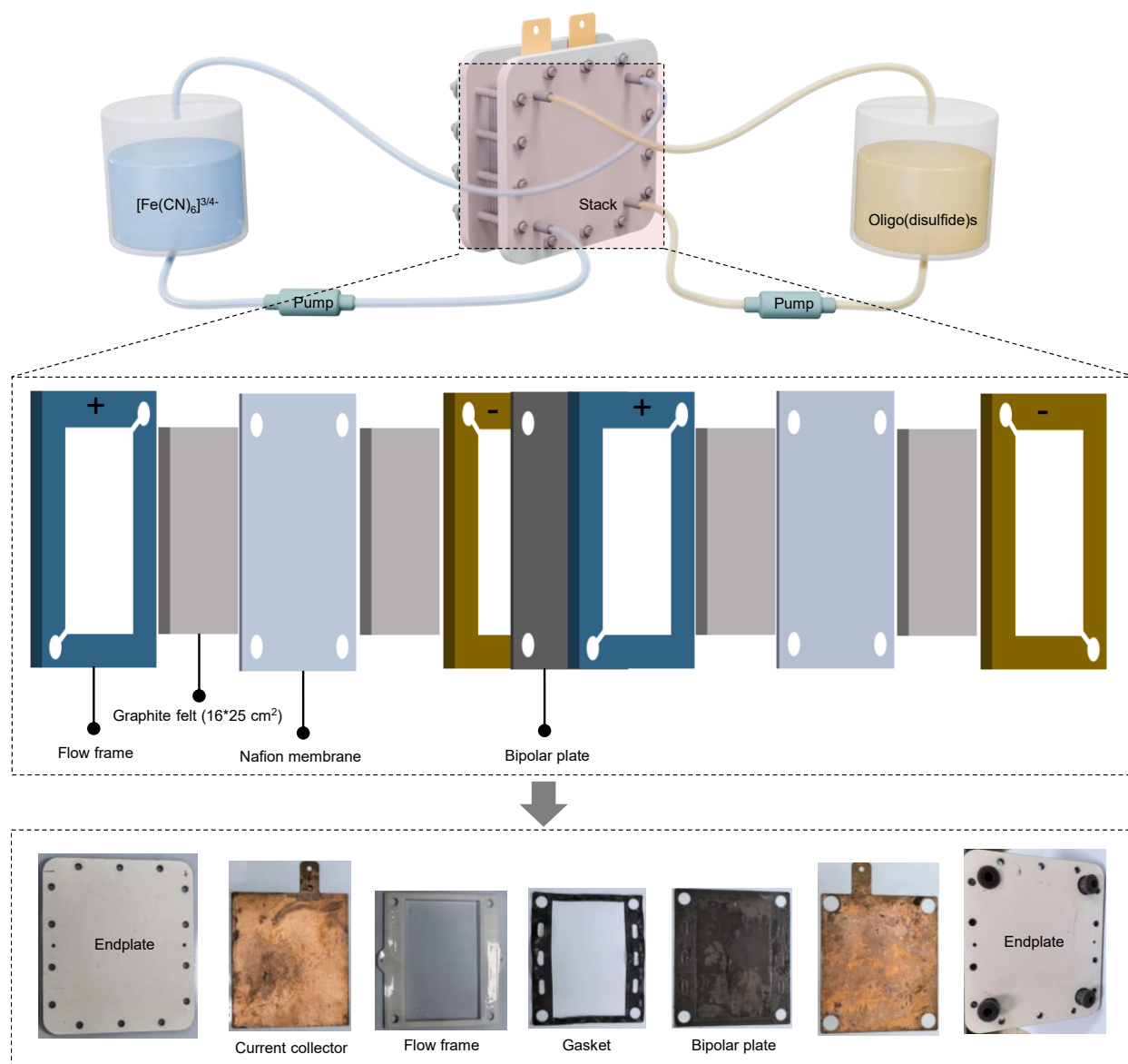
Supplementary Fig. 47. (a-c) ^1H NMR spectra of three oligo(disulfide)s-based analytes. (d) Viscosity analysis of three oligo(disulfide)s-based analytes.



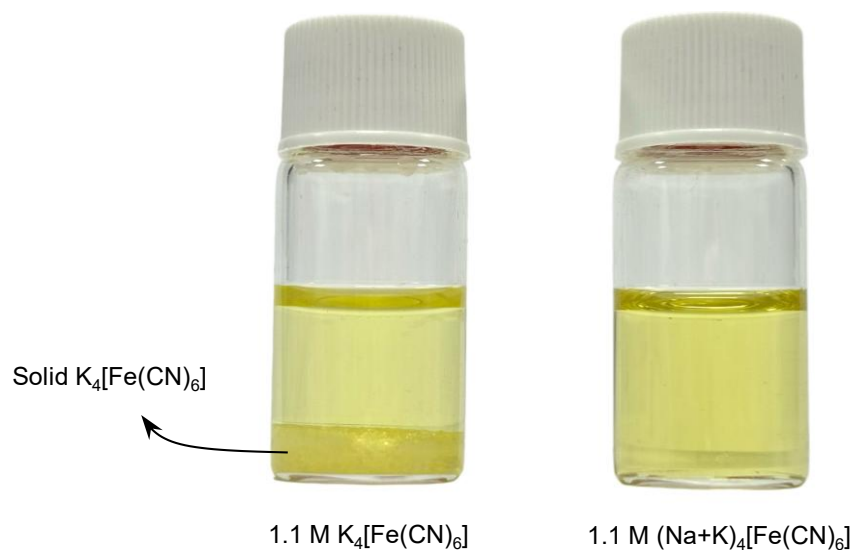
Supplementary Fig. 48. Photographs for the preparation of a 3 L oligo(disulfide)s-based anolyte with 2 M S-S bonds. NaCl/KCl and NaOH/KOH were first dissolved in water. Then, TA monomers were added under magnetic stirring.



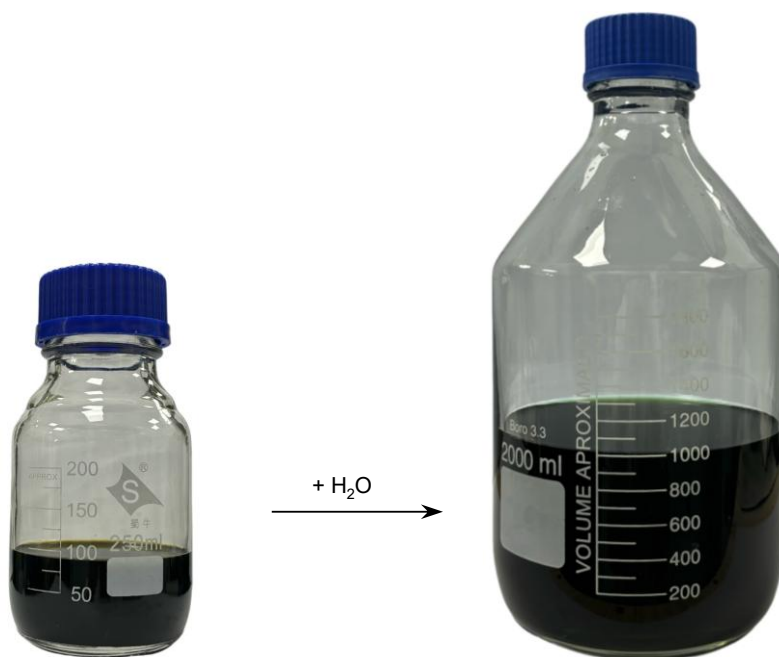
Supplementary Fig. 49. Thermodynamic stability was assessed for the above oligo(disulfide)s-based analyte (Supplementary Fig. 48) using ^1H NMR. The spectra recorded after shelving for 45 and 68 days are essentially consistent with the initial state, indicating its high chemical stability.



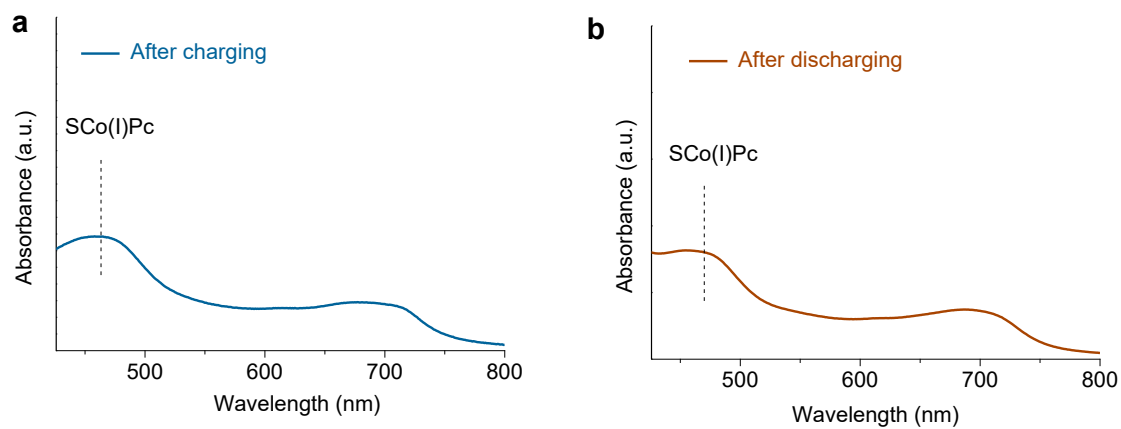
Supplementary Fig. 50. Detailed internal structure and dimensional parameters of the employed RFB stack.



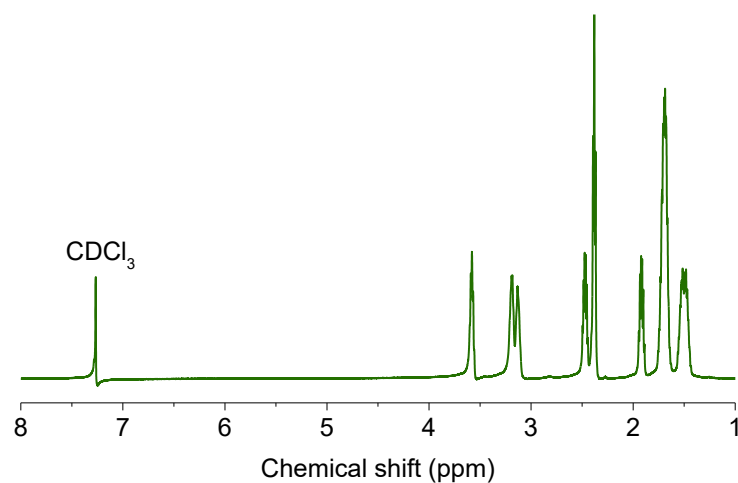
Supplementary Fig. 51. Photographs of two catholytes. Left is an undissolved $K_4[Fe(CN)_6]$, and right is a homogeneous solution with 1.1 M $[Fe(CN)_6]^{4-}$ by mixing cations (Na^+/K^+). With K^+ , the solubility of $[Fe(CN)_6]^{4-}$ in 1.0 M KCl is lower than 0.5 M. After mixing cations, the solubility of $[Fe(CN)_6]^{4-}$ increases to 1.1 M. To reduce the catholyte volume and increase the energy density of the RFB stack, 1.0 M Na/KCl was selected as the supporting electrolyte.



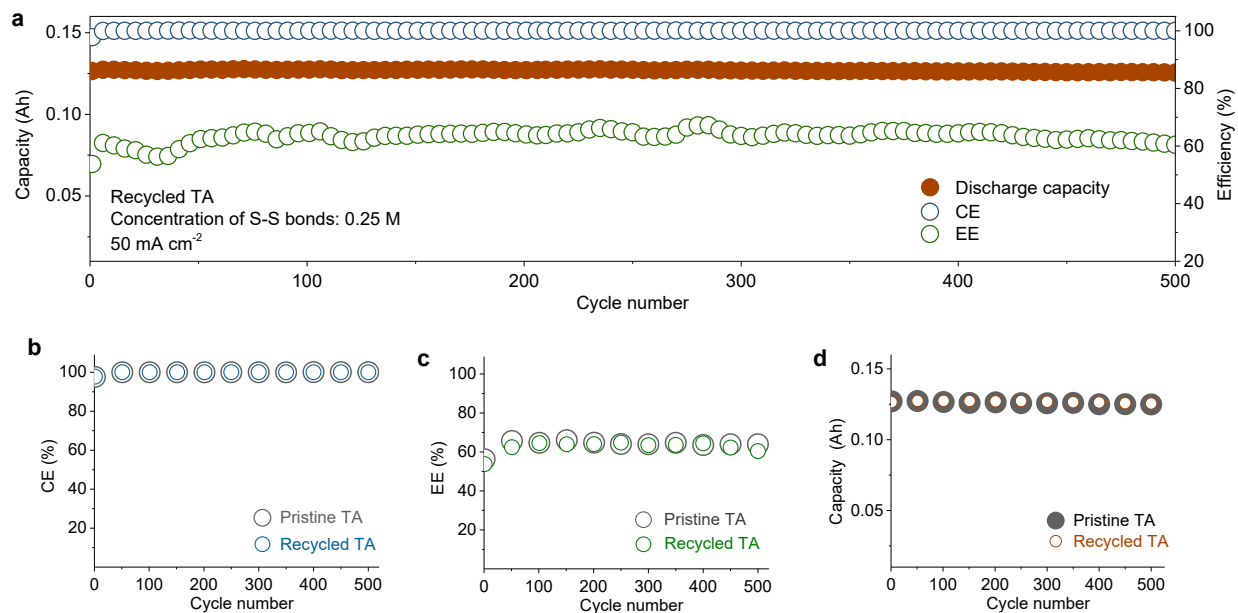
Supplementary Fig. 52. Photographs of an anolyte before and after adding H₂O. The anolyte was used in a RFB stack for cycling over 20 days. The corresponding battery performance is shown in Fig. 4c.



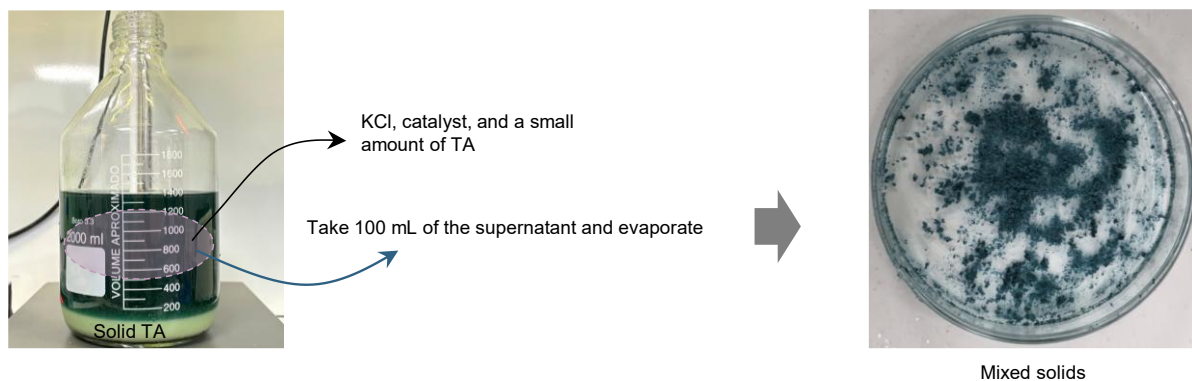
Supplementary Fig. 53. UV-vis spectrum of the anolyte after cycling over 20 days in a RFB stack. The corresponding battery performance is shown in Fig. 4c.



Supplementary Fig. 54. ^1H NMR spectrum of the recycled TA monomers from the anolyte after use in a RFB stack. The recycling isolated yield of TA monomers is 75.9%.



Supplementary Fig. 55. (a) Cycling performance of an oligo(disulfide)s-based RFB at 50 mA cm⁻². The anolyte was prepared using recycled TA as shown in Fig. 4d. Detailed RFB assembly parameters are given in Methods and Supplementary Table 1. (b-d) RFB performance comparison of recycled TA and pristine TA. The corresponding battery performance for the pristine TA is shown in Fig. 3d.



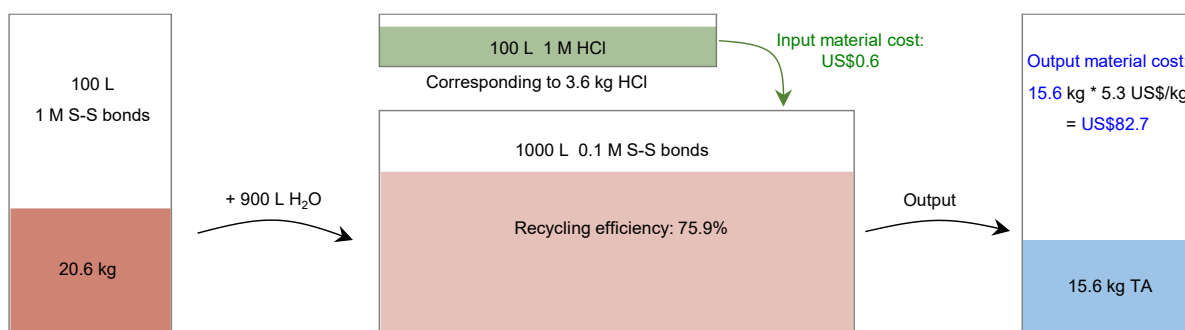
Supplementary Fig. 56. Photograph of the mixed solids obtained after evaporating 100 mL of the supernatant on the left. The left is the photograph of an anolyte after dilution and acid addition (as shown in Fig. 4d).

Supplementary Note 1:

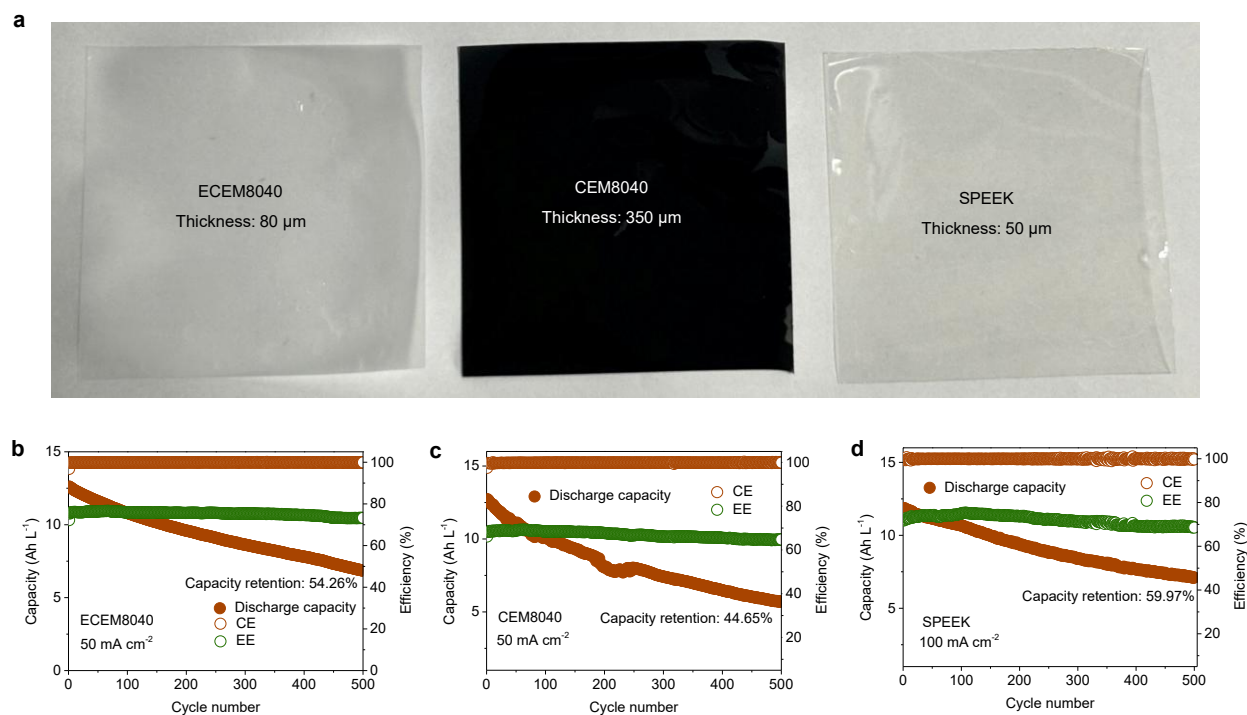
Economic analysis of the recycling process

We assumed recycling TA from a 100 L anolyte with the S-S bond concentration of 1 M as an example, and conducted an economic analysis of the recycling process.

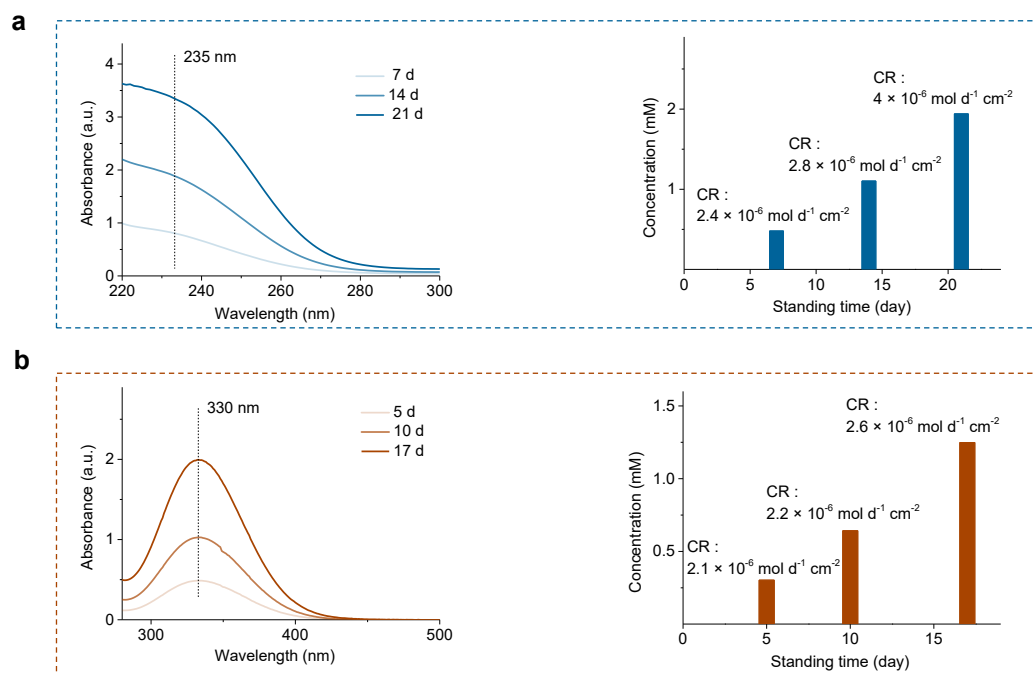
The recycling process can be accomplished simply by diluting with water and then adding acid to precipitate. The relevant material costs are shown in Supplementary Fig. 57. The input HCl cost required to recycle 100 L of anolyte is US\$0.6, while the output cost of the resulting TA can reach up to US\$82.7, indicating a notable difference between the materials consumed and the benefits generated during the recycling process. In addition, because the costs of stirring and filtration cannot be estimated from existing experiments, these expenses are not included in the calculation. Overall, the recycling process features simple operation and low auxiliary material input cost, endowing it with promising commercialization potential.



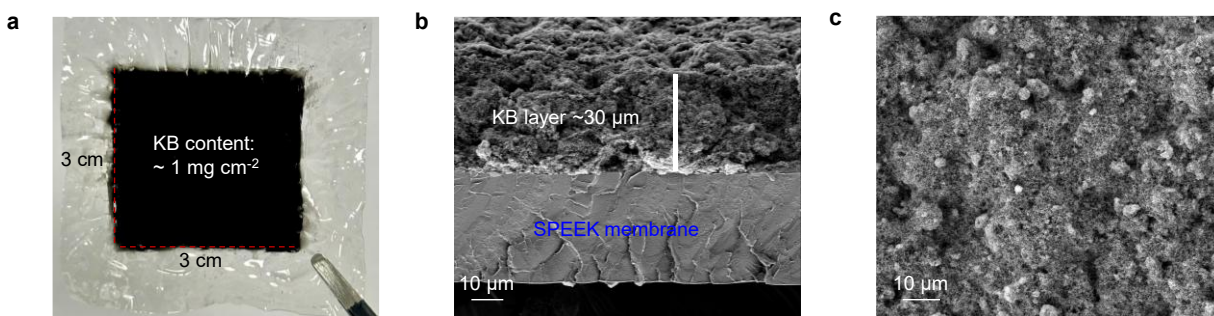
Supplementary Fig. 57. Input and output material costs for recycling TA from a 100 L solution with an S-S bond concentration of 1 M.



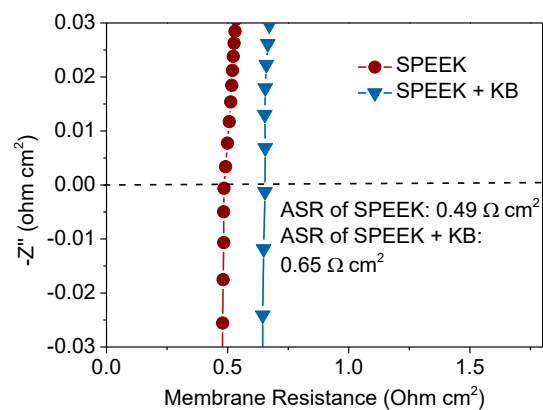
Supplementary Fig. 58. (a) Photographs of ECEM8040, CEM8040, and SPEEK membranes. Cycling performance of oligo(disulfide)s-based RFBs with (b) ECEM8040, (c) CEM8040, and (d) SPEEK membranes. The anolyte was 10 mL of 0.25 M S-S bonds. Detailed RFB assembly parameters are given in Supplementary Table 1.



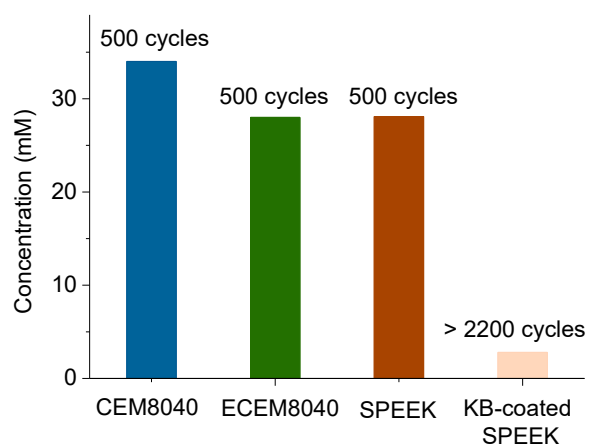
Supplementary Fig. 59. Permeability test results of reduced oligo(disulfide)s (**a**) and oligo(disulfide)s (**b**) through the SPEEK membrane. The permeability tests were conducted in a two-compartment cell, as shown in Supplementary Fig. 10. The left side contained 30 mL of 1 M S-S oligo(disulfide)s or reduced oligo(disulfide)s, while the opposite side contained 30 mL of water. UV-vis spectroscopy measurements were performed on the water side at different times. 3 mL of the solution was withdrawn for UV-vis characterization each time, followed immediately by adding the same volume of water.



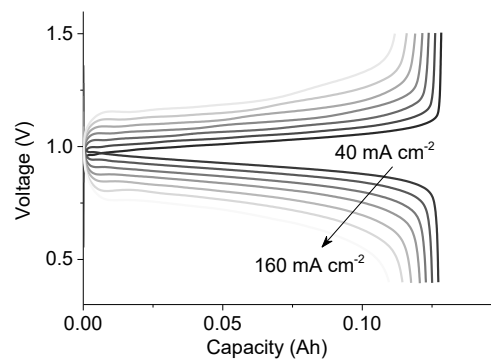
Supplementary Fig. 60. (a) Photograph of a KB-coated SPEEK membrane. The KB (ECP-600JD) powder was dispersed in 1.0 mL of 0.1 wt.% Nafion dispersion (diluted by 5 wt.% Nafion dispersion with isopropanol), followed by sonication for 2 h to ensure homogeneous dispersion, and then spray-coated onto a SPEEK membrane. (b) Cross-sectional SEM image and (c) surface SEM image of the KB-coated SPEEK membrane.



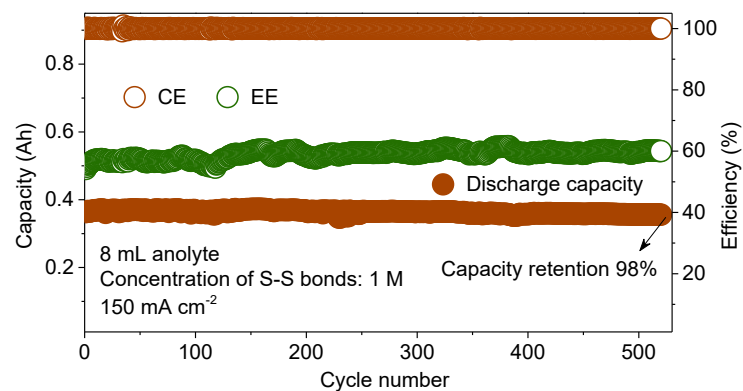
Supplementary Fig. 61. Membrane resistance measured in RFBs with an active area of 9 cm^2 , separated by a SPEEK membrane or a KB-modified SPEEK membrane. The RFBs were assembled with 1 M KCl aqueous electrolyte. The electrochemical impedance spectra of the membranes were recorded using a CHI660E electrochemical workstation with a frequency sweep from 1 to 10^5 Hz at an operating amplitude of 5 mV.



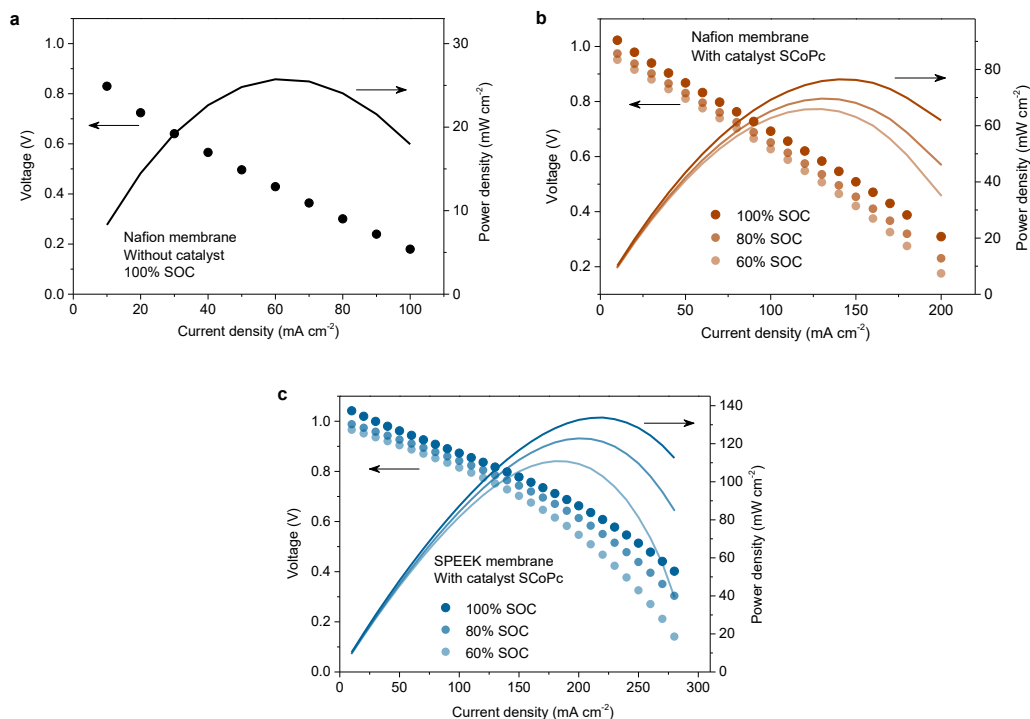
Supplementary Fig. 62. Concentration of anolyte materials detected in the catholyte after cycling. These results were obtained by ^1H NMR using sodium formate as the internal standard.



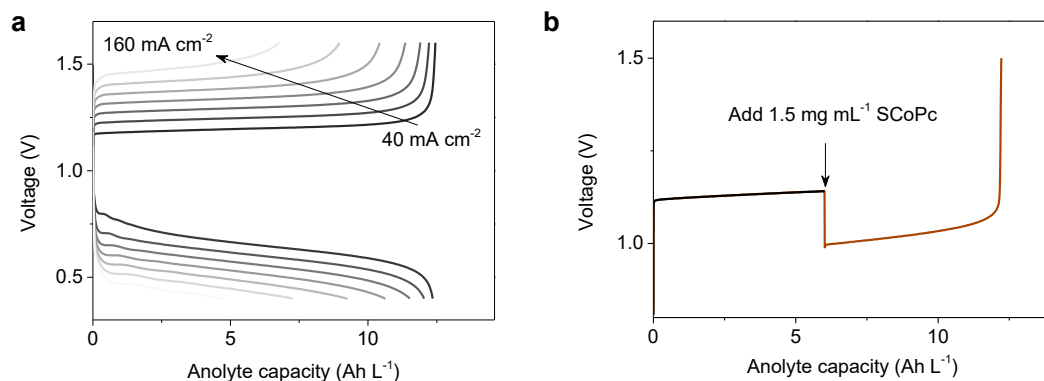
Supplementary Fig. 63. Voltage profiles of an oligo(disulfide)s-based RFB with 0.25 M S-S bonds, a KB-coated SPEEK membrane, and 1.5 mg mL⁻¹ SCoPc at current densities ranging from 40 to 160 mA cm⁻². Detailed RFB assembly parameters are given in Supplementary Table 1.



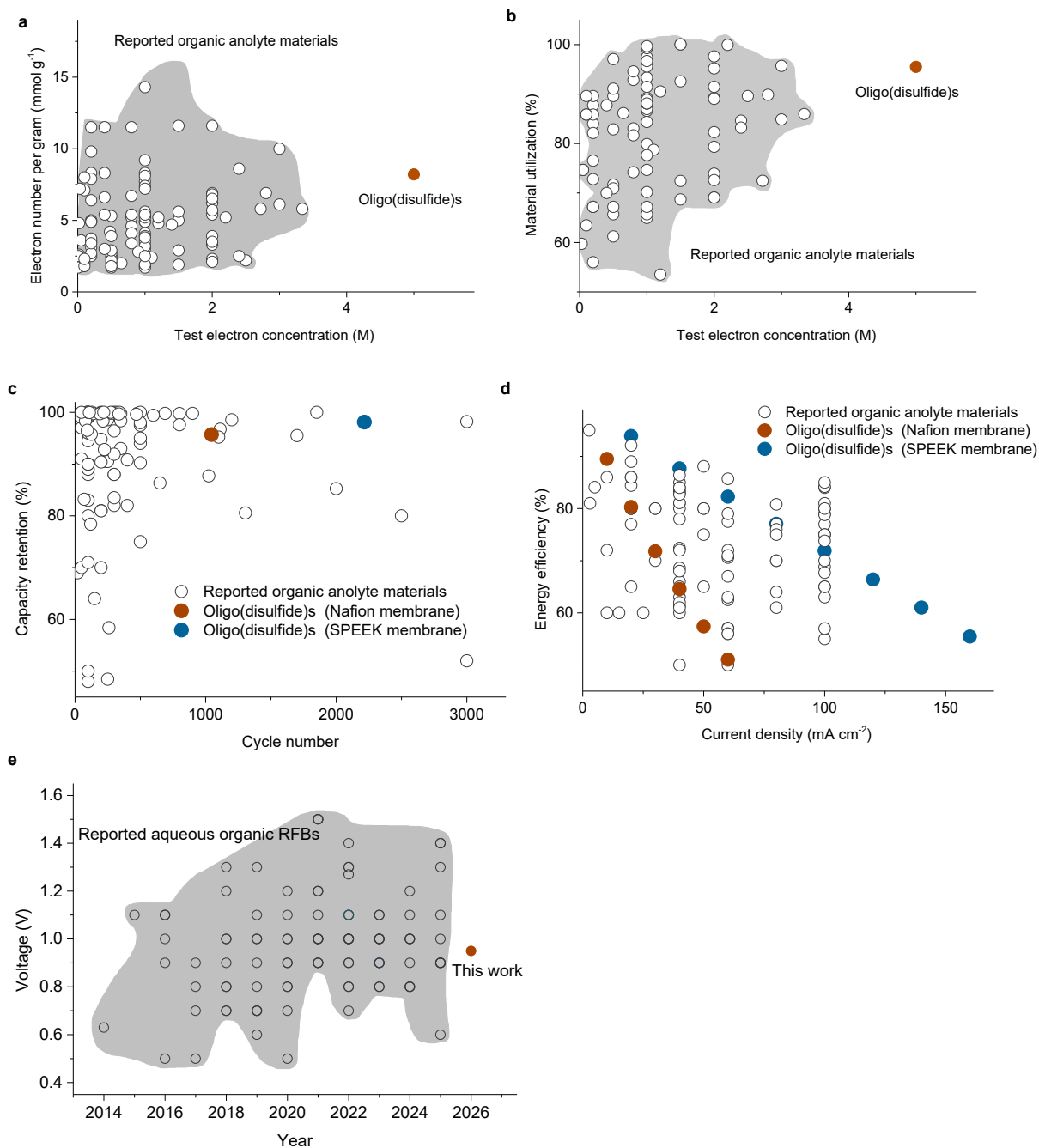
Supplementary Fig. 64. Cycling performance of an oligo(disulfide)s-based RFB with the S-S concentration of 1 M S-S bonds and a KB-modified SPEEK membrane. Detailed RFB assembly parameters are given in Supplementary Table 1.



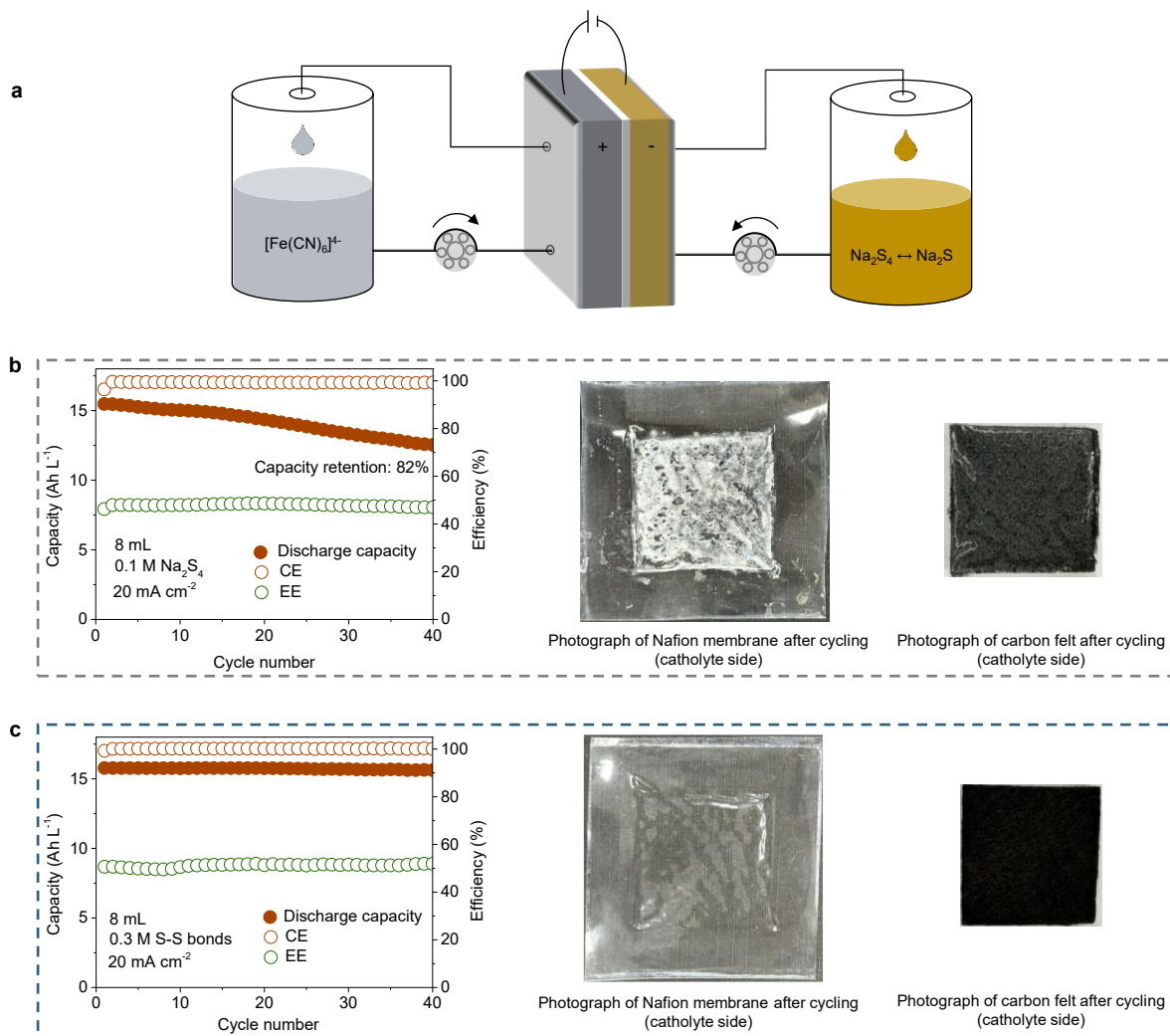
Supplementary Fig. 65. (a) Discharge polarization curves of an oligo(disulfide)s-based RFB with 0.25 M S-S bonds and a Nafion membrane, measured at 100% SOC. The cell reaches a maximum power density of 25.7 mW cm⁻². (b) Discharge polarization curves of an oligo(disulfide)s-based RFB with 0.25 M S-S bonds, 1.5 mg mL⁻¹ SCoPc, and a Nafion membrane, measured from 100% to 60% SOC. The cell reaches a maximum power density of 76.5 mW cm⁻² at 100% SOC. (c) Discharge polarization curves of an oligo(disulfide)s-based RFB with 0.25 M S-S bonds, 1.5 mg mL⁻¹ SCoPc, and a SPEEK membrane, measured from 100% to 60% SOC. The cell reaches a maximum power density of 133.9 mW cm⁻² at 100% SOC.



Supplementary Fig. 66. (a) Voltage profiles of an oligo(disulfide)s-based RFB with 0.25 M S-S bonds and a KB-coated SPEEK membrane, without SCoPc. The EE is 53.5% at 40 mA cm⁻². (b) The charge profile of an oligo(disulfide)s-based RFB with the SPEEK membrane immediately reduces after introducing 1.5 mg mL⁻¹ SCoPc at 10 mA cm⁻². Detailed RFB assembly parameters are given in Supplementary Table 1.



Supplementary Fig. 67. Comprehensive analysis of oligo(disulfide)s and prior organic anolyte materials for aqueous RFBs. These values are summarized from over 100 papers that basically cover all reported organic anolyte materials, as shown in Supplementary Table 2.



Supplementary Fig. 68. (a) Diagram of a polysulfide RFB. (b) Cycling performance of a polysulfide RFB with 0.1 M Na₂S₄ and corresponding photographs of the Nafion membrane and carbon felt after cycling. (c) Cycling performance of an oligo(disulfide)s-based RFB with 0.3 M S-S bonds and corresponding photographs of the Nafion membrane and carbon felt after cycling.

Supplementary Table 1. Detailed RFB assembly parameters (supporting electrolyte: 1 M KCl or K/NaCl).

Cell	Anolyte	Catholyte
Fig. 3a	10 mL 0.25 M TA + 0.25 M KOH	33 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. 3b	10 mL 0.25 M TA + 0.25 M KOH + 1.5 mg mL ⁻¹ SCoPc	33 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. 3d	10 mL 0.25 M TA + 0.25 M KOH + 1.5 mg mL ⁻¹ SCoPc	33 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. 3e	8 mL 1 M TA + 1 M KOH + 1.5 mg mL ⁻¹ SCoPc	106 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. 3h	8 mL 2.5 M TA + 2.75 M KOH + 1.5 mg mL ⁻¹ SCoPc	200 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. 4c	1 L 1.5 M TA + 1.65 M KOH + 1.5 mg mL ⁻¹ SCoPc	3 L 0.55 M K ₄ [Fe(CN) ₆] + 0.55 M Na ₄ [Fe(CN) ₆]
Fig. 4e	10 mL 0.25 M TA + 0.25 M KOH + 1.5 mg mL ⁻¹ SCoPc	33 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. 4g	10 mL 0.25 M TA + 0.25 M KOH + 1.5 mg mL ⁻¹ SCoPc	33 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. S22	10 mL 0.25 M TA + 0.25 M KOH	33 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. S27	20 mL 50 mM TA + 50 mM KOH + 0.15 mg mL ⁻¹ SCoPc	10 mL 0.3 M K ₄ [Fe(CN) ₆]/0.1 M K ₃ [Fe(CN) ₆]
Fig. S29	10 mL 0.25 M TA + 0.25 M KOH + 1.5 mg mL ⁻¹ SCoPc	33 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. S36	10 mL 0.25 M TA + 0.25 M KOH	33 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. S37	10 mL 0.25 M TA + 0.25 M KOH	33 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. S39	10 mL 0.25 M TA + 0.25 M KOH + 1.5 mg mL ⁻¹ SCoPc	33 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. S41	8 mL 1.5 M TA + 1.5 M KOH + 1.5 mg mL ⁻¹ SCoPc	160 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. S55	10 mL 0.25 M TA + 0.25 M KOH + 1.5 mg mL ⁻¹ SCoPc	33 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. S58	10 mL 0.25 M TA + 0.25 M KOH + 1.5 mg mL ⁻¹ SCoPc	33 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]
Fig. S64	8 mL 1 M TA + 1 M KOH + 1.5 mg mL ⁻¹ SCoPc	106 mL 0.3 M K ₄ [Fe(CN) ₆]/0.15 M K ₃ [Fe(CN) ₆]

Supplementary Table 2. Performance of reported organic-based analytes. ENPR represents electron number per gram (mmol g^{-1}), and TEC represents test electron concentration (M).

Materials (ENPR)	TEC	Performance	References
AQDS (5.4)	2	capacity fade: 0.08%/cycle (0.19%/day), 10 cycles (4.17 days), 500 mA cm^{-2}	<i>Nature</i> , 2014 , 505, 195.
2,6-DHAQ (8.3)	1	capacity fade: 0.1%/cycle (8%/day), 100 cycles (1.46 days), 84% EE at 100 mA cm^{-2}	<i>Science</i> , 2015 , 349, 1529.
FMN-Na (4.2)	0.48	capacity fade: 0.01%/cycle (0.63%/day), 200 cycles (3.17 days), $\sim 4.5 \text{ Ah L}^{-1}$, 80% EE at 50 mA cm^{-2}	<i>Nat. Commun.</i> , 2016 , 7, 13230.
TEMPO-PZ (2.6)	0.02	no capacity fade, 1851 cycles, $\sim 50\%$ EE at 4 mA cm^{-2}	<i>ACS Energy Lett.</i> , 2016 , 1, 976.
MV (3.9)	0.5	capacity fade: 0.11%/cycle, 100 cycles, 9.6 Ah L^{-1} , 62.5% EE at 60 mA cm^{-2}	<i>Adv. Energy Mater.</i> , 2016 , 6, 1501449.
MV (3.9)	2	no capacity fade, 100 cycles, $\sim 39.6 \text{ Ah L}^{-1}$	<i>Angew. Chem. Int. Ed.</i> , 2016 , 128, 14639.
ACA (7.7)	1	capacity fade: 0.023%/cycle, 400 cycles, 63% EE at 100 mA cm^{-2}	<i>Nat. Energy</i> , 2016 , 1, 102.
DHBQ (14.3)	1	capacity fade: 0.24%/cycle, 150 cycles, 23.2 Ah L^{-1} , 65% EE at 100 mA cm^{-2}	<i>Adv. Energy Mater.</i> , 2017 , 7, 1702056.
AQS (6.9)	2	15 cycles (30 h), 38.9 Ah L^{-1} , 73.5% EE at 250 mA cm^{-2}	<i>Adv. Energy Mater.</i> , 2017 , 8, 1601488.
[(Me)(NPr)V]Cl ₃ (5.3)	0.5	capacity fade: 0.18%/cycle, 50 cycles, $\sim 12 \text{ Ah L}^{-1}$, 63% EE at 60 mA cm^{-2}	<i>Chem</i> , 2017 , 3, 961.
BTMAP-Vi (2)	0.65	capacity fade: 0.0057%/cycle (0.1%/day), 250 cycles (14 days), $\sim 15 \text{ Ah L}^{-1}$, 65% EE at 50 mA cm^{-2}	<i>ACS Energy Lett.</i> , 2017 , 2, 639.
2,3-HCNQ (9.2)	1	capacity fade: 0.053%/cycle (3.4%/day), 100 cycles (1.5 days), 18.8 Ah L^{-1} , 68.8% EE at 100 mA cm^{-2}	<i>ACS Energy Lett.</i> , 2018 , 3, 2404.
(SPr) ₂ V (2.5)	0.5	capacity fade: 0.01%/cycle, 100 cycles, $\sim 12.2 \text{ Ah L}^{-1}$, 67% EE at 60 mA cm^{-2}	<i>ACS Energy Lett.</i> , 2018 , 3, 663.
(NPr) ₂ V (2)	0.5	capacity fade: 0.005%/cycle, 500 cycles, $\sim 8.8 \text{ Ah L}^{-1}$, 57.1% EE at 60 mA cm^{-2}	<i>Chem. Commun.</i> , 2018 , 54, 6871.
[(NPr) ₂ TTz]Cl ₄ (2.4)	0.5	capacity fade: 0.06%/cycle, 50 cycles, $\sim 9 \text{ Ah L}^{-1}$, 68.6% EE at 40 mA cm^{-2}	<i>Angew. Chem. Int. Ed.</i> , 2018 , 57, 231.
DHPS (6.9)	2.8	capacity fade: 0.0195%/cycle (0.68%/day), 500 cycles (> 14.3 days), 67.4 Ah L^{-1} , 75% EE at 100 mA cm^{-2}	<i>Nat. Energy</i> , 2018 , 3, 508.
Diquat (2.7)	0.5	capacity fade: 0.2%/cycle (0.8%/day), 100 cycles (24.9 days), $\sim 8.2 \text{ Ah L}^{-1}$, 84.1% EE at 5 mA cm^{-2}	<i>ACS Energy Lett.</i> , 2018 , 3, 2533.
1,8-DHAQ (8.3)	0.2	capacity fade: 0.12%/cycle (13.0%/day), 100 cycles, 77% EE at 80 mA cm^{-2}	<i>J. Power Sources</i> , 2018 , 386, 40.
NR (7.9)	0.2	capacity fade: 0.11%/cycle, 100 cycles, $\sim 3 \text{ Ah L}^{-1}$, 8.05 mA cm^{-2}	<i>ChemSusChem</i> , 2018 , 11, 1866.
2,6-DBEAQ (4.9)	1	capacity fade: 0.00069%/cycle (0.04%/day), 350 cycles (~ 6 days), $\sim 17.4 \text{ Ah L}^{-1}$, 80% EE at 100 mA cm^{-2}	<i>Joule</i> , 2018 , 2, 1894.
AQ-1,8-3E-OH (6.1)	3	capacity fade: 0.043%/cycle (0.5%/day), 220 cycles (18 days), 76.9 Ah L^{-1} , 75% EE at 50 mA cm^{-2}	<i>ACS Energy Lett.</i> , 2019 , 4, 1342.
AQDS(NH ₄) ₂ (5)	1.5	no capacity fade, 300 cycles (15 days), 29.1 Ah L^{-1} , 70.6% EE at 60 mA cm^{-2}	<i>Angew. Chem. Int. Ed.</i> , 2019 , 58, 16629.
Fc-bipy ³⁺ (1.7)	0.5	capacity fade: 0.0063%/cycle, 4000 cycles, 5.2 Ah L^{-1} , 60% EE at 10 mA cm^{-2}	<i>J. Power Sources</i> , 2019 , 417, 83.
Bislawsone (11.6)	2	capacity fade: 0.038%/cycle (0.74%/day), > 250 cycles (12.8 days), 52.3 Ah L^{-1} , 77% EE at 100 mA cm^{-2}	<i>ACS Energy Lett.</i> , 2019 , 4, 1880.
Lawsone (11.5)	0.2	capacity fade: 0.0079%/cycle, 215 cycles, $\sim 1 \text{ Ah L}^{-1}$, 60% EE at 15 mA cm^{-2}	<i>Energy Storage Mater.</i> , 2019 , 19, 62.
1,8-DHAQDS (5)	0.2	capacity fade: 0.52%/cycle (52%/day), 100 cycles (~ 1 days)	<i>ACS Appl. Energy Mater.</i> , 2019 , 2, 7893.
AMA (5.2)	0.8	capacity fade: 0.02%/cycle (0.81%/day), 350 cycles (10 days), $\sim 4.5 \text{ Ah L}^{-1}$, 84.2% EE at 100 mA cm^{-2}	<i>ACS Appl. Energy Mater.</i> , 2019 , 2, 2469.

DMBQ (9.8)	0.2	capacity fade: 0.15%/cycle (12.6%/day), 200 cycles (2.38 days), 4.7 Ah L ⁻¹ , 72% EE at 60 mA cm ⁻²	<i>Ind. Eng. Chem. Res.</i> , 2019 , 58, 3994-3999.
(2HO-V)Br ₂ (4.9)	0.2	no capacity fade, 200 cycles (> 40 h), ~ 4.1 Ah L ⁻¹ , 83.4% EE at 40 mA cm ⁻²	<i>Chem. Commun.</i> , 2019 , 55, 4801.
2,6-DPPEAQ (4.1)	1	capacity fade: 0.00036%/cycle (0.014%/day), 480 cycles (12.3 days), ~ 26.11 Ah L ⁻¹ , 65% EE at 100 mA cm ⁻²	<i>Adv. Energy Mater.</i> , 2019 , 9, 1900039.
IC-H (4.7)	1.4	capacity fade: 0.04%/cycle (0.46%/day), 200 h, 16.1 Ah L ⁻¹ , 64% EE at 80 mA cm ⁻²	<i>ACS Appl. Energy Mater.</i> , 2019 , 2, 7425.
AADA (5.3)	1	capacity fade: 0.16%/cycle, 260 cycles, ~ 25 Ah L ⁻¹	<i>Angew. Chem. Int. Ed.</i> , 2020 , 59, 22163.
K ₂ -BNDI (3.6)	0.05	100 cycles, ~ 1 Ah L ⁻¹ , 86% EE at 10 mA cm ⁻²	<i>J. Mater. Chem. A</i> , 2020 , 8, 112183.
AQDS (5.4)	1	capacity fade: 0.02%/cycle, 50 cycles, 17.6 Ah L ⁻¹ , 57% EE at 60 mA cm ⁻²	<i>Chem. Eng. J.</i> , 2020 , 383, 123085.
DPivOHAQ (4.9)	1	capacity fade: 0.00031%/cycle (0.014%/day), 690 cycles (15.6 days), 25.6 Ah L ⁻¹ , 85% EE at 100 mA cm ⁻²	<i>Chem.</i> , 2020 , 6, 1432.
BPP-Vi (1.8)	1	capacity fade: 0.00069%/cycle (0.016%/day), 280 cycles (13 days), 26.6 Ah L ⁻¹ , 85% EE at 40 mA cm ⁻²	<i>Adv. Energy Mater.</i> , 2020 , 10, 2000100.
BHPC (6.9)	1	capacity fade: 0.0149%/cycle (0.08%/day), 1305 cycles (23 days), 25.9 Ah L ⁻¹ , 80% EE at 100 mA cm ⁻²	<i>ACS Energy Lett.</i> , 2020 , 5, 411.
[(bpy(CH ₂) ₃ NMe ₃)] ₂ (2)	0.1	capacity fade: 0.5%/cycle, 100 cycles, ~ 1.7 Ah L ⁻¹ , 72% EE at 10 mA cm ⁻²	<i>J. Power Sources</i> , 2020 , 477, 228985.
d-BR5 (8)	0.1	capacity fade: 0.0005%/cycle, 200 cycles, ~ 1.1 Ah L ⁻¹ , 80% EE at 50 mA cm ⁻²	<i>ACS Appl. Energy Mater.</i> , 2020 , 3, 2290-2295.
AQDS (5.4)	0.8	capacity fade: 0.01%/cycle, 100 cycles, 17.8 Ah L ⁻¹ , 81% EE at 40 mA cm ⁻²	<i>J. Mater. Chem. C</i> , 2020 , 8, 5727.
BHOP-Vi (2.3)	2	capacity fade: 0.055%/cycle (1.128%/day), 100 cycles, 47.8 Ah L ⁻¹ , 55% EE at 100 mA cm ⁻²	<i>ChemSusChem</i> , 2020 , 13, 2245.
EV (2.7)	1	no capacity fade (80% SOC), 500 cycles (26 days), 21.4 Ah L ⁻¹ , 77% EE at 20 mA cm ⁻²	<i>Nano Energy</i> , 2021 , 84, 105897.
[(NPr) ₂ PV]·4Cl (3.5)	0.2	capacity fade: 0.06%/cycle (3%/day), 300 cycles (140 h), 4.5 Ah L ⁻¹ , 89% EE at 20 mA cm ⁻²	<i>ACS Appl. Mater. Interfaces</i> , 2021 , 13, 44174.
(TPyTz)Cl ₆ (4.8)	1.2	50 cycles (~ 0.3 days), ~ 17.2 Ah L ⁻¹ , 61% EE at 80 mA cm ⁻²	<i>Angew. Chem. Int. Ed.</i> , 2021 , 60, 20921.
R-Vi (2.2)	0.5	capacity fade: 0.021%/cycle (1.11%/day), 650 cycles (12.3 days), 11.1 Ah L ⁻¹ , 76% EE at 80 mA cm ⁻²	<i>Angew. Chem. Int. Ed.</i> , 2021 , 60, 26971.
MVdN (3.2)	1	capacity fade: 1.55%/cycle, 20 cycles, 23.3 Ah L ⁻¹ , 72.4% EE at 40 mA cm ⁻²	<i>J. Electrochem. Soc.</i> , 2021 , 168, 100532.
DCDHAQ (5.6)	1.5	capacity fade: 0.0029%/cycle (0.03%/day), 90 cycles (9 days), 40.2 Ah L ⁻¹ , 60% EE at 40 mA cm ⁻²	<i>J. Mater. Chem. A</i> , 2021 , 9, 26709.
HAQS (6.6)	0.4	capacity fade: 0.012%/cycle (0.29%/day), 300 cycles, ~ 9.4 Ah L ⁻¹ , 80% EE at 40 mA cm ⁻²	<i>ChemElectroChem</i> , 2021 , 8, 2526.
(APBPpy)Cl ₄ (3.5)	1	capacity fade: 0.04%/cycle (2.88%/day), 100 cycles (1.4 days), 20 Ah L ⁻¹ , 80.8% EE at 80 mA cm ⁻²	<i>Adv. Mater.</i> , 2021 , 33, 2005839.
[MV]Br ₂ (2.9)	0.5	no capacity fade, 100 cycles, ~ 9.5 Ah L ⁻¹ , 56% EE at 60 mA cm ⁻²	<i>ACS Energy Lett.</i> , 2021 , 6, 2891.
1,6-DPAP (5.6)	1	capacity fade: 0.000002%/cycle (0.0015%/day), 90 cycles (12 days), ~ 26.7 Ah L ⁻¹ , ~ 80% EE at 20 mA cm ⁻²	<i>Angew. Chem. Int. Ed.</i> , 2021 , 60, 5289.
DAEAQ (5.2)	1	capacity fade: 0.24%/day, 500 cycles (11.43 days), 27.78 Ah L ⁻¹ , 81% EE at 100 mA cm ⁻²	<i>Energy Storage Mater.</i> , 2021 , 36, 417.
4C7SFL (5.8)	2.72	capacity fade: 0.00293%/cycle (0.0209%/day) 1111 cycles (120 days), 52.8 Ah L ⁻¹ , 92.1% EE at 20 mA cm ⁻²	<i>Science</i> , 2021 , 372, 836-840.
1,8-PFP (6.2)	2	no capacity fade, > 130 cycles (40 days), ~ 51 Ah L ⁻¹ , 65% EE at 20 mA cm ⁻²	<i>Joule</i> , 2021 , 5, 2437.
2,6-N-TSAQ (2.5)	0.2	capacity fade: 0.00024%/cycle (0.025%/day), ~ 900 cycles, 4.8 Ah L ⁻¹	<i>Batteries Supercaps</i> , 2022 , 5, e202200009.
1,8-BDPAQCl ₂ (3.9)	0.8	capacity fade: 0.048%/cycle (0.88%/day), 200 cycles (11 days), ~ 17.5 Ah L ⁻¹ , 61.3% EE at 40 mA cm ⁻²	<i>ChemElectroChem</i> , 2022 , 9, e202200224.
AQDP (5.7)	2	capacity fade: 0.0024%/cycle (0.025%/day), 115 cycles (over 11 days), 42.5 Ah L ⁻¹	<i>ACS Energy Lett.</i> , 2022 , 7, 226.

[(NPr) ₂ FV]Cl ₄ (1.8)	0.05	capacity fade: 0.0006%/cycle (0.14%/day), 3000 cycles (13 days), 1 Ah L ⁻¹ , 63% EE at 40 mA cm ⁻²	<i>ACS Appl. Mater. Interfaces</i> , 2022 , 14, 48727.
6-QCA (11.5)	0.4	capacity fade: 0.1%/cycle, 100 cycles	<i>ACS Appl. Energy Mater.</i> , 2022 , 5, 10379.
exDMeBP (3.0)	1	capacity fade: 0.17%/cycle, 100 cycles, ~18 Ah L ⁻¹ , 75% EE at 80 mA cm ⁻²	<i>JACS Au</i> , 2022 , 2, 1214.
2,3-DHAQ (8.3)	0.4	capacity fade: 0.016%/cycle (0.8%/day), 3000 cycles (over 60 days), 75% EE at 100 mA cm ⁻²	<i>J. Power Sources</i> , 2022 , 539, 231600.
[(NPr) ₂ TV]Cl ₄ (3.1)	0.2	capacity fade: 0.04%/cycle, 300 cycles, 4.6 Ah L ⁻¹ , 62% EE at 40 mA cm ⁻²	<i>J. Mater. Chem. A</i> , 2022 , 10, 9830.
(ATBPY)Cl ₄ (1.7)	1	capacity fade: 0.008%/cycle (0.445%/day), 100 cycles (1.8 days), 23.6 Ah L ⁻¹ , 85.7% EE at 60 mA cm ⁻²	<i>Adv. Funct. Mater.</i> , 2022 , 32, 2111744.
2,6-DPPAQ (4.1)	0.8	capacity fade: 0.00189%/cycle (0.127%/day), 140 cycles (50 h), 19.9 Ah L ⁻¹ , 79% EE at 100 mA cm ⁻²	<i>Nat. Commun.</i> , 2022 , 13, 3184.
DBPZ (7.1)	0.1	capacity fade: 0.026%/cycle, 200 cycles, 2.4 Ah L ⁻¹ , 84.4% EE at 20 mA cm ⁻²	<i>Green Chem.</i> , 2022 , 24, 8783.
TPZ-2 (7.2)	0.03	capacity fade: 0.6%/cycle (55%/day), 50 cycles, 0.48 Ah L ⁻¹ , 81% EE at 3 mA cm ⁻²	<i>Chem. Commun.</i> , 2022 , 58, 13226.
3,4-S ₂ V (2.4)	1.1	capacity fade: 0.0027%/cycle (0.045%/day), 1700 cycles (100 days), 23.2 Ah L ⁻¹ , ~ 66% EE at 40 mA cm ⁻²	<i>Adv. Energy Mater.</i> , 2022 , 12, 2202085.
PV ³⁺ (1.7)	0.005	capacity fade: ~ 0.29%/cycle, 100 cycles	<i>Mater. Lett.</i> , 2022 , 314, 131876.
[PyrPV]Cl ₄ (3.2)	1	capacity fade: 0.206%/cycle (5.73%/day), 250 cycles (~9 days), 23.9 Ah L ⁻¹ , 84% EE at 40 mA cm ⁻²	<i>Adv. Energy Mater.</i> , 2022 , 12, 2103478.
THAQ (7.4)	1	capacity fade: 0.00435%/cycle (0.36%/day), 1100 cycles (13.3 days), 20.8 Ah L ⁻¹ , ~ 75% EE at 100 mA cm ⁻²	<i>J. Power Sources</i> , 2022 , 524, 231001.
(PPBPY)Br ₂ (2.8)	0.9	no capacity fade, 320 cycles (> 8.8 days), ~ 11.1 Ah L ⁻¹ , 77.5% EE at 60 mA cm ⁻²	<i>Angew. Chem. Int. Ed.</i> , 2022 , 61, e202208223.
Dex-Vi (1.9)	1.5	no capacity fade, ~ 340 cycles (30 days), 40.2 Ah L ⁻¹	<i>ACS Energy Lett.</i> , 2022 , 7, 2428.
[(DMAE-Pr) ₂ -Vi]Cl ₄ (1.8)	0.1	capacity fade: ~ 0.027%/cycle (~ 1.51%/day), 300 cycles (5.3 days), ~ 2.3 Ah L ⁻¹ , 81.1% EE at 40 mA cm ⁻²	<i>Batteries Supercaps</i> 2023 , 6, e202200355.
LAQD (4.8)	0.02	capacity fade: 0.095%/cycle, 200 cycles, 0.15 Ah L ⁻¹ , ~ 86% EE at 20 mA cm ⁻²	<i>Int. J. Biol. Macromol.</i> , 2023 , 229, 236.
4A ⁴⁺ -NDI-4Br ⁻ (2.1)	2	capacity fade: 0.004%/cycle (0.044%/day), 500 cycles (45 days), ~ 37 Ah L ⁻¹ , ~ 60% EE at 25 mA cm ⁻²	<i>Adv. Mater.</i> , 2023 , 35, 2210859.
2-2PEAQ (6.8)	2	capacity fade: 0.01%/day, ~ 190 cycles (~ 27 days), 49 Ah L ⁻¹ , ~ 68% EE at 40 mA cm ⁻²	<i>Adv. Funct. Mater.</i> , 2023 , 33, 2211338.
DpivOHAQ (4.9)	0.2	capacity fade: 0.0012%/cycle, 1200 cycles, ~ 3.8 Ah L ⁻¹	<i>Angew. Chem. Int. Ed.</i> , 2023 , 62, e202214819.
Dex-DiOH-Vi (2.2)	2.5	no capacity decay, ~ 275 cycles (14 days), 60 Ah L ⁻¹ , 80% EE at 30 mA cm ⁻²	<i>Adv. Energy Mater.</i> , 2023 , 13, 2203919.
HATNTA (11.6)	1.5	capacity fade: 0.021%/cycle (0.168%/day), 80 cycles (10 days), 37.2 Ah L ⁻¹ , 78% EE at 40 mA cm ⁻²	<i>Energy Storage Mater.</i> , 2023 , 59, 102789.
[(DMAE-Pr) ₂ -Vi]Cl ₄ (1.8)	0.5	capacity fade: ~ 0.18%/cycle (~ 1.7%/day), 120 cycles (12.4 days), ~ 13 Ah L ⁻¹ , 86.4% EE at 40 mA cm ⁻²	<i>Adv. Energy Sustain. Res.</i> , 2023 , 4, 2300077.
(SPR) ₃ 4TpyTz (3)	0.4	capacity fade: 0.012%/cycle (0.44%/day), 500 cycles (14 days), ~ 50% EE at 60 mA cm ⁻²	<i>ACS Appl. Mater. Interfaces</i> , 2023 , 15, 36242.
2,6-D2PEAQ (5.2)	2.2	capacity fade: 0.0008%/cycle (0.013%/day), 470 cycles (27 days), 58.9 Ah L ⁻¹ , ~ 70% EE at 100 mA cm ⁻²	<i>ACS Energy Lett.</i> , 2023 , 8, 600.
4C7SFL (5.8)	3.34	capacity fade: 0.0307%/day, > 2000 cycles (> 480 days), ~ 76.9 Ah L ⁻¹ , 80% EE at 20 mA cm ⁻²	<i>Joule</i> , 2023 , 7, 1609.
Lawsone (11.5)	0.8	capacity fade: 0.1%/cycle, 100 cycles, 20.27 Ah L ⁻¹ , 57% EE at 100 mA cm ⁻²	<i>Chem. Eng. J.</i> , 2023 , 464, 142661.
NDI (3.72)	0.2	capacity fade: 0.0047%/cycle (0.58%/day), 350 cycles, 4.4 Ah L ⁻¹ , 61% EE at 40 mA cm ⁻²	<i>CCS Chem.</i> , 2023 , 5, 2334.
3-NH ₂ -2-2PEAQ (6.5)	2	capacity fade: 0.00095%/cycle (0.01%/day), 336 cycles (32 days), 47.7 Ah L ⁻¹	<i>ACS Appl. Energy Mater.</i> , 2023 , 6, 12259.
2,7-AQDS (5.4)	0.4	120 cycles, 7.5 Ah L ⁻¹ , 56% EE at 60 mA cm ⁻²	<i>Adv. Energy Mater.</i> , 2024 , 14, 2400022.
dex-NDI (2.5)	2.4	no capacity decay, 100 cycles (6.7 days), 54.4 Ah L ⁻¹ , 83% EE at 40 mA cm ⁻²	<i>Angew. Chem. Int. Ed.</i> , 2024 , 63, e202405427.

DBEP (5.2)	1.2	capacity fade: 0.0012%/cycle (0.024%/day), 1024 cycles (50 days), 29.1 Ah L ⁻¹ , 88.1% EE at 50 mA cm ⁻²	<i>J. Am. Chem. Soc.</i> , 2024 , 146, 3293.
NDI-DEtOH (2.7)	0.2	capacity fade: 0.045%/cycle (4.5%/day), 400 cycles (4 days), ~ 3.6 Ah L ⁻¹ , ~ 72% EE at 40 mA cm ⁻²	<i>Mater. Horiz.</i> , 2024 , 11, 1283.
[(NPr) ₂ SV]Cl ₄ (1.9)	1	capacity fade: 0.034%/cycle, 125 cycles, 23.6 Ah L ⁻¹ , 82.7% EE at 40 mA cm ⁻²	<i>Energy Storage Mater.</i> , 2024 , 73, 103824.
3HAAQ (6.4)	0.2	40 cycles, ~ 2.3 Ah L ⁻¹ , < 50% EE at 40 mA cm ⁻²	<i>Adv. Energy Sustain. Res.</i> , 2024 , 5, 2400118.
SulEstC1- α ViO (2.3)	0.1	capacity fade: 0.055%/cycle (3.19%/day), 300 cycles, ~ 2.3 Ah L ⁻¹ , < 70% EE at 30 mA cm ⁻²	<i>ACS Appl. Mater. Interfaces</i> , 2024 , 16, 28645.
MMV (3.4)	0.8	capacity fade: 0.05%/cycle, 500 cycles, ~8.5 Ah L ⁻¹ , 71% EE at 60 mA cm ⁻²	<i>J. Mater. Chem. A</i> , 2024 , 12, 25934.
3-AFNQ (7.2)	1	capacity fade: 0.01%/cycle (0.27%/day), 500 cycles (13.8 days), 23.7 Ah L ⁻¹ , < 70% EE at 80 mA cm ⁻²	<i>ACS Energy Lett.</i> , 2024 , 9, 586-593.
1,4-CDHAQ (6.7)	0.8	capacity fade: 0.008%/cycle (0.28%/day), 2500 cycles (72 days), 15.9 Ah L ⁻¹ , 84% EE at 40 mA cm ⁻²	<i>Electrochim. Acta</i> , 2024 , 475, 143570.
Cys-DHAQ (3.9)	1	capacity fade: 0.00096%/cycle (0.05%/day), 600 cycles (11.5 days), 24.5 Ah L ⁻¹ , 78.8% EE at 100 mA cm ⁻²	<i>Nat Commun.</i> , 2025 , 16, 4727.
Cys-AE (5.4)	1	capacity fade: 0.00031%/cycle (0.013%/day), 800 cycles (19.1 days), 23.8 Ah L ⁻¹ , 80% EE at 100 mA cm ⁻²	<i>Nat. Commun.</i> , 2025 , 16, 2965.
(CBu) ₂ NDI (3.3)	2	no capacity fade, 220 cycles (~27 days), 44.1 Ah L ⁻¹ , 80% EE at 20 mA cm ⁻²	<i>Natl. Sci. Rev.</i> , 2025 , 12, nwaf123.
TMAP-bisV (2.9)	1.5	no capacity fade, ~50 cycles, 27.6 Ah L ⁻¹ , 80% EE at 30 mA cm ⁻²	<i>Angew. Chem. Int. Ed.</i> , 2025 , 64, e202501458.
Ph-BTMAP-Vi (3.1)	2	capacity fade: 0.095%/cycle (0.75%/day), 200 cycles (25.4 days), ~37 Ah L ⁻¹ , 79% EE at 60 mA cm ⁻²	<i>Angew. Chem. Int. Ed.</i> , 2025 , 137, e202514131.
PEG2-BPy-PEG2-2Cl (2.5)	1	capacity fade: 0.037%/cycle (0.29%/day), 94 cycles (12 days), 23.6 Ah L ⁻¹ , > 65% EE at 40 mA cm ⁻²	<i>ACS Appl. Energy Mater.</i> , 2025 , 8, 181.
PQQPS (3.8)	1	capacity fade: 0.003%/cycle (0.13%/day), 800 cycles (18 days), 22.63 Ah L ⁻¹ , 70% EE at 80 mA cm ⁻²	<i>Nano Energy</i> , 2025 , 144, 111404.
PPA (10)	3	capacity fade: 0.032%/cycle (0.095%/day), 225 cycles (80 days), 68.2 Ah L ⁻¹ , 86% EE at 20 mA cm ⁻²	<i>Adv. Sci.</i> , 2025 , 12, e14452.
BTMEP-Vi (3.4)	0.2	capacity fade: 0.04%/cycle (14.88%/day), 300 cycles (19.4 h), 3.6 Ah L ⁻¹ , 67.7% EE at 100 mA cm ⁻²	<i>ACS Omega</i> , 2025 , 10, 18641.
DAPQ (8.6)	2.4	capacity fade: 0.00034%/cycle (0.0069%/day), 110 cycles (~ 5.4 days), 53.5 Ah L ⁻¹ , 73.8% EE at 100 mA cm ⁻²	<i>J. Am. Chem. Soc.</i> , 2025 , 147, 46582.

Supplementary Table 3. Comparative analysis of V₂O₅ and TA.

Materials	V ₂ O ₅	TA
Redox reaction	$V^{3+} + e^- \leftrightarrow V^{2+}$	$\sim S-S \sim + 2e^- \leftrightarrow 2 \cdot S \sim$
Price (US\$ kg ⁻¹)	14.1	5.3
Molecular weight (g mol ⁻¹)	181.9	206.3
Cost per stored charge (US\$ kWh ⁻¹)	43	18
Toxicity	Carcinogen	Endogenous
Achieved capacity (Ah L ⁻¹)	< 80	128
Supporting electrolyte	Strong acid	Near neutral

Supplementary Note 2

Techno-economic analysis of an oligo(disulfide)s-based RFB

Techno-economic analysis was performed based on a reported PSIB (*Nat. Energy*, **2021**, 6, 517) that features a similar battery structure with the oligo(disulfide)s-based RFB. An RFB stack (Fig. 4b) was used to calculate the techno-economic. The corresponding material costs were obtained from the PSIB system reported above or from *www.alibaba.com*. Also, the corresponding analysis parameters were based on the PSIB system reported above.

The cost per stored charge (CPSC) for active materials was calculated using the following formula, as shown in Supplementary Table 4:

$$\text{CPSC} = \frac{\text{Cost per kg}}{\text{Capacity per kg}}$$

Supplementary Table 4. Price, capacity, and CPSC of PT and S₂K₂.

Materials	Price (US\$ kg ⁻¹)	Molecular weight (g mol ⁻¹)	Capacity (Ah kg ⁻¹)	CPSC (US\$ kWh ⁻¹)
S ₂ K ₂	0.5	142	377	1.3
PT	6.1	244	220	27.7

Supplementary Table 5. Cost of materials for constructing a RFB with a capacity of 1 kWh.

	Anolyte cost			Catholyte cost	
	PT	KCl	SCoPc	K ₄ [Fe(CN) ₆] + Na ₄ [Fe(CN) ₆]	KCl
Material usage	18.4 M (4.5 kg)	12.3 M (0.9 kg)	1.8 g	18.4 M + 18.4 M (6.8 kg + 5.6 kg)	36.8 M (2.7 kg)
Price US\$ kg ⁻¹	6.1	0.3	28	2.2 + 1.7	0.3
Cost (US\$)	27.5	0.27	0.05	15 + 9.5	0.8
Total cost (US\$)		27.8			25.3

We then assumed an RFB with an energy capacity of 1000 Wh. The total electrolyte volume (V) is:

$$V = \frac{\text{Capacity}}{\text{Energy density}} = \frac{1000 \text{ Wh}}{15 \text{ Wh L}^{-1}} = 66.7 \text{ L}$$

The unit tank cost is US\$0.15 L⁻¹; thus, the total tank cost (C_{tank}) is:

$$C_{\text{tank}} = 66.7 \text{ L} \times \text{US\$}0.15 \text{ L}^{-1} = \text{US\$}10$$

The total cost of materials (C_{material}), which includes active materials and supporting salts, is:

$$C_{\text{material}} = \frac{C_{\text{anolyte}} + C_{\text{catholyte}}}{V_d} = \frac{27.8 + 25.3}{0.82} = \text{US\$}65$$

V_d is the discharge voltage (0.82 V) at 40 mA cm⁻².

The investment cost energy (C_{energy}) is calculated as follows:

$$C_{\text{energy}} = \frac{C_{\text{material}} + C_{\text{tank}}}{\epsilon_{\text{sys,d}} \epsilon_{\text{q,rt}} \epsilon_{\text{v,d}}}$$

Where $\varepsilon_{v,d}$ is the discharge voltage efficiency (0.7); $\varepsilon_{q,rt}$ represents the round-trip coulombic efficiency (0.9992); $\varepsilon_{sys,d}$ represents the system efficiency, which can be considered as 0.94. Thus, the C_{energy} is:

$$C_{energy} = \frac{US\$65 + US\$10}{0.7 \times 0.9992 \times 0.94} = US\$114$$

The cost of the battery stack per unit area ($US\$ m^{-2}$) includes the Nafion membrane, graphite felt, flow field, and other components, and can be assumed to be $US\$573 m^{-2}$. Thus, the power cost (C_p) is:

$$C_p = \frac{US\$573 m^{-2}}{\varepsilon_{sys,d} j_d V_d} = \frac{US\$573 m^{-2}}{0.94 \times 0.4 kA m^{-2} \times 0.82 V} = US\$1858 kW^{-1}$$

Where j_d is the working current density ($40 mA cm^{-2}$).

The energy-normalized installed cost ($C_{installed}$, $US\$ kWh^{-1}$) mainly includes C_{energy} , C_p , balance-of-plant cost (C_{bop}), and additional cost (C_{add}). Among the C_{bop} reflects the costs of attachments, such as pipelines and pumps, assumed to be $US\$202.5 kW^{-1}$, and the C_{add} reflects other costs of RFBs, such as operation and administration, assumed to be $US\$87.5 kW^{-1}$. Therefore, the $C_{installed}$ is calculated as follows:

$$C_{installed} = C_{energy} + \frac{C_p + C_{bop} + C_{add}}{t_d}$$

Where t_d represents the storage duration of the RFB, which is determined as the ratio of energy and power (E/P) of RFBs. When the t_d is 1 h, the $C_{installed}$ is:

$$US\$114 + \frac{US\$1858 + US\$87.5 + US\$202.5}{1 h} = US\$2262$$

When the t_d is 6 h, the $C_{installed}$ is:

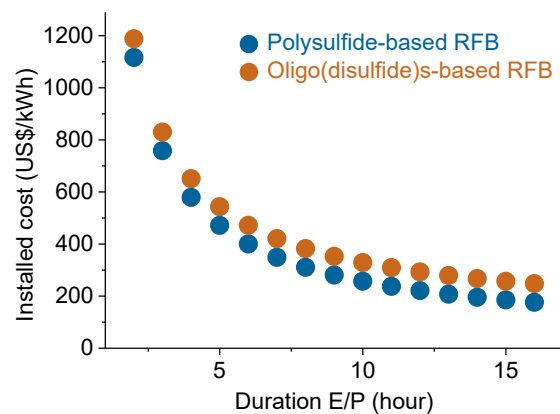
$$US\$114 + \frac{US\$1858 + US\$87.5 + US\$202.5}{6 h} = US\$472$$

Because the oligo(disulfide)s-based RFB is basically consistent with state-of-the-art inorganic polysulfide RFBs (*Nat. Energy* **2021**, 6, 517; *Nat Energy* **2023**, 8, 1355) in terms of operating voltage, current density, and battery structure composition. Thus, the C_p , C_{bop} , and C_{add} for both RFBs are theoretically close. Here, the C_p , C_{bop} , and C_{add} for a polysulfide RFB were chosen to be the same values as the oligo(disulfide)s-based RFB, and the C_{energy} for a polysulfide RFB is $US\$42.4$. Thus, the $C_{installed}$ is:

$$US\$42.4 + \frac{US\$1858 + US\$87.5 + US\$202.5}{t_d}$$

When the t_d is 6 h, the $C_{installed}$ is:

$$US\$42.4 + \frac{US\$1858 + US\$87.5 + US\$202.5}{6 h} = US\$400.4$$



Supplementary Fig. 69. Installed costs for polysulfide and oligo(disulfide)s RFBs with varying storage durations.

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