

A fluorinated macrocyclic organodisulfide cathode for lithium organic battery

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Experimental:

Materials and chemicals

2,5-Difluorobenzene-1,4-dithiol ($C_6H_4F_2S_2$) was purchased from Shanghai KinaChemical Co. Ltd., the purity is 99%. Dimethyl sulfoxide (DMSO, 99.8%, Macklin), acetone (CH_3COCH_3 , 99.5%), trichloromethane ($CHCl_3$, $\geq 99.0\%$), methanol (CH_3OH , $\geq 99.0\%$), aligned multiwalled carbon nanotubes (CNTs, 95+%, OD: 10-20 nm, L: 30-100 μm , Nanostructured and Amorphous Materials, Inc.) were used as received. The electrolyte is composed of 1.0 M Lithium bis(trifluoromethanesulfonyl)amide (LiTFSI) and 1.0% lithium nitrate ($LiNO_3$) in a mixture solvent of 1,2-dimethoxyethane (DME)/1,3-dioxolane (DOL) (1:1 v/v) which was purchased from Canrd.

Synthesis of fluorinated macrocyclic organodisulfide (F-MCDS)

2,5-Difluorobenzene-1,4-dithiol (36 mg) was added to 144 μL of DMSO, and the solution became deep orange. After stirring for 1 h at room temperature, the crystal precipitated quickly and the solution color faded with the formation of the product. Then it was washed with acetone and dried in a vacuum oven at 50°C overnight. The light yellow solid was obtained. These procedures were carried out inside an argon-filled glovebox.

F-MCDS@CNTs electrode fabrication

F-MCDS (54 mg) and CNTs (70 mg) were dispersed in 400 mL of anhydrous ethanol through ultrasonication for 15 mins. Following this, the mixture was vacuum filtered onto a 7-cm-diameter filter paper. The filter cake was dried in a vacuum oven at 60 °C overnight. The filter cake was cut into small disks (diameter = 12 mm) and transferred into an argon-filled glovebox for further testing.

Cell fabrication and electrochemical evaluation

The mass loading of cathode material was determined by thermogravimetric analysis (TGA). The F-MCDS electrode has an active material loading of 2.0-2.3 mg. CR2032 type coin cells were fabricated inside the argon-filled glovebox. First, 20 μL of electrolyte was added into a F-MCDS electrode. Then a Celgard 2400 separator was placed on the top of the electrode followed by adding 20 μL of electrolyte. This was topped off with a lithium foil and nickel foam spacer before the coin cell was crimped. Cyclic voltammetry (CV) was performed on a Bio-Logic VSP electrochemical workstation. The potential was swept from open-circuit voltage to 1.9 V and then swept back to 3.0 V at a scanning rate of 0.05 $mV s^{-1}$. Cells were Galvanostatically cycled on a LAND battery cycler at various C-rates (1 C = 304.2 $mA g^{-1}$). The cells were discharged to 1.9 V at 0.1 C and 0.3 C, 1.8 V at 0.5 C, 1 C, and 2 C, 1.7 V at 3 C, and 1.6 V at 4 C to ensure material utilization. All cells were recharged to 3 V.

Materials characterizations

Materials characterizations were performed on cells that were cycled at 0.05 C rate to the appropriate cut-off voltage. Waters Xevo G2-XS QT mass spectrometer was used to

characterize the synthesized sample and the cycled products. The cathode was separated from the cell in the glovebox and then immersed in the mixture of chromatographic methanol and dimethyl sulfoxide (4:1 v/v) to obtain the solution of active material. At last, the solutions were transferred out of the glovebox and we used Atmospheric Solids Analysis Probe (ASAP) mass spectrometry to identify the charge-discharge products of F-MCDS during cycling. ASAP allows direct analysis of samples using an atmospheric pressure chemical ionization (APCI) source in the QToF-MS. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor II infrared spectrometer, which can directly test solid or liquid samples without tablet compression. The synthesized solid powder was directly placed on the test platform for measurement. Scanning electron microscopy (SEM) was performed on a Zeiss Sigma 500 SEM. Sulfur, fluorine, and carbon elemental mappings were carried out to understand the material distribution using energy-dispersive X-ray spectroscopy (EDS) detector attached to the SEM. X-ray diffraction (XRD) characterization was performed by Rigaku SmartLabSE X-ray diffractometer with Cu K α radiation source. The scanning rate was 2° min⁻¹ for 2 θ from 10° to 50°. Thermogravimetric Analysis (TGA) was tested by Mettler Toledo TGA2 Simultaneous Thermal Analyzer. The temperature test range was 30-800 °C, and the carrier gas was nitrogen.

Computational method

In this work, all the synthesized compounds of (C₆H₂F₂S₂)₂, (C₆H₂F₂S₂)₃ and (C₆H₂F₂S₂)₄ were calculated using density functional theory (DFT) at PBE0/def2SVP level by Gaussian 16 program,¹ the solvent effect was mimicked by the implicit solvent models based on the density (SMD) approach with the static dielectric constant of DOL/DME set to 7.07.^{2,3} The electrostatic potential involved in the analyses were evaluated by Multiwfn.⁴ based on the highly effective algorithm proposed in Ref S5.

Supporting Figures:

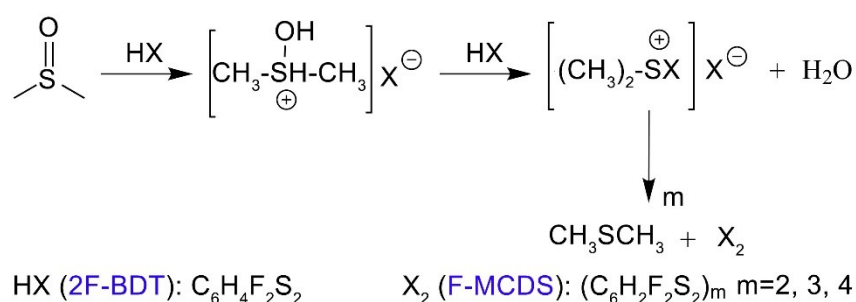


Figure S1. The proposed mechanism for the synthesis of macrocyclic organodisulfide (F-MCDS).

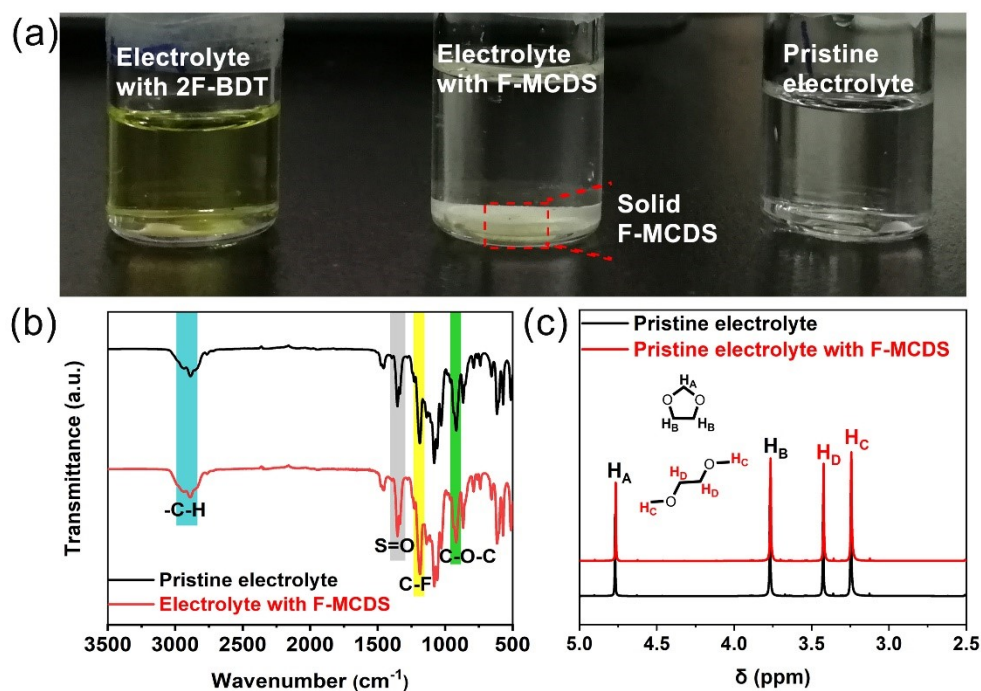


Figure S2. (a) Optical image of 2F-BDT and F-MCDS in the pristine electrolyte composed of 1.0 M LiTFSI and 1.0% LiNO_3 in a mixture solvent of DME/DOL (1:1 v/v). (b) FTIR spectra of electrolyte containing F-MCDS and blank electrolyte. (c) Comparison of ^1H NMR spectra of two different electrolytes.

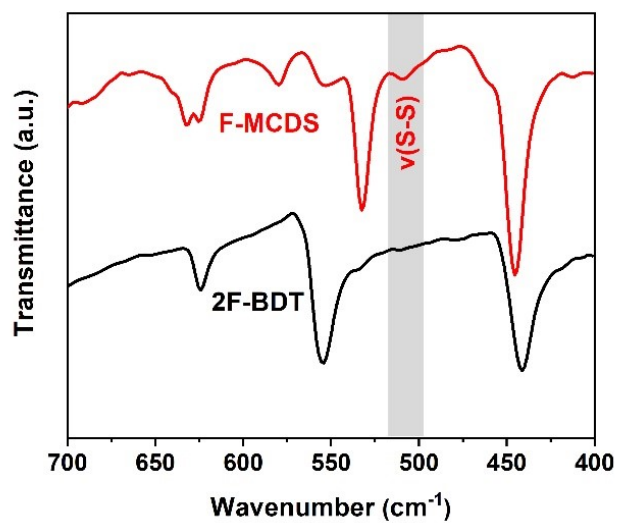


Figure S3. FTIR spectra of F-MCDS and 2F-BDT between 400 to 700 cm^{-1} .

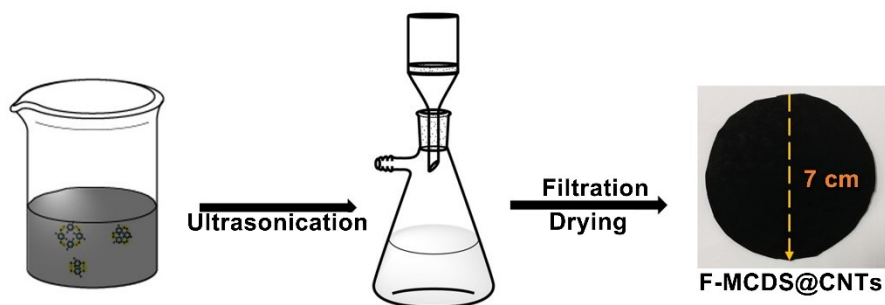
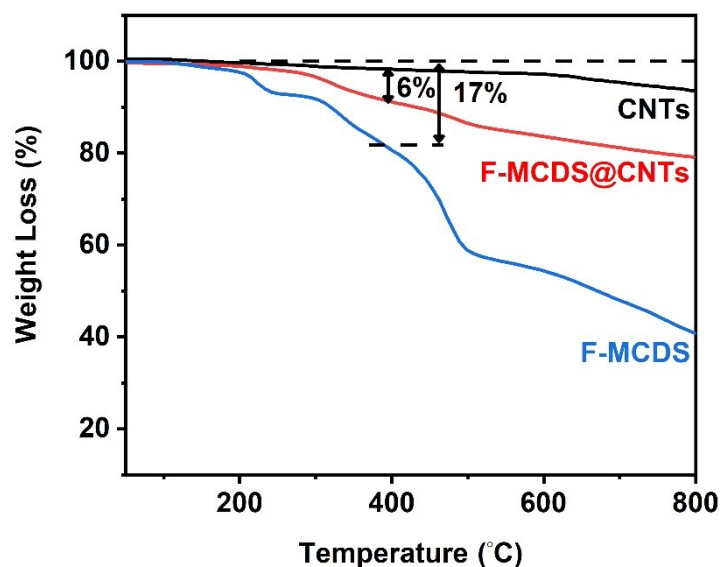


Figure S4. Schematic illustration of the experimental procedure for the preparation of the F-MCDS@CNTs composite electrode.



$$A_{F-MCDS} = \frac{W_{F-MCDS@CNTs}}{W_{F-MCDS}} M_{cathode}$$

Figure S5. TGA analysis of CNTs, F-MCDS and F-MCDS@CNTs composite. $W_{F-MCDS@CNTs}$ is the percentage of the mass reduction of F-MCDS@CNTs composite at 400°C (6%). W_{F-MCDS} is the weight loss percentage of F-MCDS at 400°C (17%). $M_{cathode}$ is the total mass of the F-MCDS@CNTs composite. A_{F-MCDS} is the mass of F-MCDS in the composite electrode. According to the formula, the F-MCDS@CNTs composite electrode contains ~35% F-MCDS.

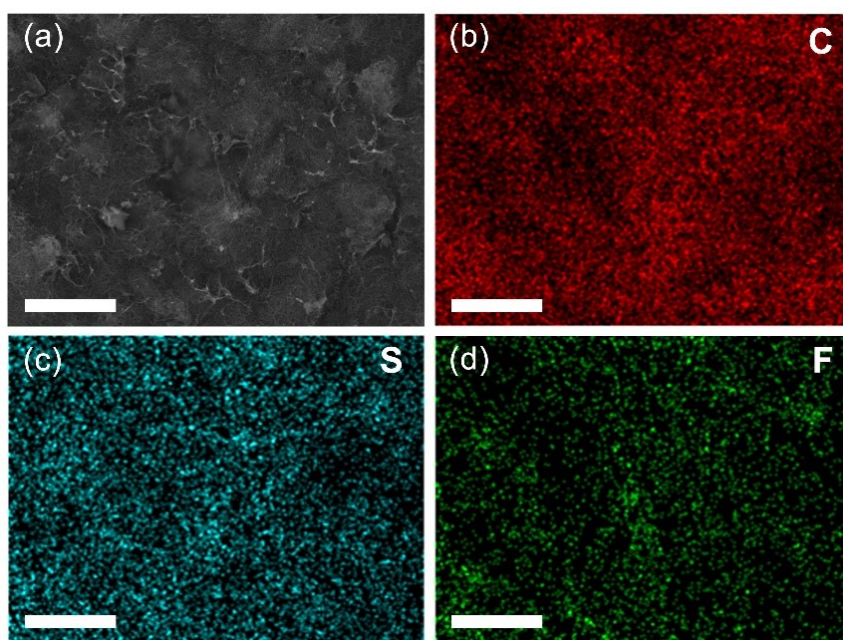


Figure S6. SEM image of the prepared F-MCDS@CNTs composite electrode (a) and EDS elemental maps for carbon (b), sulfur (c), and fluorine (d). All scale bars represent 5 µm.

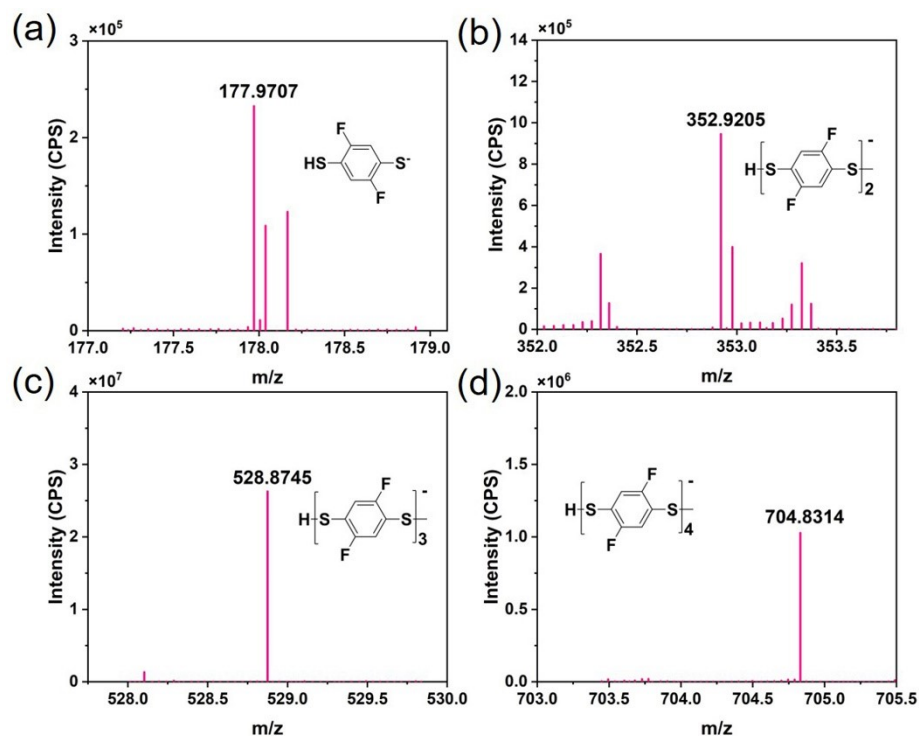


Figure S7. MS spectra of the intermediate products in the discharge of F-MCDS to 2.3 V.

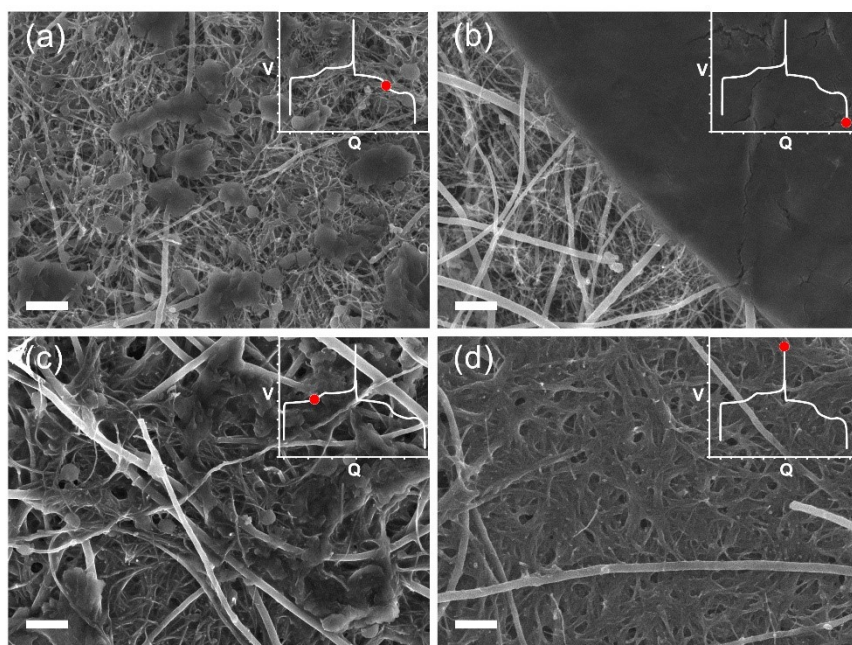


Figure S8. SEM images of the F-MCDS@CNTs composite cathode taken at different stages of cycling as represented by the inset figure. All scale bars represent 1 μm .

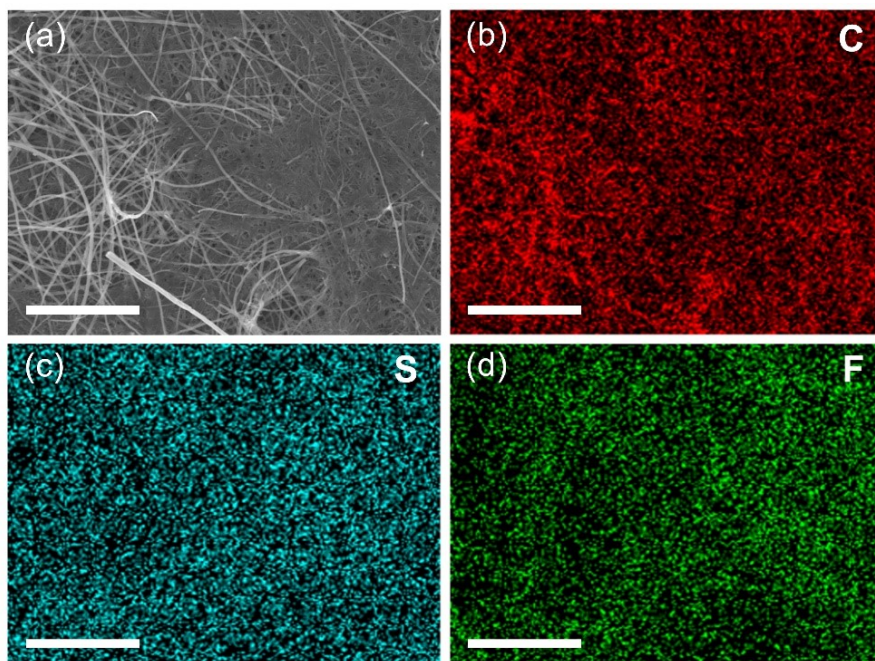


Figure S9. SEM image of the cathode after 5 cycles at the charged state (a) and EDS elemental maps for carbon (b), sulfur (c), and fluorine (d). All scale bars represent 10 μm .

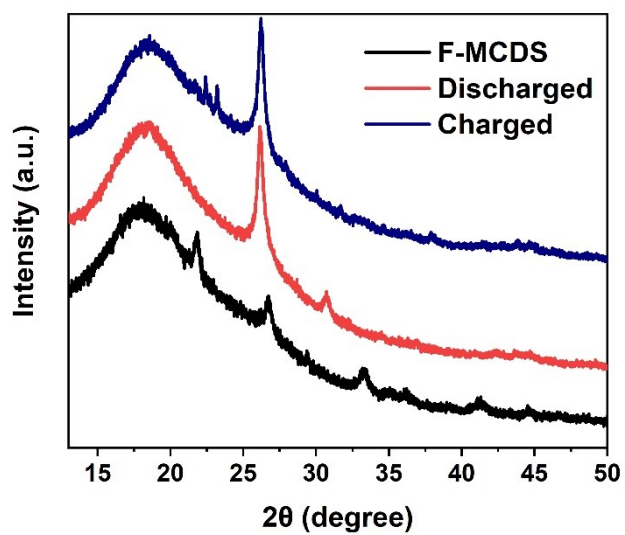


Figure S10. XRD patterns of pristine, discharged and charged F-MCDS.

Notes and references:

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