

Supporting Information

Covalent Organic Frameworks as the Coating Layer of Ceramic Separator for High Efficiency Lithium-Sulfur Batteries

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Experimental Method

Chemicals. All the reagents and raw materials were used directly without further purification. Tetrakis(4-aminophenyl)ethane(ETTA, 95%),

2,5-Dimethoxy-1,4-Dicarboxaldehyde (DMTA, 95%), tetrahydrofuran (THF, 99.0%), acetone (99.5%), 1,4-dioxane (96%), mesitylene (97%) and sublimed sulfur (99.5%)

were purchased from alpha. Lithium plate (99.98%),

bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.95%), super-P (98%), Lithium nitrate

(99%), 1,3-dioxolane (DOL, 99.9%), LA132 water-soluble binder (LA132, 99%) and

1,2-dimethoxyethane (DME, 99.9%) were purchased from nanwu-lab.

Preparation of DMTA-COF. ETTA (0.5 g) and DMTA (0.5 g) monomers were

added in a glass bottle with 1, 4-dioxane and mesitylene mixture(50 ml, v: v=1:1) as

solvent. When the solid were dissolved under stirring, 5ml acetic acid aqueous

solution (6 M) was added into the above solution. Then the mixture was placed in an

oven at 110 °C for 72 h. The resulting red solid was washed with 1, 4-dioxane,

tetrahydrofuran and acetone, sequentially. Finally, the obtained powder was dried in a

vacuum oven (80 °C) over night.

Preparation of DMTA-COF/S composite. The DMTA-COF (0.5 g) and sublimed

sulfur (0.5 g) were dropped in the mortar and ground uniformly. Then the mixture

was transferred into the Teflon reaction kettle and heated at 155 °C for 15 h. After

cooling to room temperature, the COF encapsulated sulfur composite powder was

obtained.

Preparation of the DMTA-COF/ceramic separator. The as-synthesized

DMTA-COF powder (0.24 g) and super-P (0.12 g) were mixed and ground in a mortar, and then transferred into a test tube. LA132 water-soluble binder (0.8 g) and alcohol-water solution (2ml, v: v=1:3) were then added into the tube. To get the uniform slurry, the mixture was stirred by a high-speed dispersion machine spitting for 6 min. Then, the well-dispersed mixture was coated onto the ceramic separator by the doctor-blade method and dried in a vacuum oven at 60 °C overnight (**Figure S12**, Supporting Information). Finally, the DMTA-COF/ceramic separator was cut into discs with a diameter of 19mm.

Characterization of DMTA-COF, DMTA-COF/S and DMTA-COF/ceramic separator. Solid-state ^{13}C NMR spectra were carried out on the Bruker 400 M. Fourier transform infrared spectroscopy with potassium bromide tableting range of 4000–400 cm^{-1} were obtained by a Nicolet/Nexus-670 FT-IR spectrometer. The powder X-ray diffraction patterns were measured on a Bruker D8 Advance diffractometer (from 4° to 30°, Cu K α radiation). Thermo-gravimetric analyses (TGA) were performed on a Netzsch Thermo Microbalance TG 209 F3Tarsus from room temperature to 900 °C with a heating rate of 10 °C/min under a flowing nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) was recorded on an ESCA Lab250 XPS spectrometer using Al K α radiation. The nitrogen adsorption and desorption isotherms were measured at 77 K and using Bel sorp Max surface area size analyzer. Scanning electron microscope (SEM) images were taken on Tescan Maia3.EDX elemental mapping (Oxford Instruments) was performed on the Tescan Maia3.

Assembling of the Lithium-sulfur batteries. DMTA-COF/S (0.24 g), super-P (0.12 g) and LA132 (0.04 g) were mixed together and then an alcohol-water solution(2 ml)was added. After being dispersed with high-speed dispersion machine, the slurry was coated on aluminum foil and first dried at room temperature and then vacuum dried at 60 °Cfor 12 h. After that, the films were cut into circular pieces with a diameter of 12 mm. The weight was recorded on an electronic balance(0.6 mg/cm²or 1.5 mg/cm²sulfur-loaded).Finally, the DMTA-COF/S cathode, separator, lithium plate and electrolyte (DOL/ DME (v: v=1:1) with 1 M LITFSI and 0.1 M LiNO₃) were assembled into CR2032 button batteries in a glove box containing an argon atmosphere, with sealing machine sealed and standing for 300 min before test.

Electrochemical performance test. The galvanostatic charge/discharge tests were performed between 1.8 V and 2.8 V using a LAND CT2001A multichannel battery testing system at room temperature. The electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were obtained using a CHI660C electrochemical workstation, with an EIS frequency range of 0.01-100000 Hz and an amplitude of 5 mV, CV curves were recorded at a scan rate of 0.1 mV/s in a potential range of 1.8–3.0 V (vs. Li⁺/Li).

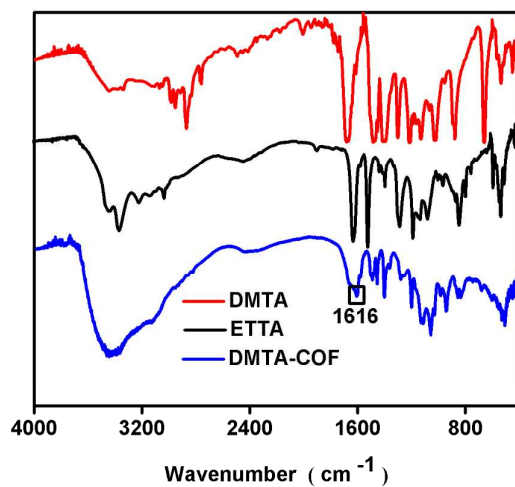


Figure S1. FT-IR spectra of Tetrakis(4-aminophenyl)ethane(ETTA, black), 2,5-Dimethoxy-1,4-Dicarboxaldehyde (DMTA, red), and DMTA-COF (blue).

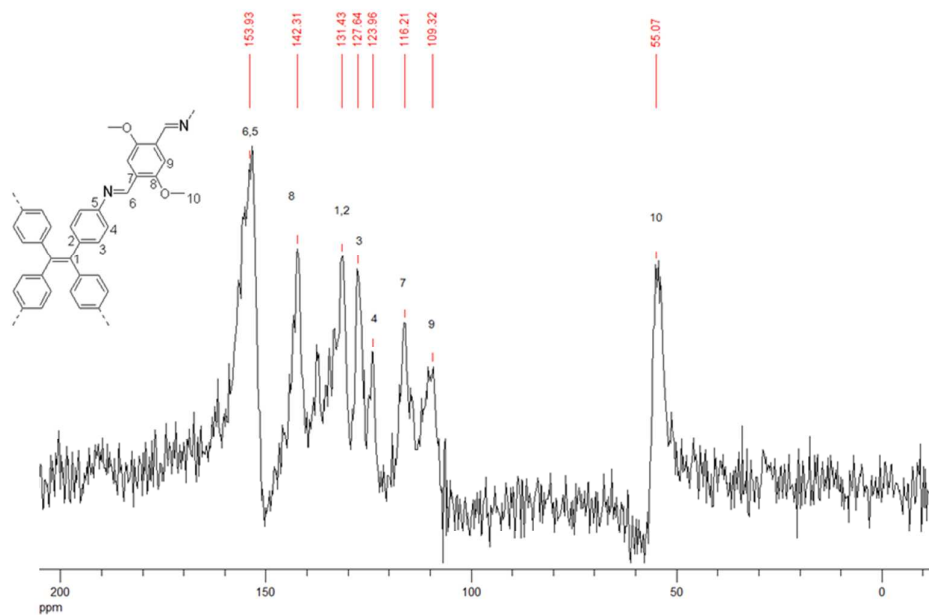


Figure S2. Solid-state ^{13}C NMR spectrum of DMTA-COF.

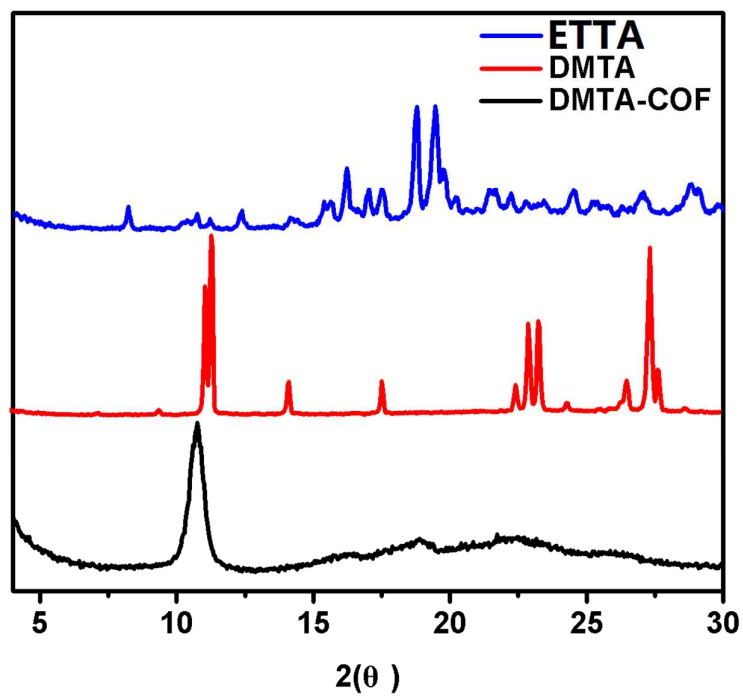


Figure S3. Powder X-ray diffraction patterns of Tetrakis(4-aminophenyl)ethane (ETTA, blue), 2,5-Dimethoxy-1,4-Dicarboxaldehyde (DMTA, red), and DMTA-COF (black).

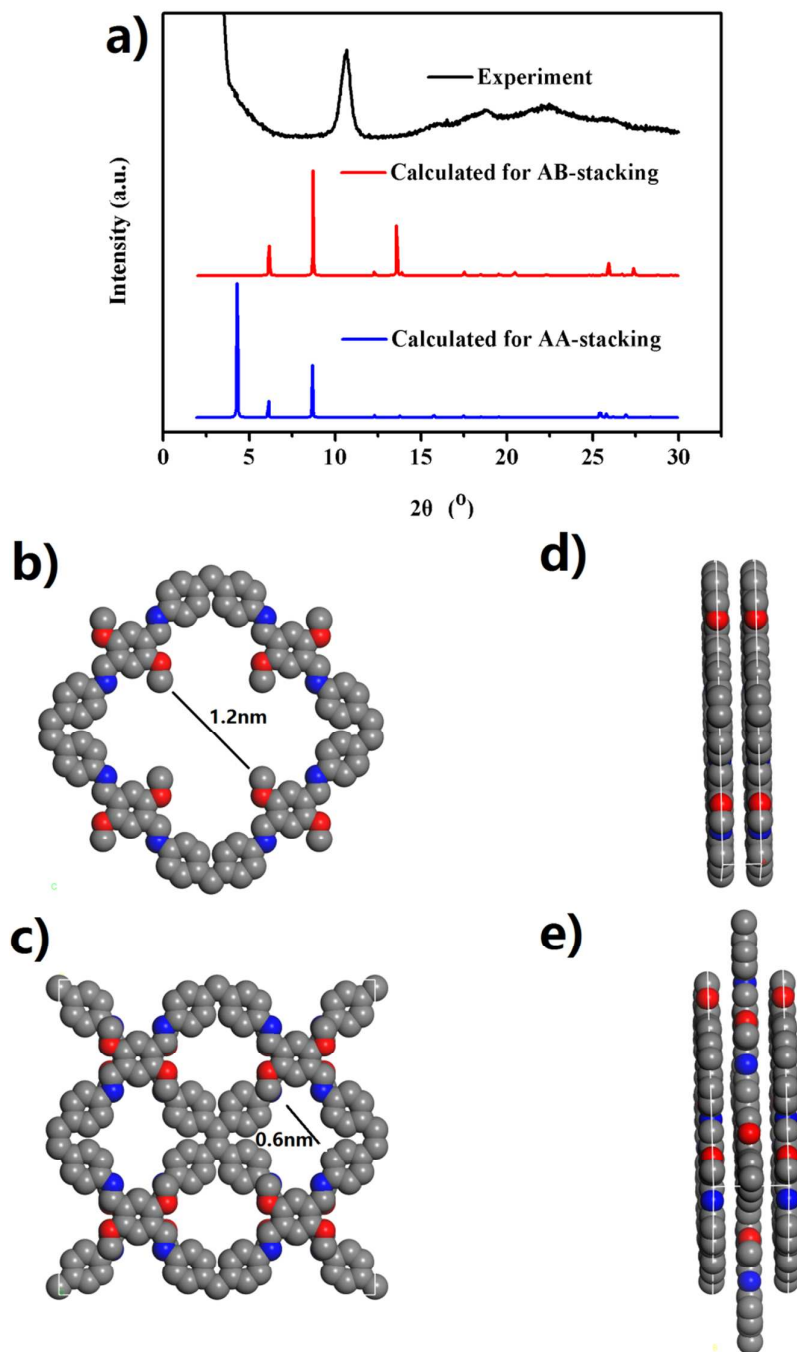


Figure S4. (a) PXRD pattern of the DMTA-COF: experiment (red), calculated for AA-stacking (red), and calculated for AB-stacking (blue). Space-filling models of the DMTA-COF in (b and d) AA and (c and e) AB-stacking modes.

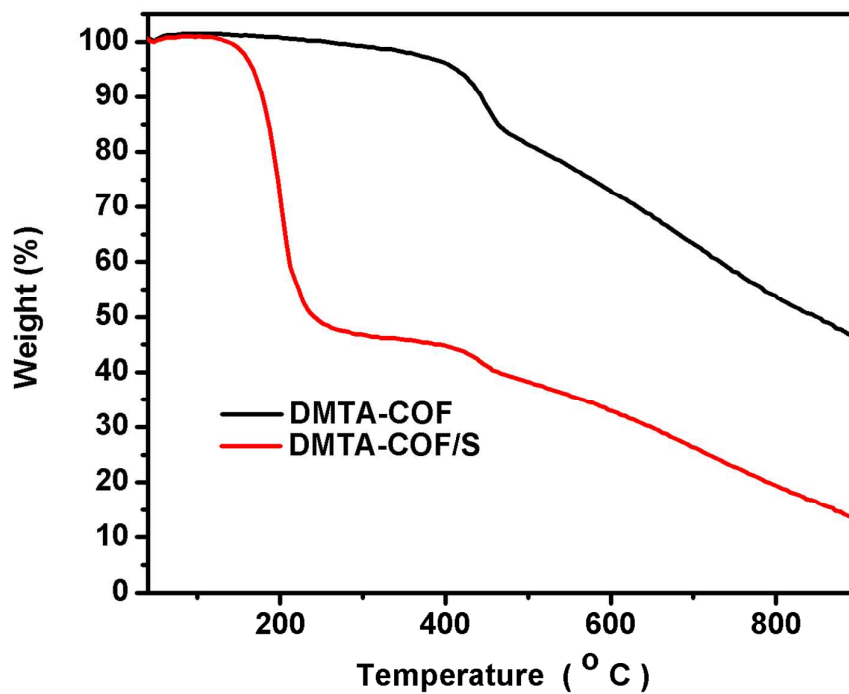


Figure S5. TGA curves of DMTA-COF (black) and DMTA-COF/S (red) composite recorded in an N₂ atmosphere.

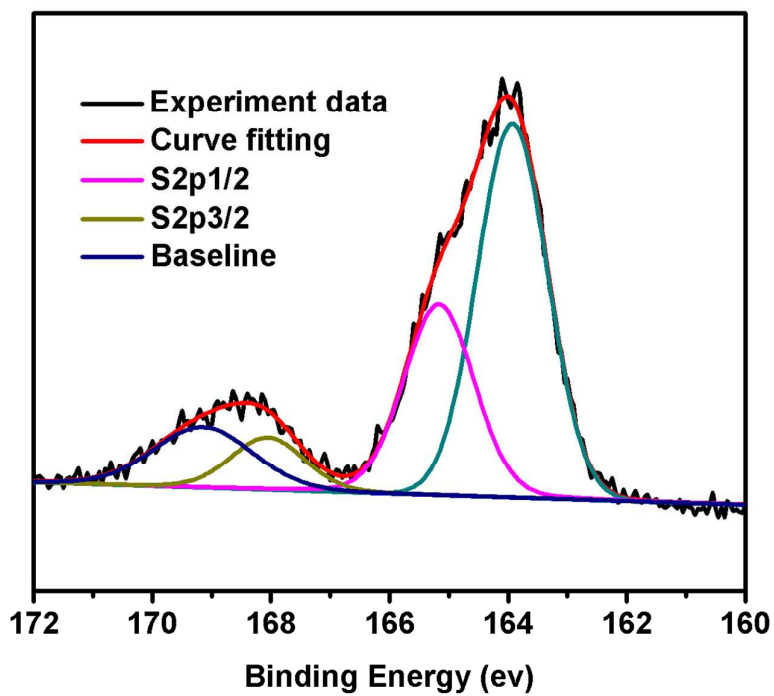


Figure S6. XPS S2p spectra of DMTA-COF/S composite.

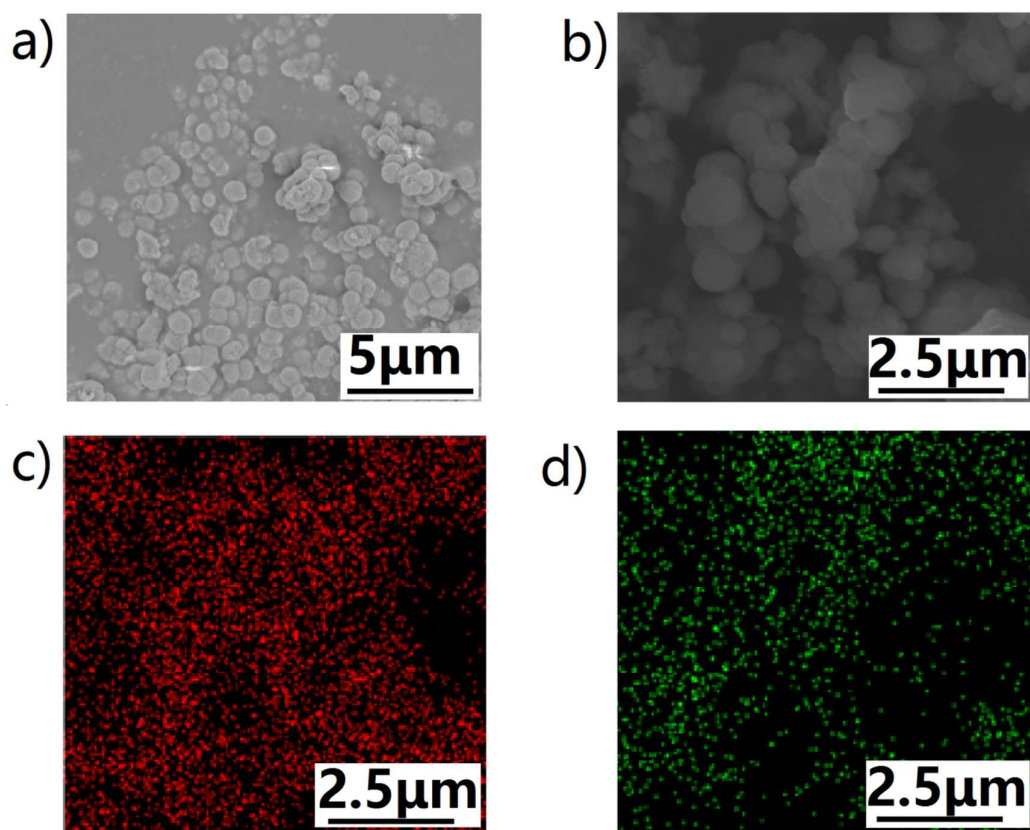


Figure S7.(a) SEM image of the DMTA-COF/S composite, (b)–(d) characterization of DMTA-COF/S composite: elemental mapping of S (c) and C (d).

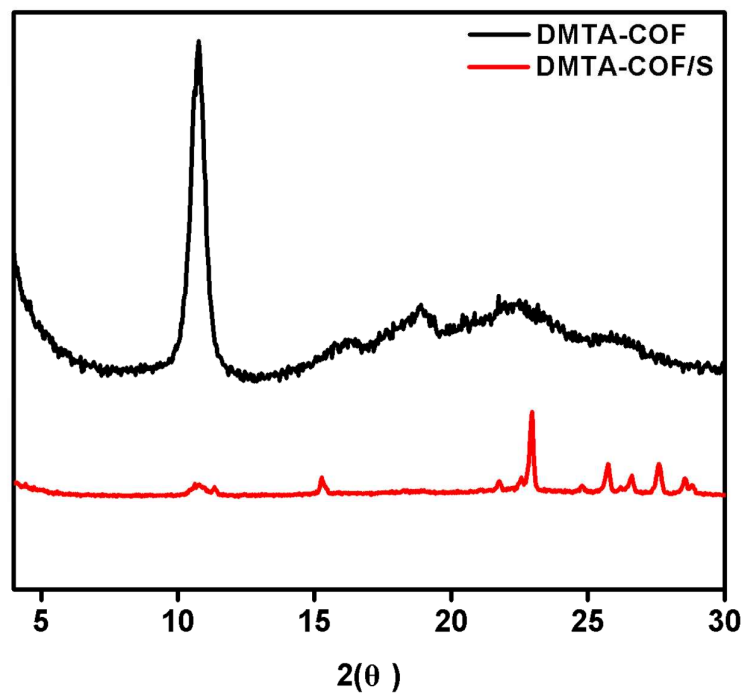


Figure S8. Powder X-ray diffraction patterns of DMTA-COF (black) and DMTA-COF/S composite (red).

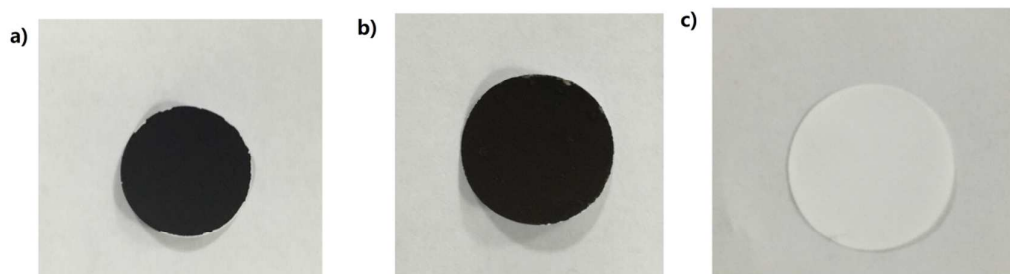


Figure S9. Photograph of DMTA-COF/ceramic separator (a), super-P/ceramic separator (b) and pristine ceramic separator (c).

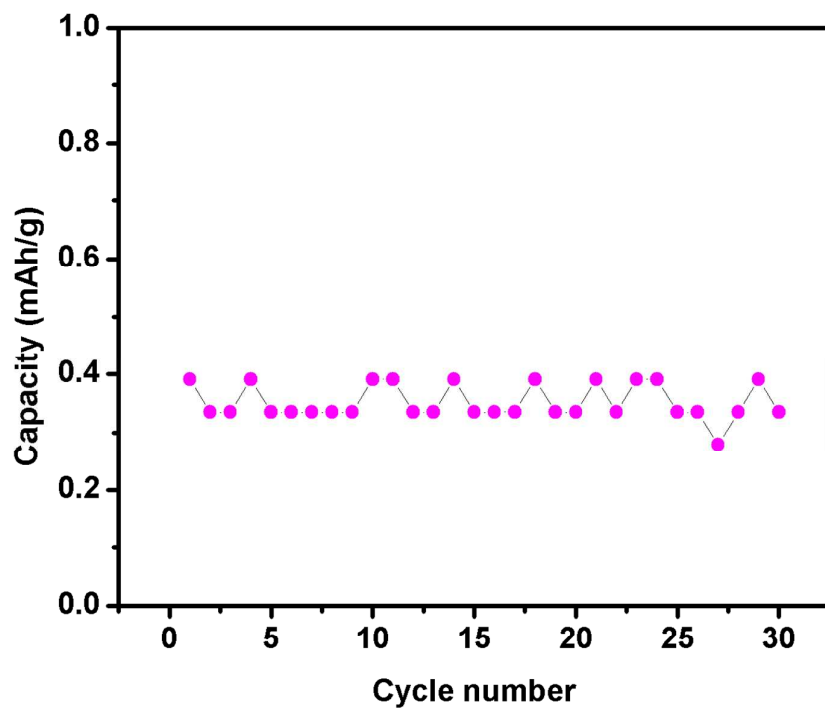


Figure S10. The cycle performance of the pure DMTA-COF cathode.

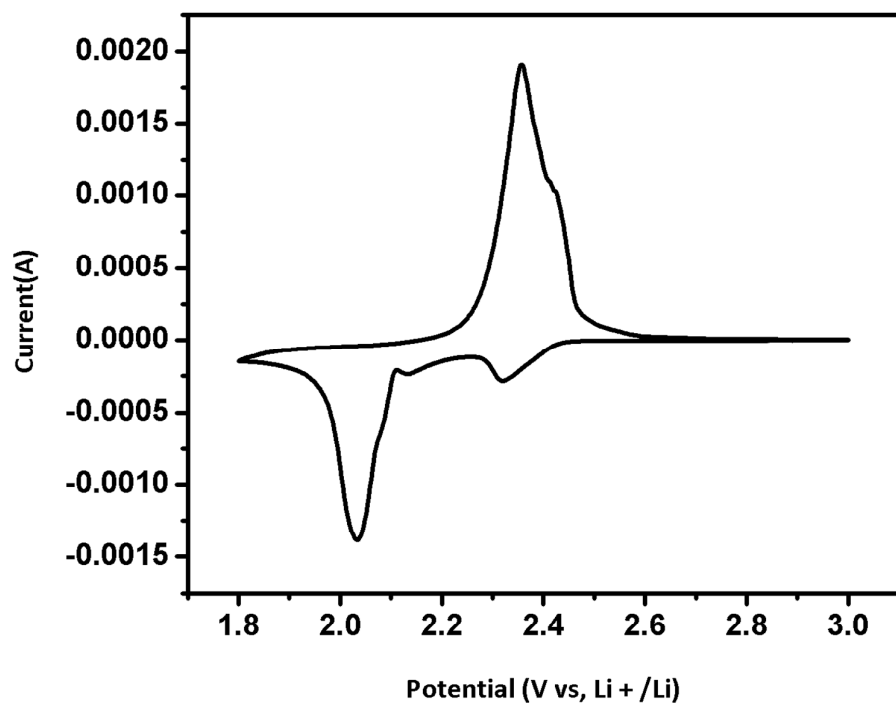


Figure S11. The first CV curve of the DMTA-COF/ceramic separator with DMTA-COF/S composite cathode at a scan rate of 0.1 mV^{-1} .

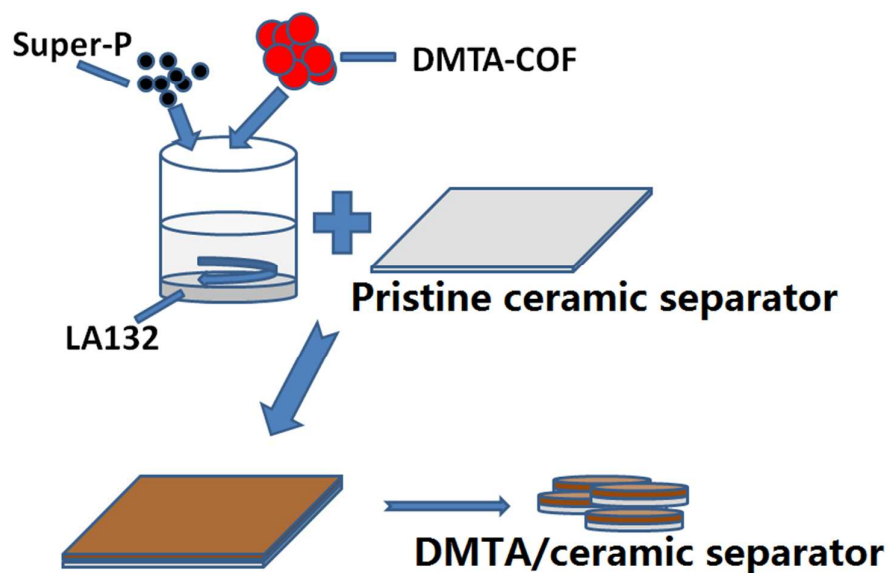


Figure S12. Schematic of the preparation process to produce DMTA-COF/ceramic separator. The DMTA-COF powder and super-P powder are ground together and added to LA132 and isopropyl alcohol-water solution, all mixed together to coat a ceramic separator forming a DMTA-COF/ceramic separator.



Figure S13.(a), (b) and (c) are photographs of DMTA-COF/ceramic separator, super-P/ceramic separator and pristine ceramic separator, respectively.

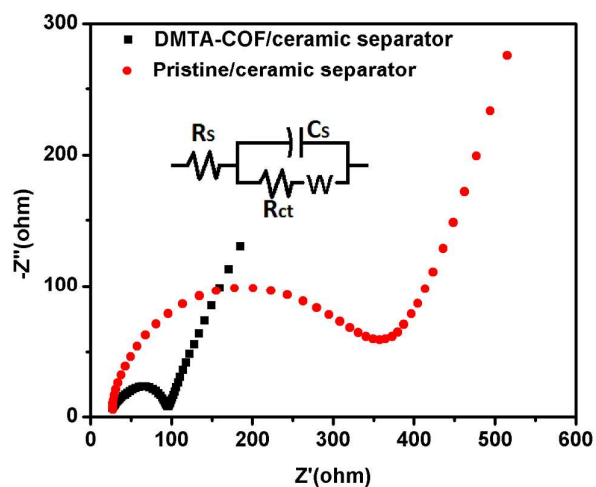


Figure S14. Electrochemical impedance spectra of Li-S cells with a DMTA-COF/ceramic separator and a pristine ceramic separator (the inset is the magnified plot for the cell with a DMTA-COF/ceramic separator).

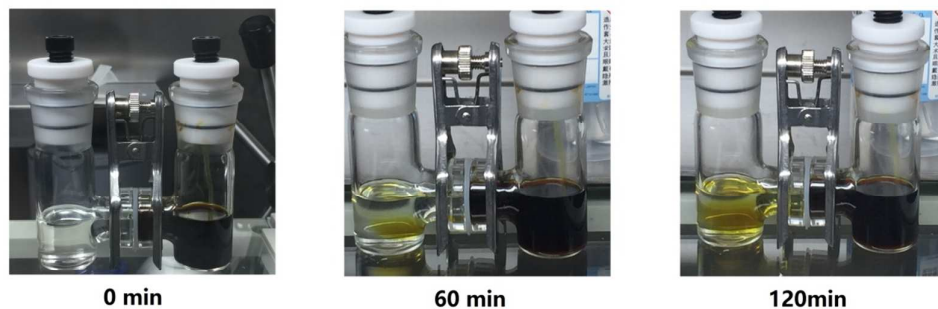


Figure S15. Photographs recording the polysulfide diffusion process across the separator. In the beginning (0 minute), the polysulfide was totally blocked by the separator from the vinicolor electrolyte. After 60 minutes of diffusion, the polysulfide filled the separator. When the diffusion time reached 120 minutes, the polysulfide fully filled the pores of COFs and moved through the gap of particles of COFs and towards to another side of separator.

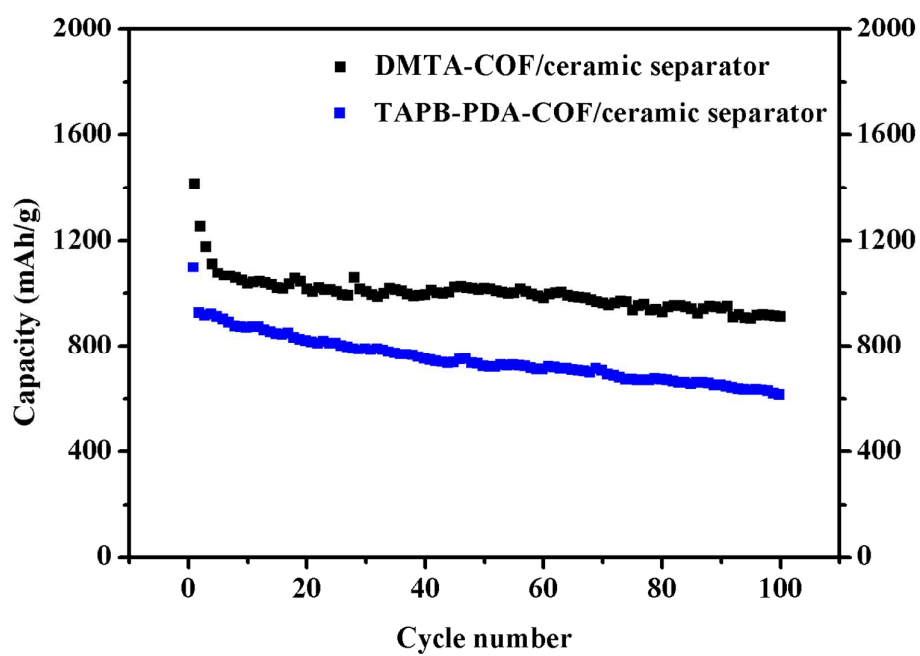


Figure S16. Cycling performance of DMTA-COF/ceramic separator (black) and TAPB-PDA-COF/ceramic separator (blue) cathodes at a current rate of 0.5 C (1 C = 1680 mA g⁻¹) for 100 cycles.