Supplementary Information

Intermolecular cyclic polysulfides as cathode materials for rechargeable

lithium batteries

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Experimental Section

Materials:

1,3-benzenedithiol was purchased from Toyko Chemical Industry (TCI). Sulfur was purchased from Aladdin. Toluene was purchased from Kermel. Carbon disulfide was purchased from J&K. The electrolyte is composed of 1.0 M LiTFSI and 0.1% LiNO₃ in mixture solvent of 1,2-dimethoxyethane (DME)/1,3-dioxolane (DOL) (1:1 v/v) which was purchased from Canrd. All reagents were used as received.

Synthesis of intermolecular cyclic polysulfides and electrode fabrication:

1,3-benzenedithiol (0.2 mmol, 28.5 mg) and sulfur (0.4 mmol, 12.8 mg) were dissolved in 1 mL of a mixture solvent of toluene/carbon disulfide (1:1 v/v). It was stirred continuously for 12 h to form a green transparent solution. To fabricate electrodes, commercial binder-free multi-walled carbon nanotube (CNT) paper called buckypaper was used as substrates. The paper was cut into ~1.1 cm² discs (d = 12 mm, about 2.0 mg each). Part of the reacted solution was added into the paper discs and the solvent was removed by heating at 60 °C for 12 h in a vacuum oven to form ICPSs/CNT electrodes.

Typical cell fabrication:

CR2032 type coin cells were fabricated inside an Ar-filled glove box. First, 20 μ L of blank electrolyte was added into an ICPSs/CNT electrode. Then a Celgard 2400 separator was placed on the top of the electrode followed by adding 20 μ L of blank electrolyte. This was topped off with a lithium foil and nickel foam spacer before the coin cell was crimped. The cell was taken out of the glove box for the electrochemical evaluation.

Electrochemical cell testing:

Cyclic voltammetry (CV) was performed on a Bio-Logic SAS VMP-3 potentiostat. The potential was swept from open circuit voltage (OCV) to 1.8 V and then swept back to 3.0 V at a scanning rate of 0.05 mV s⁻¹. Cells were galvanostatically cycled between 1.8 and 3.0 V on a LANHE battery cycler at different C rates ($1C = 623.4 \text{ mA g}^{-1}$).

Materials characterization:

X-ray diffraction (XRD) was conducted on a Rigaku MiniFlex600 X-ray diffractometer with Cu K α radiation. The samples were protected in the sample holder with kapton film. The scanning rate was 2° min⁻¹ between 10° and 70°. Fourier transform infrared (FTIR) absorption spectra were collected on NEXUS 470 FTIR spectrometer. The scanning region is from 400 cm⁻¹ to 4000 cm⁻¹. Raman spectroscopy was performed on Lab RAM HR Evolution Laser Raman spectrometer. Scanning electron microscopy (SEM) was performed on Phenom Pro. X-ray photoelectron spectroscopy (XPS) were performed with a 5000 VersaProbe II PS spectrometer with monochromatic Al Ka radiation. Ultrahigh performance

liquid chromatography quadrupole time-of-flight mass spectrometry (UPLC-QTof-MS, Waters Acquity UPLC coupled with a Xevo G2-XS QTof mass spectrometer) was used to analyze the synthesized, discharged, and recharged products of ICPS. The mass range was set between 50-1200 Da. The eluent consists of mobile phase A (water) and mobile phase B (acetonitrile). The used column is a Acquity UPLC BEH C18 with an inner diameter of 2.1 and 100 mm length. The injection volume of the samples was 2 μ L.

Computational methods:

All geometry optimizations were carried out with density functional theory (DFT) by using the M06-2X functional combined with the 6-31G(d) basis set.¹⁻³ Harmonic vibrational frequencies were obtained by analytical differentiation of gradients in order to determine the structures were local minima. The static electric field from DME and DOL is mimicked by using the solvation model based on density (SMD),⁴ and the static dielectric constant of DME was set to $\epsilon = 7.07$ at 298.15K.⁵ All the DFT calculation were implemented with the Gaussian 16 computational chemistry package.⁶ For the mechanisms of formation of three cyclic polysulfides, all the reactants, intermediates (transition states) and products were optimized. In particular, the optimized radical fragments were investigated with open-shell method at the M06-2X/6-31G(d) level, due to the adequate allowance for spin polarization. The 'stable=opt' was used to check the stability of the wavefunctions. The Milliken spin density were further calculated to make sure the spin density is highest locate on the center of the center atoms, such as sulfur atoms for 1,3-BDT in current system. Supporting figures and tables:



Figure S1. Optical images: (a) ICPSs in a mixture solvent of toluene/carbon disulfide (1:1 v/v); (b) lead acetate-based test strip was used to confirm the H₂S evolution.



Figure S2. MS of the aged HDBCO sample in air for six months.

Atoms	Х	Y	Ζ
С	-1.200897	1.803029	0.3330520
С	0.000000	1.726047	-0.368932
С	1.200897	1.803029	0.3330520
С	1.208191	2.024970	1.7117650
С	0.000000	2.156876	2.3910680
С	-1.208191	2.024970	1.7117650
Н	0.000000	1.573439	-1.444954
Н	0.000000	2.324316	3.463420
Н	-2.149452	2.077267	2.250459
S	-2.783076	1.671250	-0.499413
S	-2.533961	0.000000	-1.700549
S	-2.783076	-1.671250	-0.499413
С	-1.200897	-1.803029	0.333052
С	-1.208191	-2.024970	1.711765
С	0.000000	-2.156876	2.391068
С	1.208191	-2.024970	1.711765
С	1.200897	-1.803029	0.333052
С	0.000000	-1.726047	-0.368932
Н	-2.149452	-2.077267	2.250459
Н	0.000000	-2.324316	3.463420
Н	0.000000	-1.573439	-1.444954
Н	2.149452	-2.077267	2.250459
Н	2.149452	2.0772670	2.250459
S	2.783076	1.671250	-0.499413
S	2.783076	-1.671250	-0.499413
S	2.533961	0.000000	-1.700549

Table S1. Coordinate of HDBCO optimized with DFT at M062X/6-31G(d) level.



Figure S3. XIC of C₁₂H₈S₆.



Figure S4. XIC of $C_{18}H_{12}S_6$ (a) and $C_{18}H_{12}S_7$ (b); MS of $C_{18}H_{12}S_6$ (c) and $C_{18}H_{12}S_7$ (d).



Figure S5. UV absorption spectrum of the synthesized sample with the 1,3-BDT:sulfur ratio of 1:5 (a); and XIC of $C_{12}H_8S_6$ (b), $C_{18}H_{12}S_6$ (c), and $C_{18}H_{12}S_7$ (d).

carbon	carbon	hydrogen	hydrogen	sulfur	sulfur
(theoretical)	(experimental)	(theoretical)	(experimental)	(theoretical)	(experimental)
41.8%	42.1%	2.32%	2.43%	55.8%	56.7%

Table S2. The results of elemental analysis of ICPSs.



Figure S6. ¹H-NMR spectra of 1,3-BDT (a) and ICPSs (b).



Figure S7. FTIR spectra of ICPSs and sulfur between 400 to 700 cm⁻¹.



Figure S8. Raman spectra of ICPSs and sulfur.



Figure S9. XRD pattern of ICPSs and sulfur.



Figure S10. SEM image of an ICPSs/CNT electrode.



Scheme S1. The possible lithiation and delithiation processes of ICPSs in lithium batteries.



Figure S11. UPLC-QTof-MS of the discharged electrode. (a) XIC of 1,3-BDT; (b) MS of 1,3-BDT.



Figure S12. (a) XIC and (b) MS of HDBCO; (c) XIC and (d) MS of HTBCN; (e) XIC and (f) MS of HTBCD.



Figure S13. Voltage-profiles of a Li/ICPSs cell in different cycles at C/2 rate.



Figure S14. Rate performance of a Li/ICPSs cell.

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