

**Single-ion quasi-solid-state electrolytes based on sulfonimide-functionalized covalent organic framework**

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## A. General Information

All commercially available reagents and solvents were used as received without further purification unless noted.

NMR spectra were taken on BRUKER AVANCE III 400 MHz and BRUKER AVANCE III HD 500 MHz. (CH<sub>3</sub>)<sub>2</sub>SO (2.5 ppm) was used as internal reference in <sup>1</sup>H NMR spectra, and (CH<sub>3</sub>)<sub>2</sub>SO (39.51 ppm) for <sup>13</sup>C NMR.

Solid-state <sup>13</sup>C NMR and <sup>7</sup>Li NMR were recorded on BRUKER AVANCE III HD 500 MHz. The FT-IR spectra of starting materials, intermediate product and as synthesized COFs were taken on NICOLET iS10. Thermogravimetric analyses (TGA) were tested on a Rigaku TG8120 under flowing N<sub>2</sub> with 10 K min<sup>-1</sup> ramp rate to 1073K. The morphologies of COFs samples were observed by a scan electron microscopy (SEM) (S-4800) equipped with a camera operated at 20 kV. The powder X-ray diffraction pattern (PXRD) were tested on a BRUKER D8 ADVANCE diffractometer with a Cu K $\alpha$  X-ray source ( $\lambda = 1.540598 \text{ \AA}$ ).

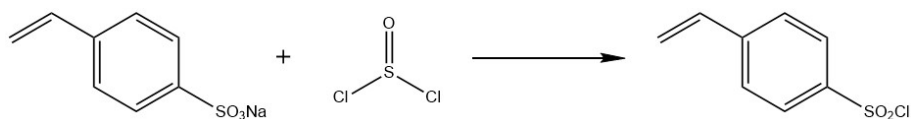
The Micromeritics ASAP 2020 automatic volumetric instrument was used to measure N<sub>2</sub> adsorption isotherm. The samples were heated at 373 K under vacuum for 6 hours for activation. Ultra-high purity grade (99.999% purity) N<sub>2</sub> were used for all free space corrections and measurements. The gas adsorption tests were under 77 K which was controlled by using a refrigerated bath of liquid N<sub>2</sub>. The surface areas were measured with the data based on the Brunauer-Emmett-Teller (BET) model. The pore size distribution of the samples was calculated by nonlocalized density functional theory (NLDFT).

Elemental analysis was performed at center of modern analysis of Nanjing University, by using analytik jena novAA350/ZEE nit650p analyzer. The lithium content was measured through atomic absorption spectroscopy.

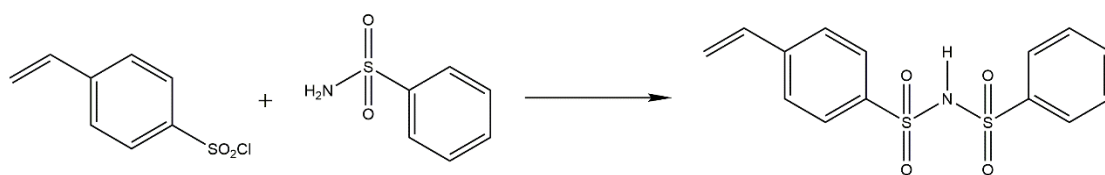
Ionic conductivity, lithium transference numbers were performed on CHI660E from CH instruments.

Battery performances were test on LAND system.

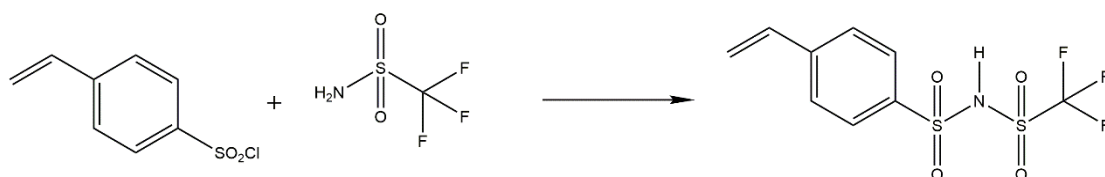
## B. Synthetic Procedures



**Synthesis of 4-vinylbenzenesulfonyl chloride:** To a three-neck round-bottomed flask, sodium 4-vinylbenzenesulfonate (14.7g, 72 mmol) and dried DMF (75 mL) were added under Ar atmosphere, thionyl chloride (7.5 mL, 86 mmol) was slowly added into the solution in 15 minutes with ice-water bath. After drip process, the solution mixture was stirred for 10 minutes at room temperature, then reacted at 333 K for 2 hours. After cooling down to room temperature, the solution mixture was drip into icy water, and extracted by ether (80 mL each time, 3 times). After dried by using anhydrous sodium sulfate, the red-orange liquid product was obtained by using a rotavapor. The product was used in next step without further purification. The physical data of the product:  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ): ;  $^{13}\text{C}$  NMR (400 HMz, DMSO- $d_6$ ): .

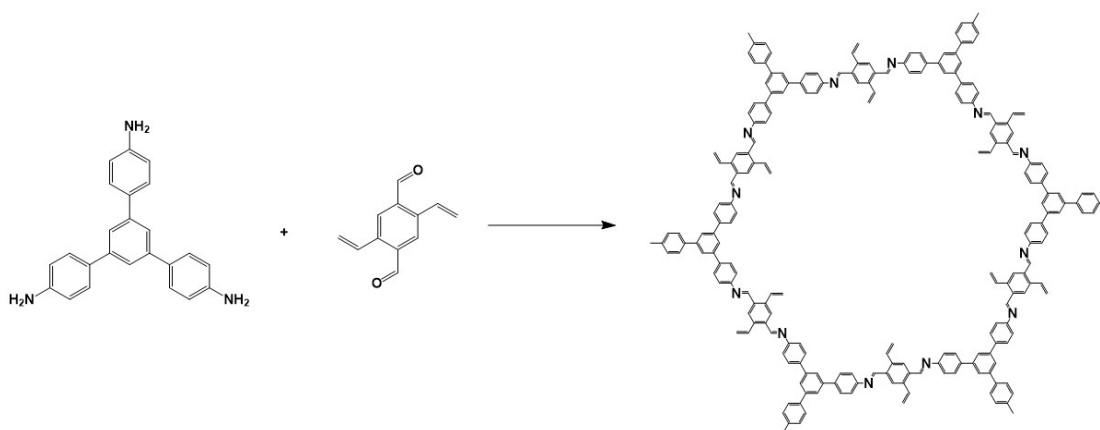


**Synthesis of 4-bz-SPSI:** To a three-neck round-bottomed flask, 4-vinylbenzenesulfonyl chloride (3.92 g, 19.3 mmol) were added under Ar atmosphere, the solution mixture that contained dried acetonitrile (20 mL), trimethylamine (9.25 mL, 66.2 mmol), DMAP (0.54g, 4.4 mmol) and benzenesulfonamide (3.46g, 22.0 mmol) was added in 15 minutes with ice-water bath. After drip process, the solution mixture was stirred at 358 K for 3 hours. The yellow-brown solution was washed by 4wt %  $\text{NaHCO}_3$  (20 mL each time, 3 times), and 1 M HCl (20 mL each time, 2 times). After dried by using anhydrous sodium sulfate, the product was obtained by using a rotavapor. The product was used in next step without further purification.

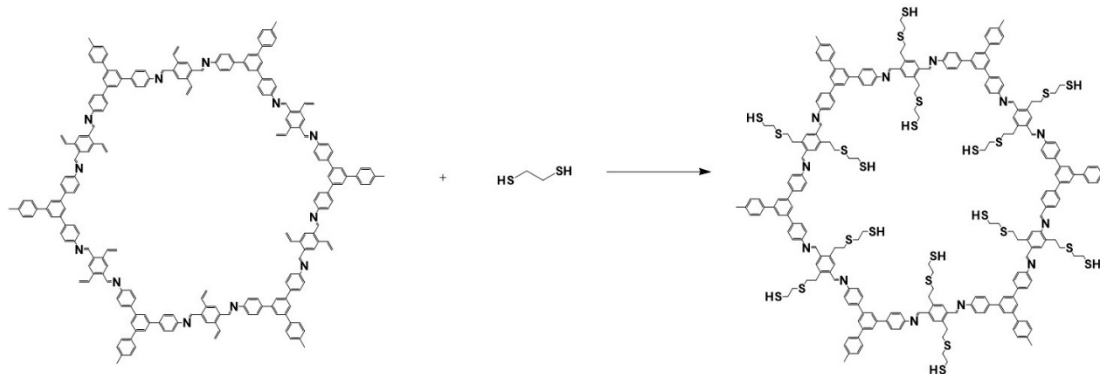


**Synthesis of 4-bz-TFSI:** To a three-neck round-bottomed flask, 4-vinylbenzenesulfonyl chloride (3.92 g, 19.3 mmol) were added under Ar atmosphere, the solution mixture that contained dried

acetonitrile (20 mL), trimethylamine (9.25 mL, 66.2 mmol), DMAP (0.54g, 4.4 mmol) and trifluoromethanesulfonamide (3.28g, 22.0 mmol) was added in 15 minutes with ice-water bath. After drip process, the solution mixture was stirred at 358 K for 3 hours. The yellow-brown solution was washed by 4wt % NaHCO<sub>3</sub> (20 mL each time, 3 times), and 1 M HCl (20 mL each time, 2 times). After dried by using anhydrous sodium sulfate, the product was obtained by using a rotavapor. The product was used in next step without further purification.



**Synthesis of COF-V:** To a Pyrex tube, 2,5-divinylterephthalaldehyde (Dva) (0.06 mmol) and 1,3,5-tris(4-aminophenyl)benzene (Tab) (0.04 mmol) were added. Then 5 mL of a 1:1 (v:v) solution of mesitylene:dioxane and 0.5 mL of 6 M acetic acid were added to the tube and the solution mixture was sonicated for 1 hour. The tube was flash frozen at 77 K (liquid N<sub>2</sub> bath), evacuated to an internal pressure of 150 mtorr and flame sealed. The reaction mixture was heated at 373 K for 72 h yielding a yellow solid at bottom of the tube which was isolated by filtration and washed with acetone (30 mL). The powder was dried under high vacuum at 358 K for 24 hours.



**Synthesis of COF-S-SH:** To a round-bottomed flask, the mixture of COF-V (100 mg) and

azobis(isobutyronitrile) (AIBN, 10 mg) were added. 1,2-ethanedithiol (4.0 mL) was introduced under Ar atmosphere. After stirring at 353 K for 48 hours, the product was isolated by filtration, washed with acetone 3 times, and dried under high vacuum at 353 K for 24 hours.

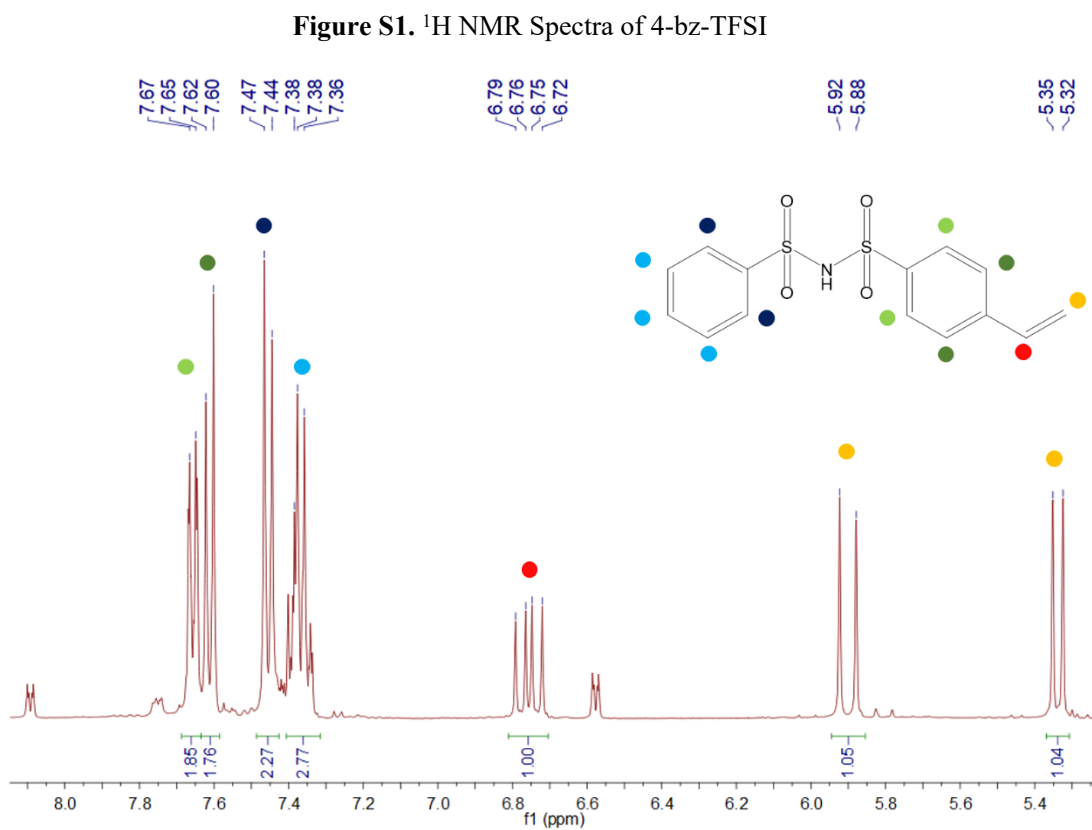
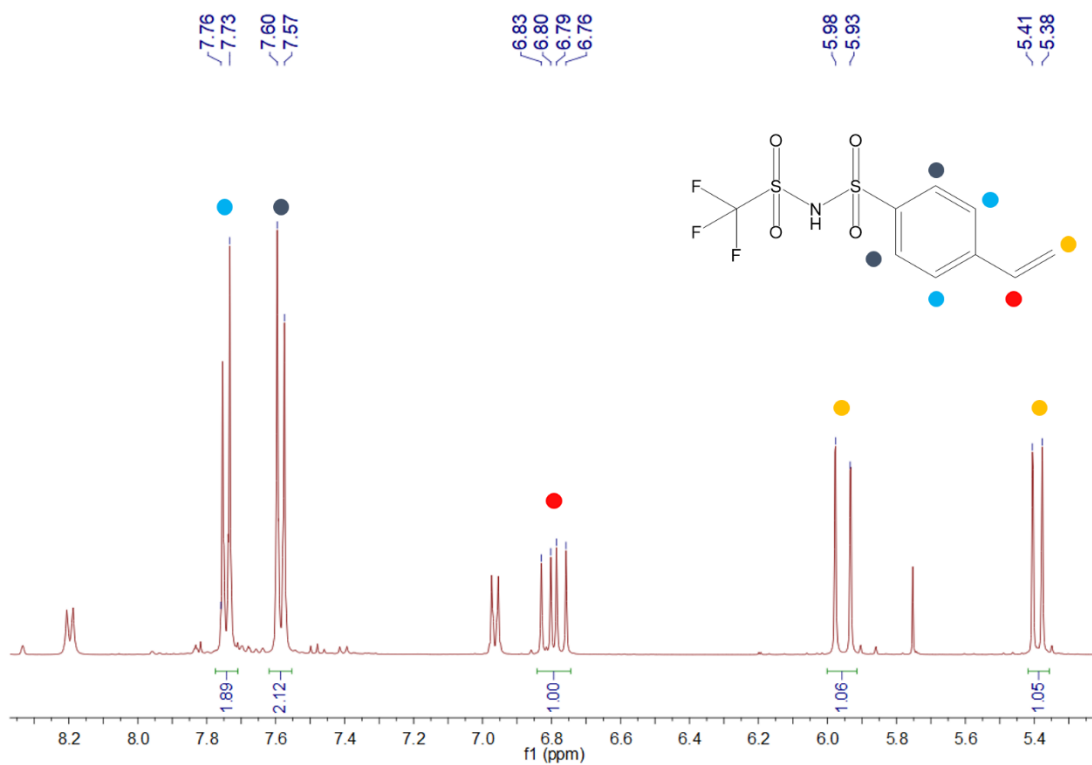
**Synthesis of COF-S-S-SPSI:** To a round-bottomed flask, COF-S-SH (100 mg) and 4-bz-SPSI (117 mg) were added with azobis(isobutyronitrile) (AIBN) (10 mg) and 4 mL of DMF under Ar atmosphere. After stirring at 353 K for 48 hours, the product was collected by filtration, washed with acetone 3 times, and dried under high vacuum at 353 K for 24 hours.

**Synthesis of COF-S-S-TFSI:** To a round-bottomed flask, COF-S-SH (100 mg) and 4-bz-TFSI (116 mg) were added with azobis(isobutyronitrile) (AIBN) (10 mg) and 4 mL of DMF under Ar atmosphere. After stirring at 353 K for 48 hours, the product was collected by filtration, washed with acetone 3 times, and dried under high vacuum at 353 K for 24 hours.

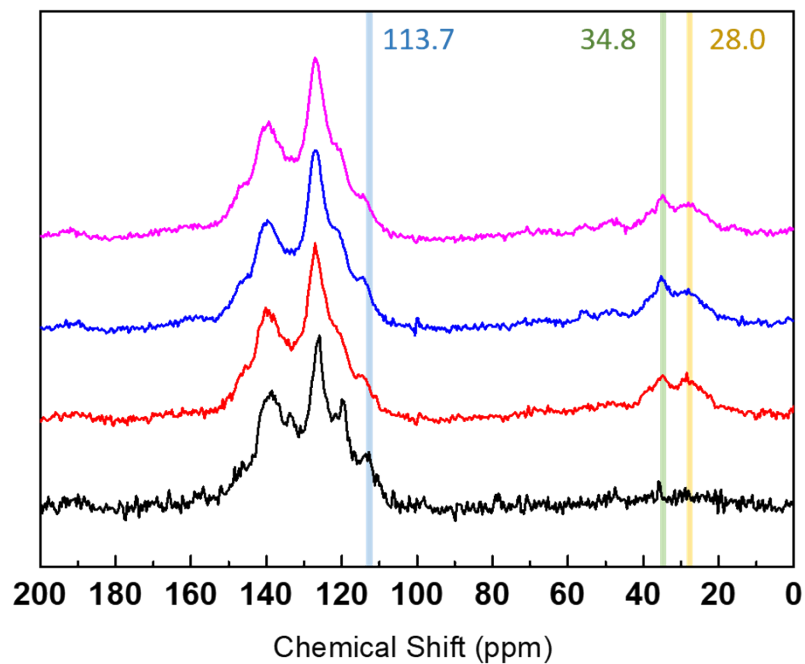
**Synthesis of COF-S-S-SPSILi:** To a round-bottomed flask, COF-S-S-SPSI (100 mg) and 4wt % LiOH (5 mL) were added. After stirring for 24 hours, the yellow-brown powder was collected by vacuum filtration. The final product was obtained by dialysis for 24 hours, and dried under vacuum at 353 K for 24 hours.

**Synthesis of COF-S-S-TFSILi:** To a round-bottomed flask, COF-S-S-TFSI (100 mg) and 4wt % LiOH (5 mL) were added. After stirring for 24 hours, the yellow-brown powder was collected by vacuum filtration. The final product was obtained by dialysis for 24 hours, and dried under vacuum at 353 K for 24 hours.

### C. <sup>1</sup>H NMR Spectra of 4-bz-TFSI and 4-bz-SPSI

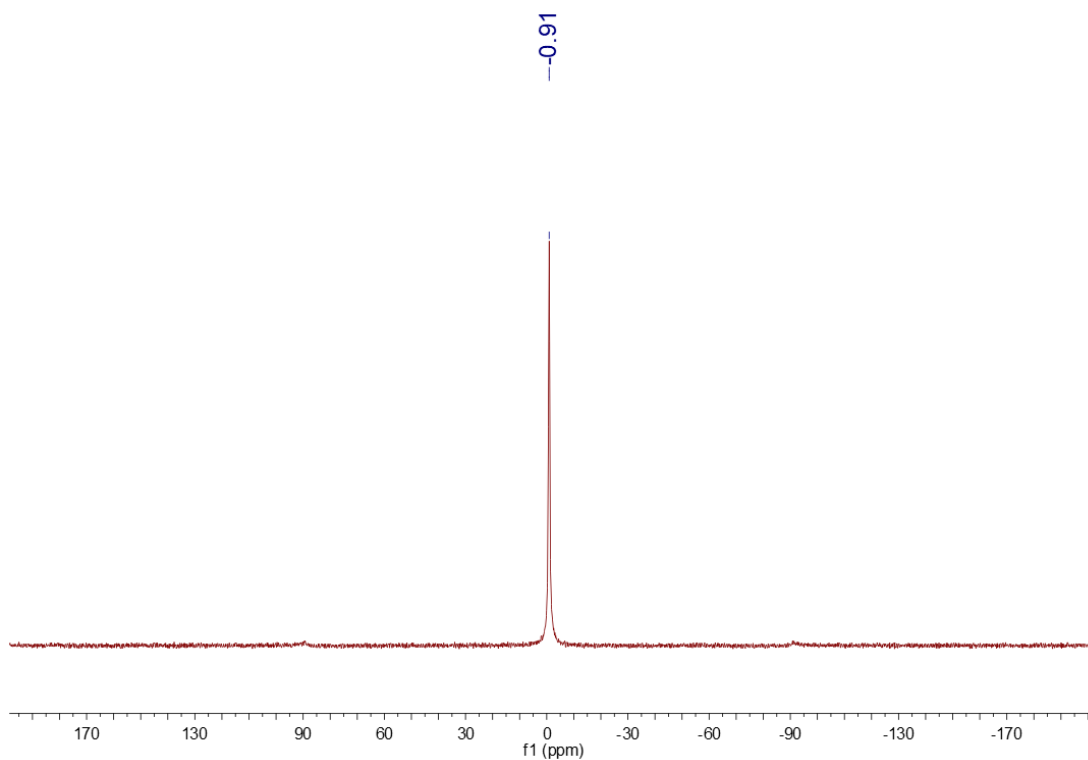


#### D. $^{13}\text{C}$ Solid-state NMR Spectra of COFs



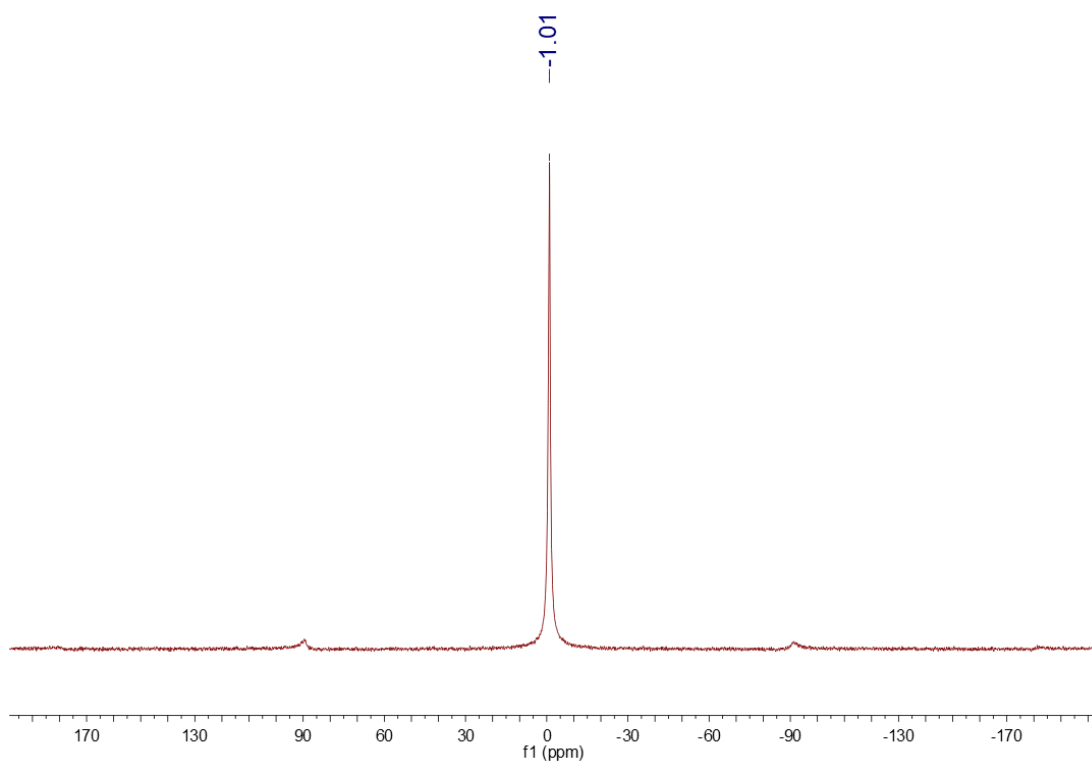
**Figure S3.**  $^{13}\text{C}$  Solid-state NMR spectrum of COF-V(black), COF-S-SH(red), COF-S-S-TFSiLi(blue) and COF-S-S-SPSiLi(purple)

**E.  $^7\text{Li}$  Solid-state NMR Spectra of COFs**

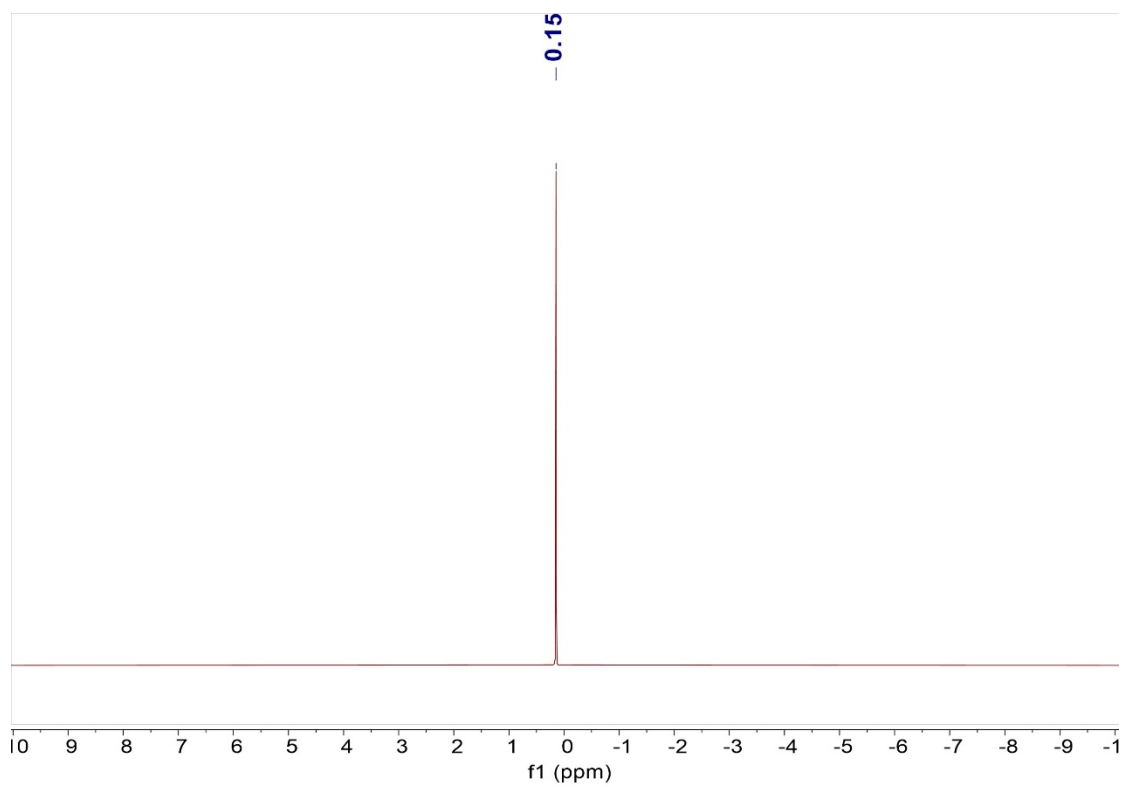


**Figure S4.**  $^7\text{Li}$  Solid-state NMR spectrum of COF-S-S-TFSiLi



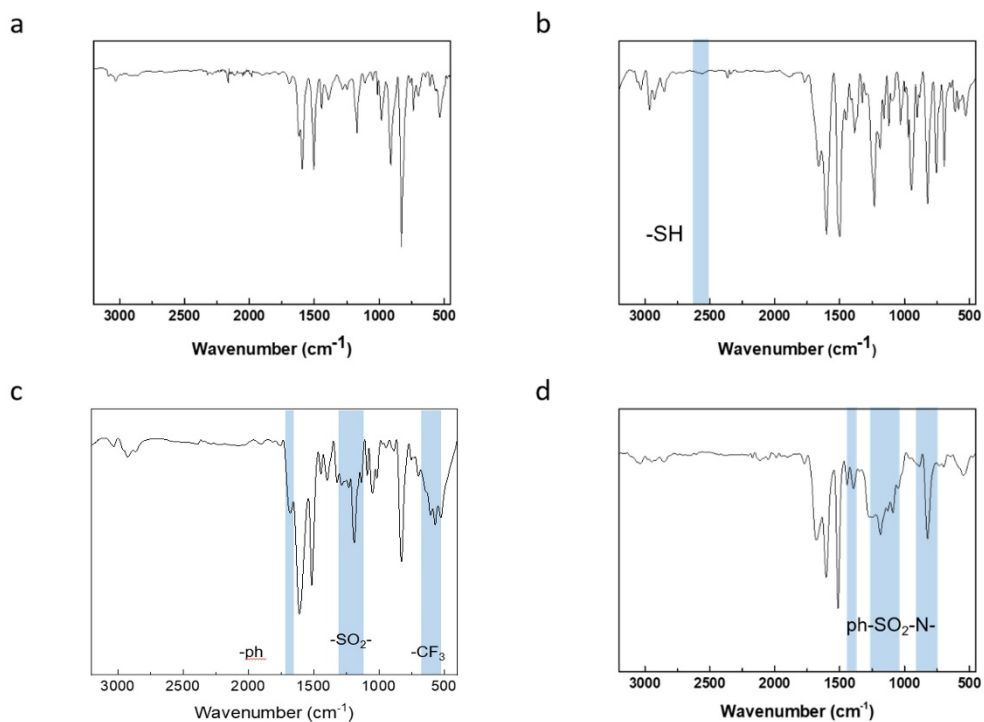


**Figure S5.**  ${}^7\text{Li}$  Solid-state NMR spectrum of COF-S-S-SPSILi

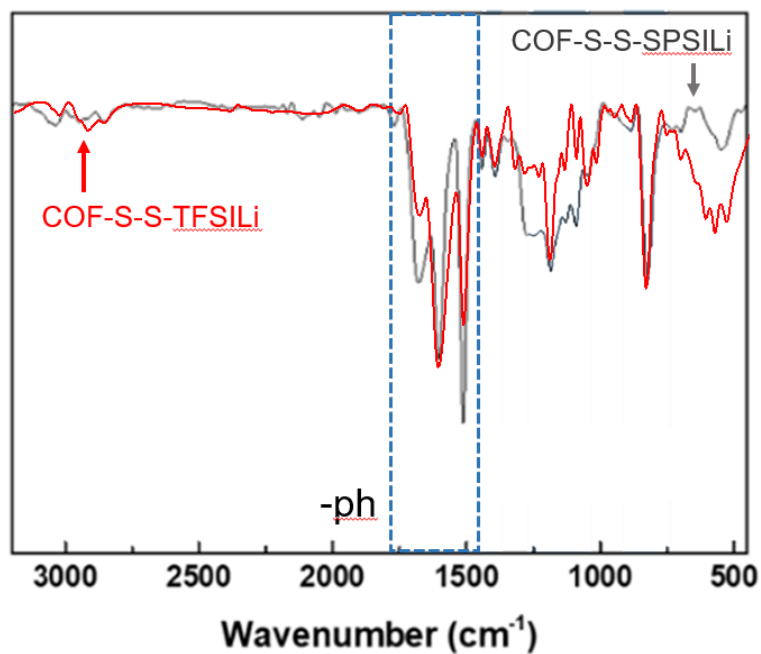


**Figure S6.**  ${}^7\text{Li}$  NMR spectrum of LiCl

## **F. FT-IR Spectra of the monomers and COFs**

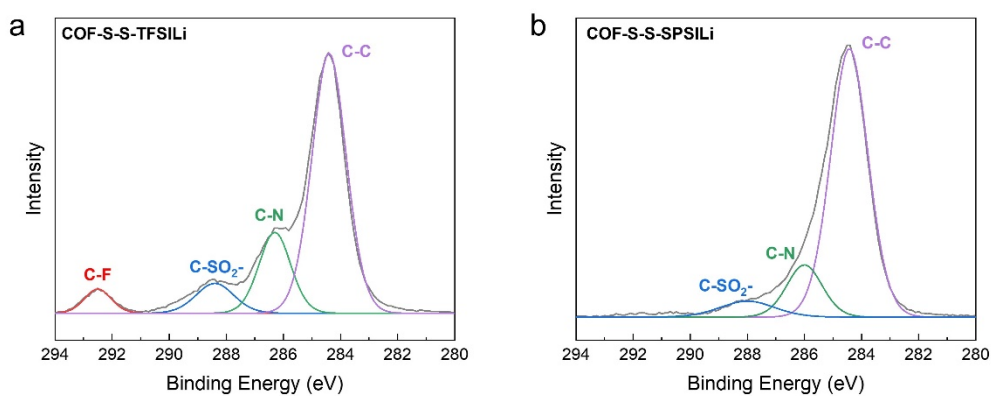


**Figure S7.** FT-IR spectra of COF-V (a), COF-S-SH (b), COF-S-S-TFSILi (c) and COF-S-S-SPSILi (d).



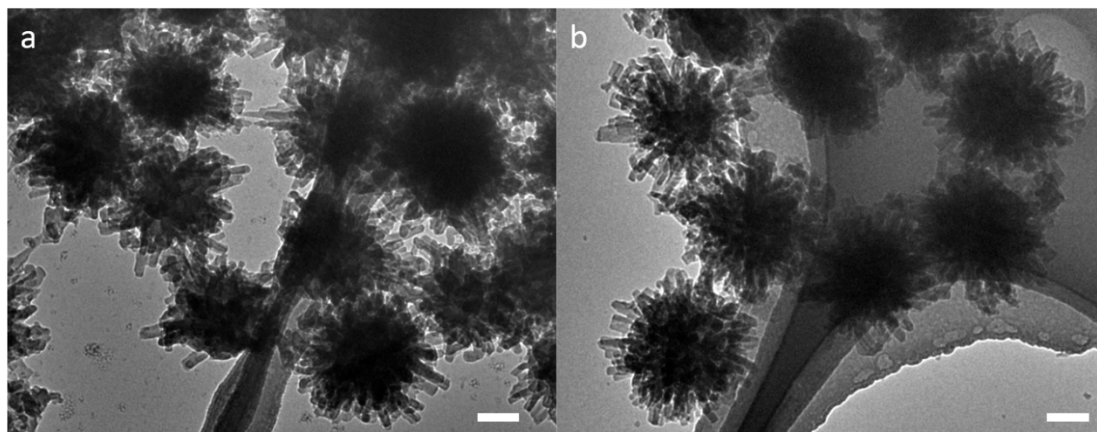
**Figure S8.** FT-IR spectra of COF-S-S-TFSILi (red) and COF-S-S-SPSILi (black).

### G. XPS of COF-S-S-TFSILi and COF-S-S-SPSILi



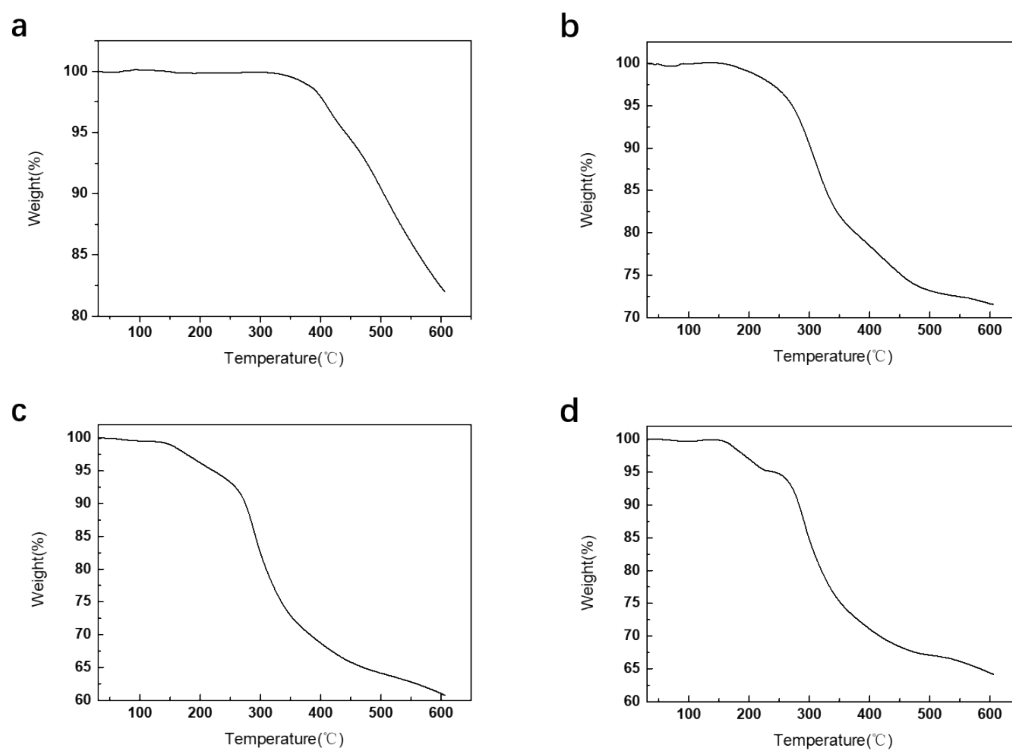
**Figure S9.** XPS of COF-S-S-TFSILi (a) and COF-S-S-SPSILi (b)

## H. TEM Images of COFs



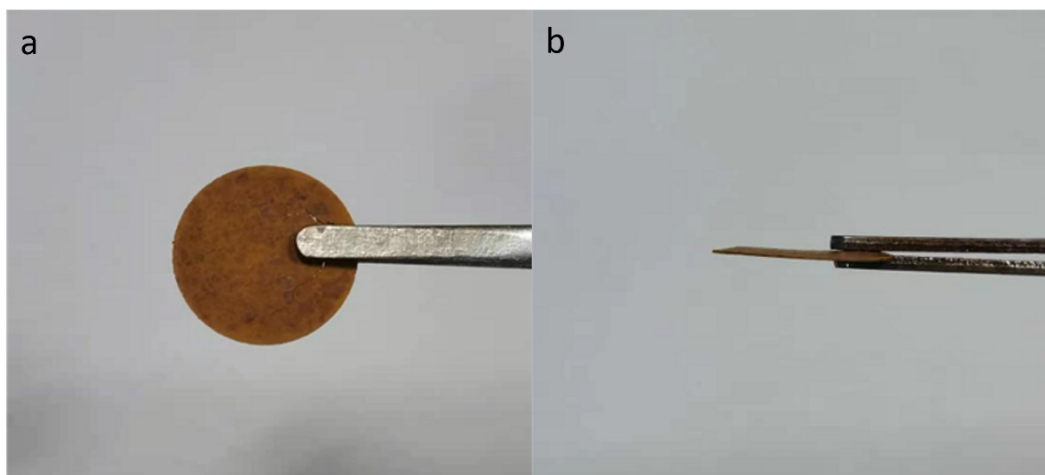
**Figure S10.** TEM images of COF-S-S-TFSILi (a) and COF-S-S-SPSILi (b). Scale bars: 200 nm

## I. TGA Analyses of COFs

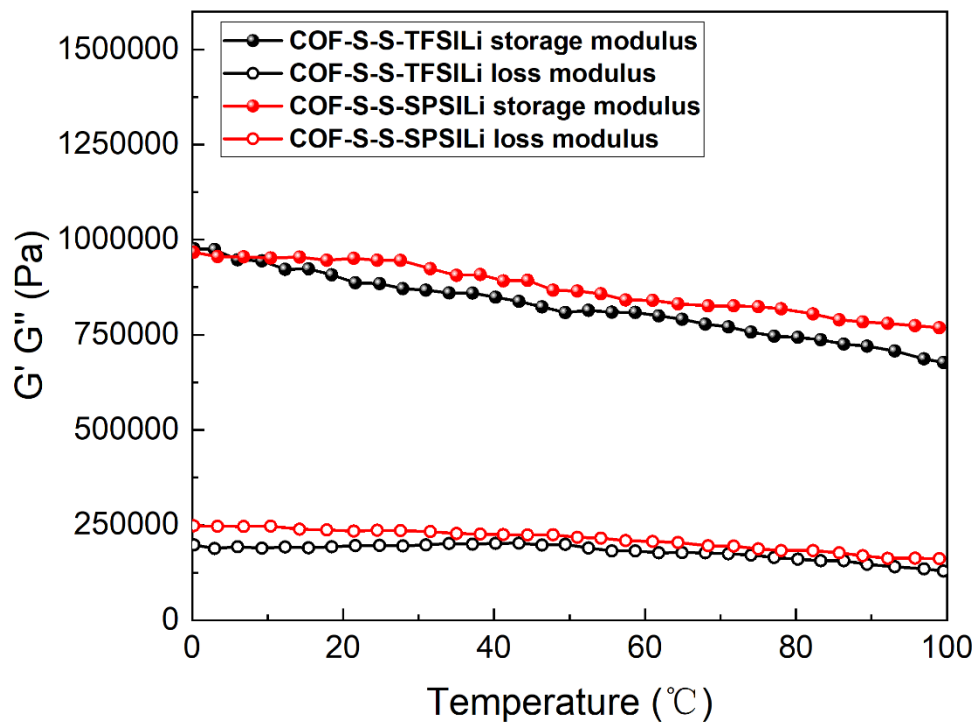


**Figure S11.** Thermogravimetric curves of COF-V(a), COF-S-SH(b), COF-S-S-TFSILi(c) and COF-S-S-SPSILi(d).

## J. Rheological and mechanical properties of COFs

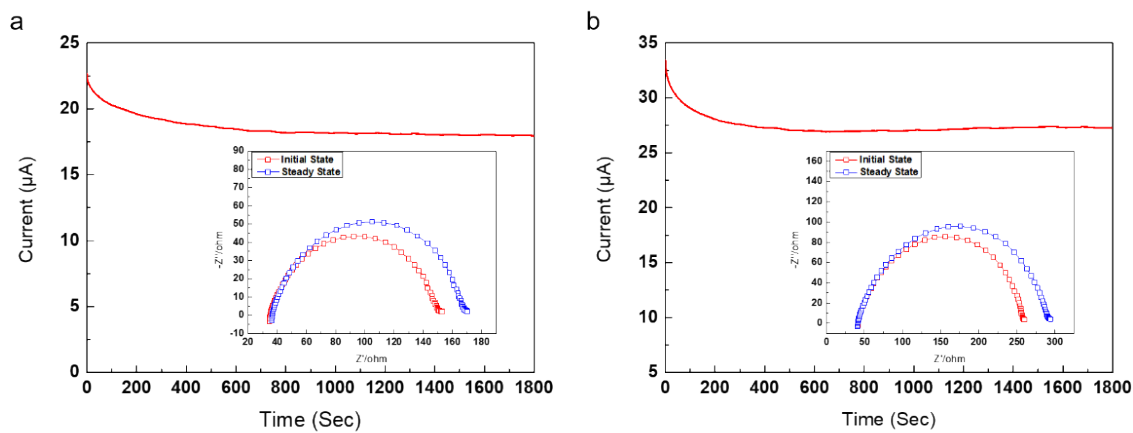


**Figure S12.** Images of COF based electrolyte film after soaked in PC

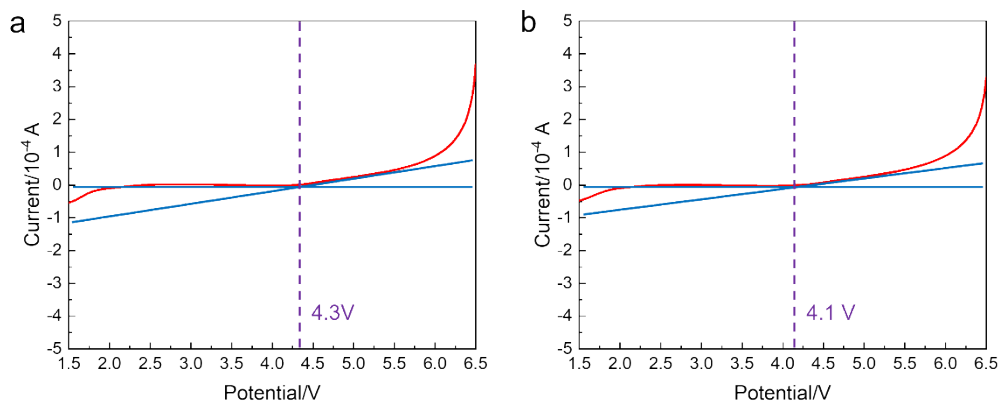


**Figure S13.** Rheology measurements of COF-S-S-TFSILi and COF-S-S-SPSILi

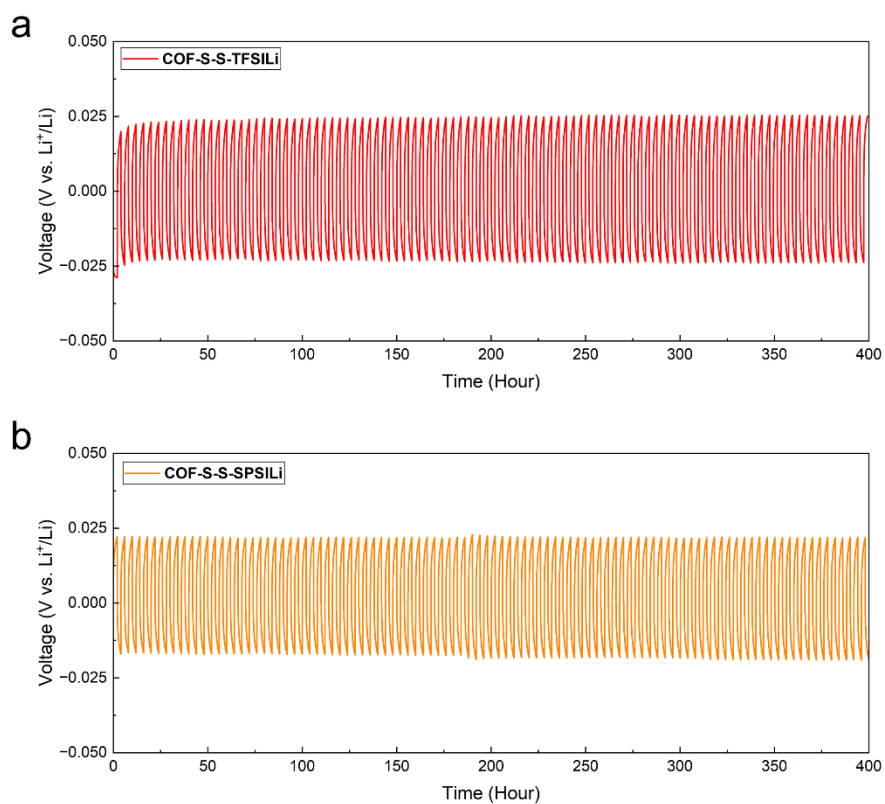
### K. Li-ion Conductivity Measurements



**Figure S14.** Lithium-ion transference number measurements of 4-bz-TFSILi@COF-V(a) and 4-bz-SPSILi@COF-V(b)

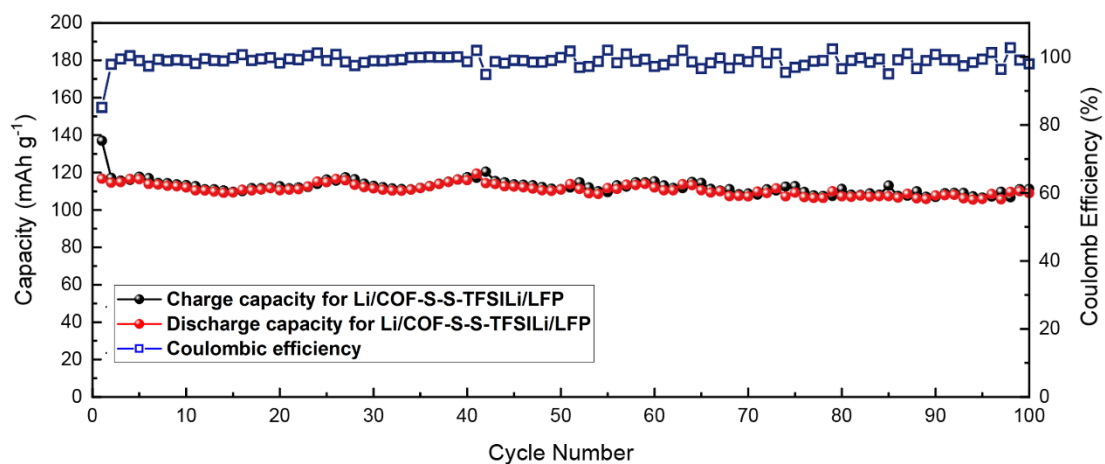


**Figure S15.** Electrochemical stable windows of COF-S-S-TFSILi(a) and COF-S-S-SPSILi(b)

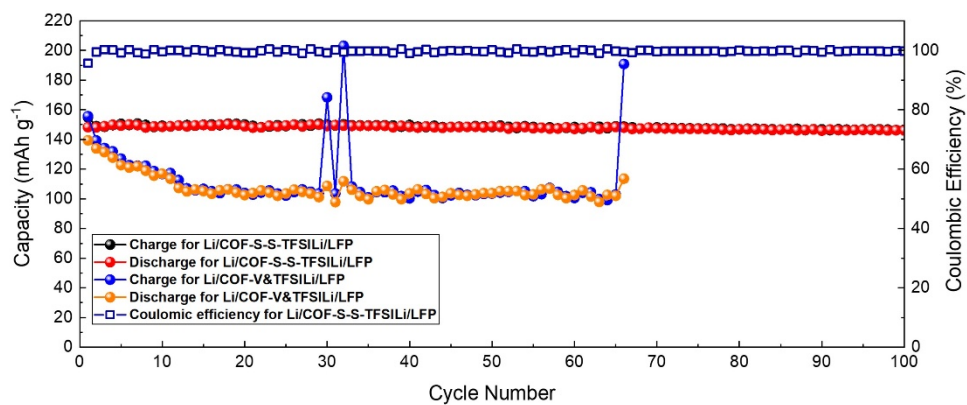


**Figure S16.** Galvanostatic Li plating/stripping profile of the Li/Li symmetric cell containing COF-S-S-TFSILi(a) and COF-S-S-SPSILi(b).

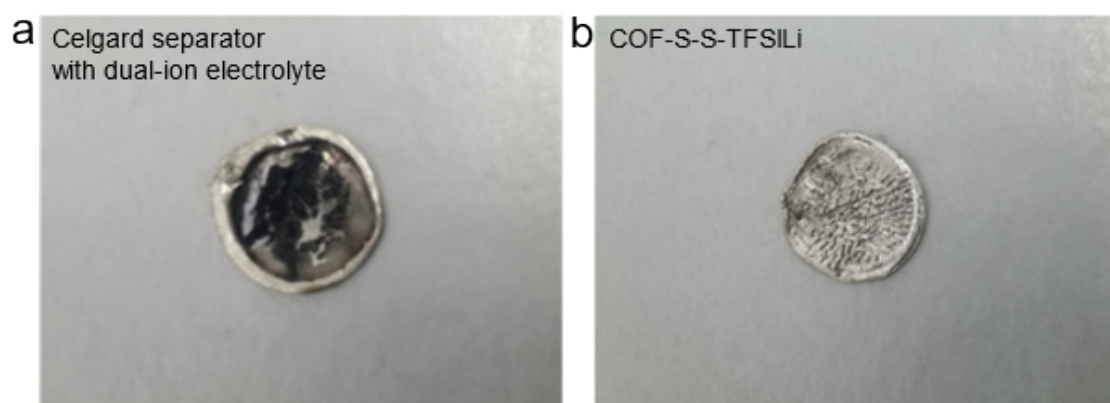
## L. LFP/Li Battery Performance



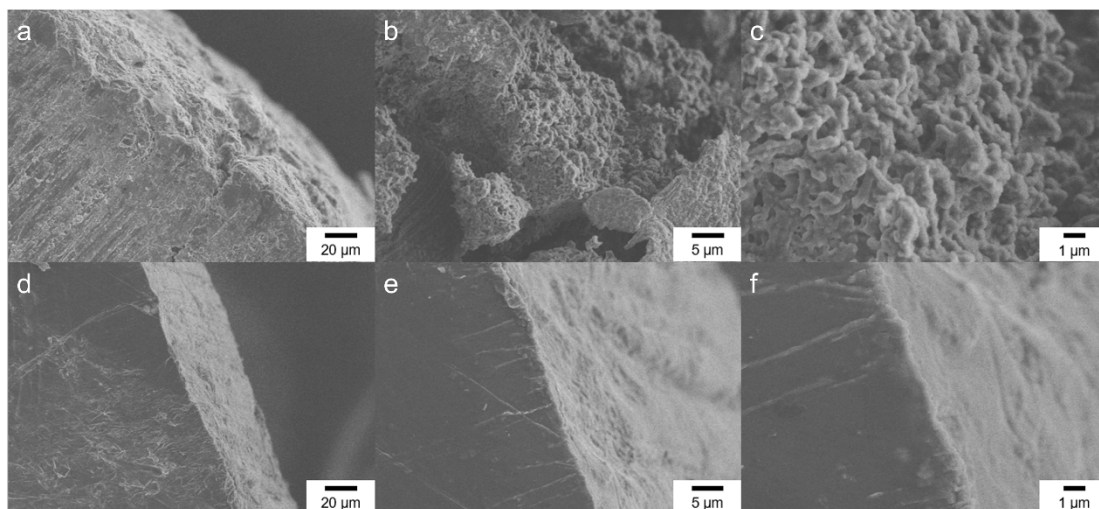
**Figure S17.** Cycle stability of Li/COF-S-S-TFSiLi/LFP cell at 1.0C



**Figure S18.** Cycle stability of the Li/COF-S-S-TFSiLi/LFP and Li/COF-V&TFSiLi/LFP cell at 0.2C



**Figure S19.** Images of Li foil after 50 cycles in Li/TFSiLi&Celgard/LFP (a) and Li/COF-S-S-TFSiLi/LFP(b).



**Figure S20.** Intersecting surface morphologies of Li foil after 50 cycles in Li/TFSILi&Celgard/LFP (a, b and c) and Li/COF-S-S-TFSILi/LFP (d, e and f).