Supporting Information

Covalent-organic frameworks rich in nitrogen and oxygen as modified separators for lithium-sulfur batteries: pore sizes effects

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S1. Materials and Methods

Experimental reagents

All commercially available reagents and solvents were used as received without further purification, unless otherwise noted. 2,6-diaminoanthraquinone (DAAQ), 1,3,5-triformylphloroglucinol (TFP), 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPT) was purchased from Alfa, 2,5-dihydroxyterephthalaldehyde (DHTA) was purchased from Sanbang Chemical. All solvents used, pure sulfur, conductive carbon black, and polyvinylidene fluoride (PVDF) were purchased from Aladdin.

Characterizations

PXRD data were collected on a Rigaku model RINT Ultima III diffractometer over the range of 2θ = 2.5 - 40° with 0.02° increment. Fourier transforms Infrared (FT-IR) spectra were obtained on a Perkin-Elmer model FT-IR-frontier infrared spectrometer with potassium bromide pellet. UV-vis spectra were used for Jasco V-770 spectrometer. ^{13}C cross-polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) analysis was conducted using AVANCEIII/WB-400. Field-emission scanning electron microscopy (FE-SEM) images were obtained on a JEOL model JSM-6700. Thermogravimetric analysis (TGA) was acquired by using a Q5000IR analyzer (TA Instruments) with an automated vertical overhead thermobalance under N_2 atmosphere. X-ray photoelectron spectra (XPS) were carried out by ESCALAB250XI electron spectrometer (VG scientific, USA). N_2 sorption tests were measured at 77 K with Bel Japan Inc. Model BELSORP-max analyzer. Before measurement, the samples were degassed in vacuum at 120 °C for more than 10 h.

S2. Synthetic procedures

Synthesis of DTQ-COF

DTQ-COF was synthesized based on the similar procedure in previous literature.[S1] 1,3,5-triformylphloroglucinol (TFP, 6.3 mg, 0.03 mmol), 2,6-diaminoanthraquinone (DAAQ, 11.9 mg, 0.05 mmol), N,N-dimethylacetamide (DMA, 0.5 mL), 1,3,5-mesitylene (0.2 mL). dilute acetic acid (6 M, 0.2 mL) were added to a Pyrex tube. After sonication for 5 mins, the tube was frozen in liquid nitrogen at 77 K rapidly, and

degassed by three freeze-pump-freeze cycles, sealed under vacuum. Afterwards, the tube was heated at 120 °C for three days, after cooling to room temperature, and the red brown powder was isolated by filtration, washed repeatedly with acetone and vacuum drying at 80 °C. The isolated yield of DTQ-COF was about 74%.

Synthesis of DHTA-COF

DHTA-COF was synthesized by solvothermal synthesis method according to previous literature.[S2] 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPT, 40 mg, 0.112 mmol), 2,5-dihydroxyterephthalaldehyde (DHTA, 20 mg, 0.145 mmol), 1,2-dichlorobenzene (1.6 mL), ethanol (0.5 mL), and acetic acid (6 M, 0.2 mL) were added to a Pyrex tube. Then the tube was sonicated for 5 mins, frozen in liquid nitrogen at 77 K rapidly, and degassed by three freeze-pump-freeze cycles, sealed with flame. The mixture was heated at 120 °C for three days to afford a red precipitate, which was isolated by filtration, washed with anhydrous acetone repeatedly, and vacuum drying at 80 °C to red powders with 83% isolated yield.

S3. Assembly of batteries and their electrochemical testing

Complexes of carbon sulfur (C/S) complex and cathode electrode sheet

In order to make carbon-sulfur complex C/S, Super-p and sublimated sulfur were mixed in a 2.5:7.5 wt. ratio and transferred to a reaction kettle lined, and heated at 155 °C for 20 h under argon atmosphere by the melt-diffusion method. Afterwards, the obtained carbon-sulfur complex C/S, Super P and the binder polyvinylidene fluoride (PVDF) were fully combined in N-methylpyrrolidone (NMP) of 8:1:1 wt. ratio. The slurry was then coated on the carbon coated aluminum foil collector, and dried in vacuum oven at 50 °C overnight. After drying, they were cut into 12 mm diameter discs to prepare cathode sheets (sulfur content 1 ~ 1.5 mg cm^{-2}).

Preparation of modified separators

A slurry was constantly prepared by mixed COFs, PVDF and Super-P (6:1:3 in weight ratio) in NMP and ball-milled for 1 h. The resulting uniformly slurry was evenly coated on the PP membrane surface and then dried in a vacuum oven at 60 ℃ overnight. Whereafter, the obtained separator was cut into discs with a diameter of 16

mm. The coated DTQ-COF and DHTA-COF layers thickness were measured 5.06 and 5.50 μm. The mass loading of the coating materials were 1.85 and 1.87 mg for DTQ-COF and DHTA-COF modified separators.

Preparation of electrolyte

The electrolyte was prepared by adding 1 mol L^{-1} LiTFSI and 1 wt% $LiNO_3$ additive in a 1:1 vol. ratio of DME (1,2-dimethoxyethane) and DOL (1,3-dioxolane) magnetically stirred for 24 h. The amount of electrolyte used was 40 μL.

Preparation of Li-S battery

Coin cells were assembled inside a glovebox under argon atmosphere (O_2 < 0.01 ppm, H_2O < 0.01 ppm), using CR2025 button battery assembly, and put the sulfur cathode plate (diameter 12 mm), separator (diameter 16 mm), electrolyte and lithium-chip anode sheet (the lithium sheet is from Coruide and has diameter of 16 mm and thickness of 0.6 mm) in turn.

Electrochemical testing

The battery test system (LANHE CT2001A) was employed to evaluate the cycling performance with a voltage range from 1.7 to 2.8 V. CV (1.7 - 2.8V, 0.1 mV s^{-1}), electrochemical impedance spectra (EIS) (10^{-1}-10^5 Hz) and I-t curves were measured on CHI 660E, Chenhua.

The conductivity of Li^+ in the separator can be calculated using the EIS of a stainless steel symmetrical battery and formula (1-1):

$$\sigma = \frac{L}{RA} \qquad (1-1)$$

In equation (1-1), L and A represent the thickness and area of the separator, respectively, and R is the bulk ohmic resistance of the electrolyte.

Using the constant potential polarization method, the I-t curve of Li/separator/Li battery structure was tested, with a polarization voltage of 0.02 V and a polarization time of 1000 s. The Li^+ migration number was calculated using formula (1-2):

$$t_{Li^+} = \frac{I_S(\Delta V - I_0 R_0)}{I_0(\Delta V - I_S R_S)} \#(1-2)$$

In equation (1-2), ΔV represents the constant voltage applied, R_0 and R_S represent the initial resistance and polarization resistance, respectively, and I_0 and I_S represent the initial and steady-state current, respectively.

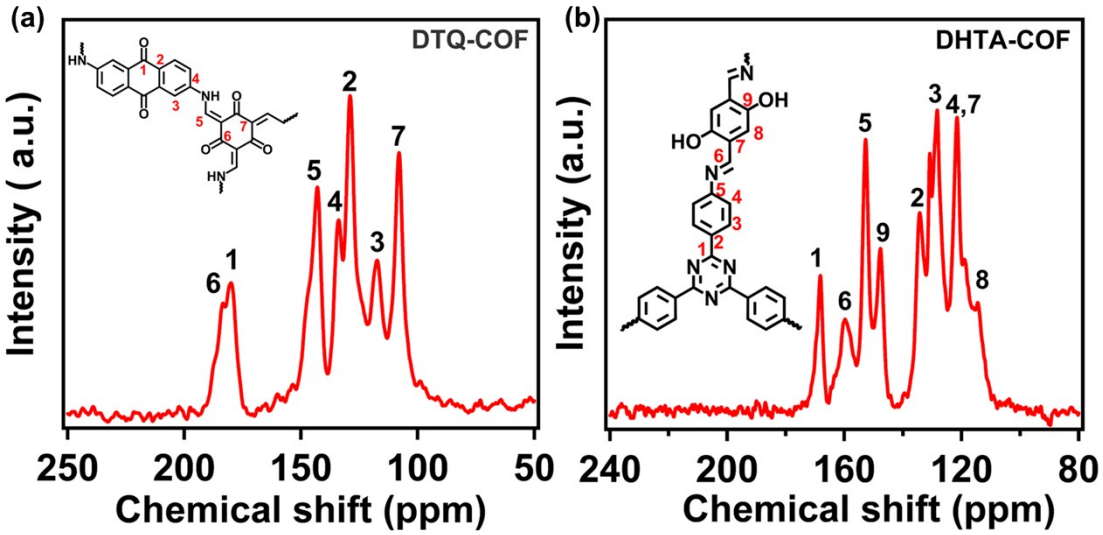

Fig. S1 The solid-state ^{13}C CP-MAS NMR of (a) DTQ-COF and (b) DHTA-COF.

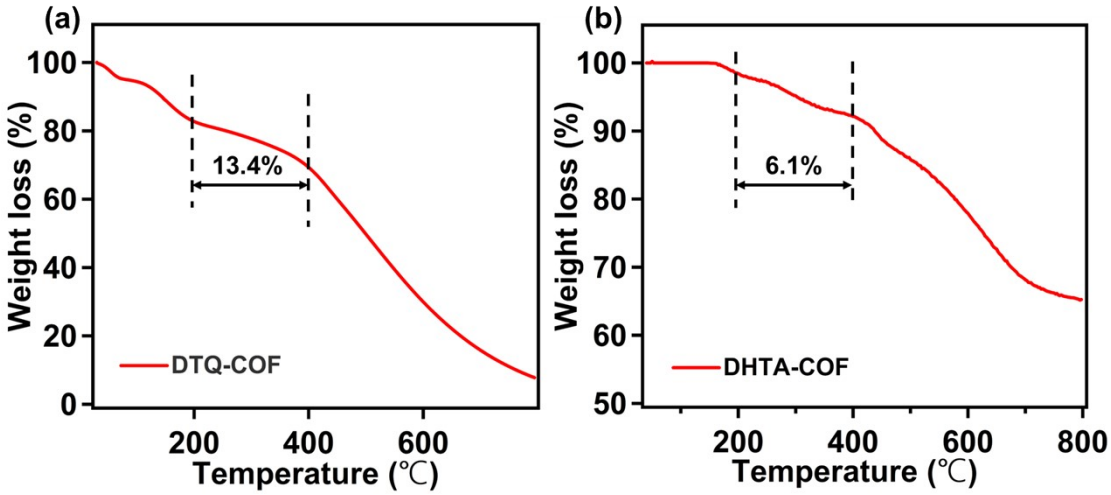

Fig. S2 TGA curves of as-synthesized (a) DTQ-COF and (b) DHTA-COF under nitrogen gas atmosphere.

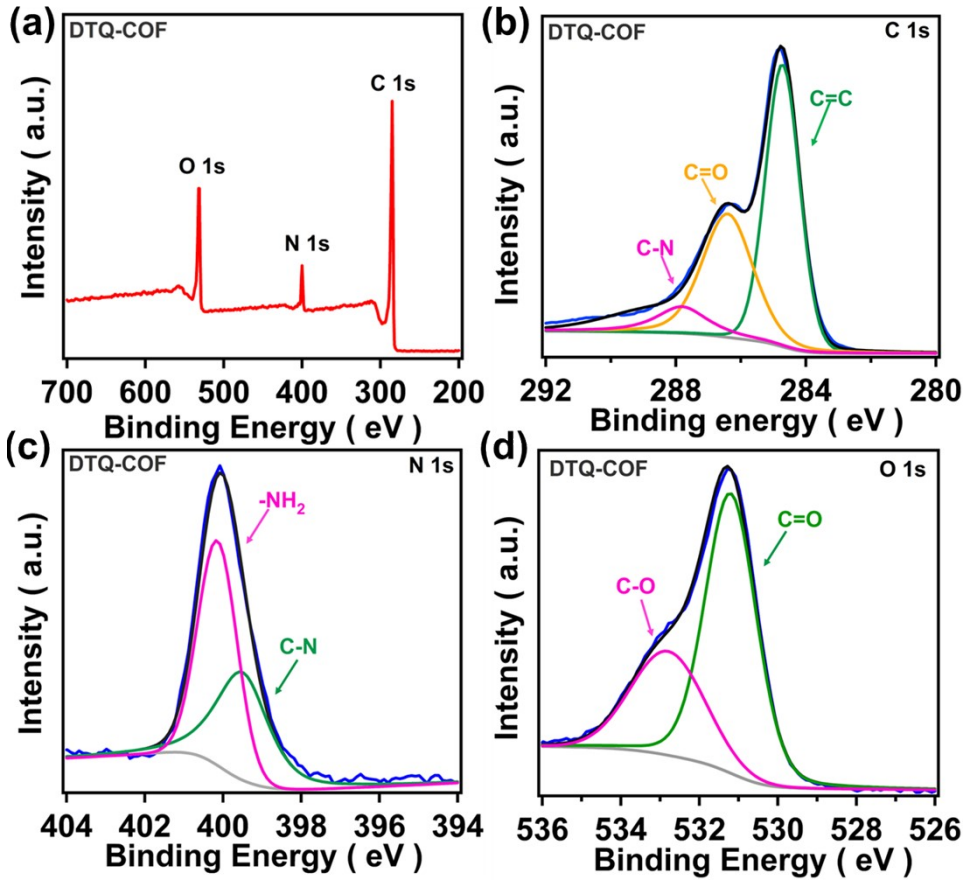

Fig. S3 (a) XPS survey spectra of DTQ-COF, (b) C 1s, (c) N 1s and (d) O 1s spectra of DTQ-COF.

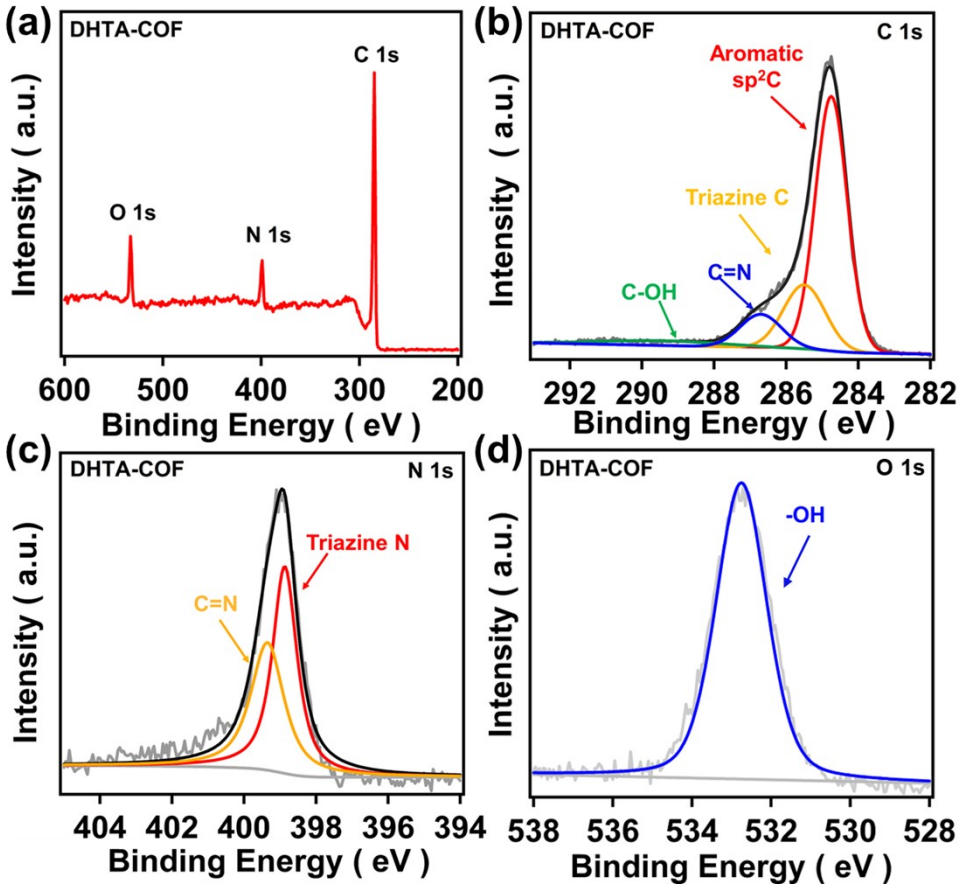

Fig. S4 (a) XPS survey spectra of DHTA-COF, (b) C 1s, (c) N 1s and (d) O 1s spectra of DHTA-COF.

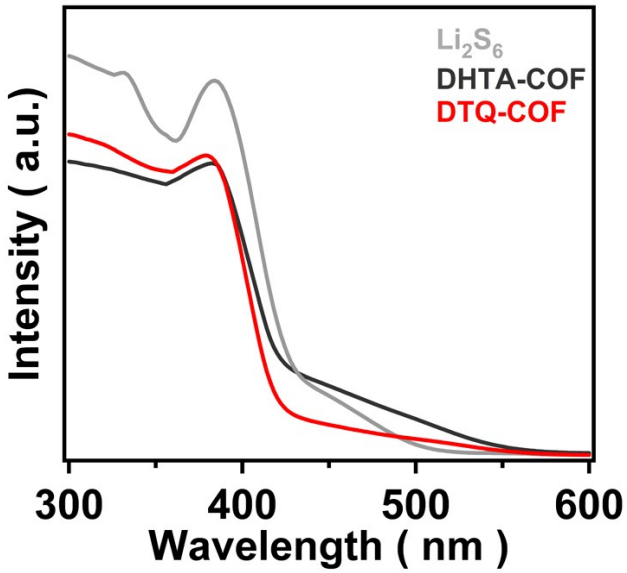

Fig. S5 UV-vis absorption spectra of DHTA-COF and DTQ-COF in Li_2S_6 solution.

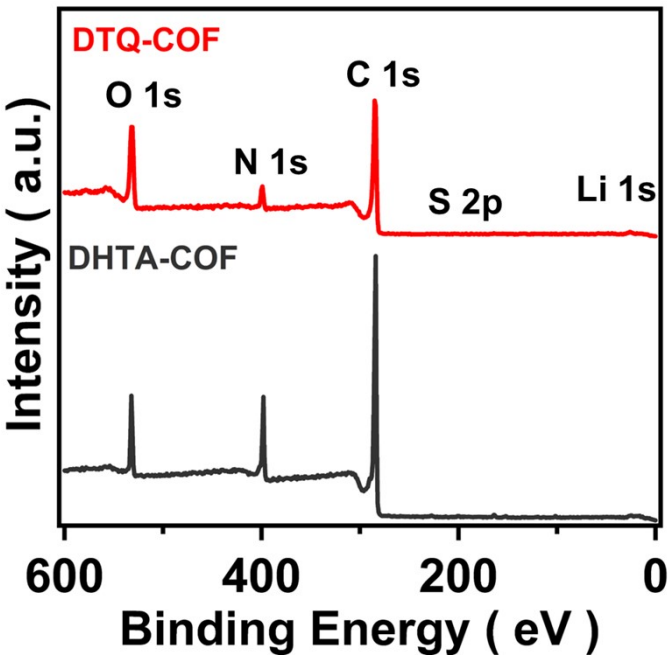

Fig. S6 XPS survey spectra of DHTA-COF and DTQ-COF in Li_2S_6 solution.

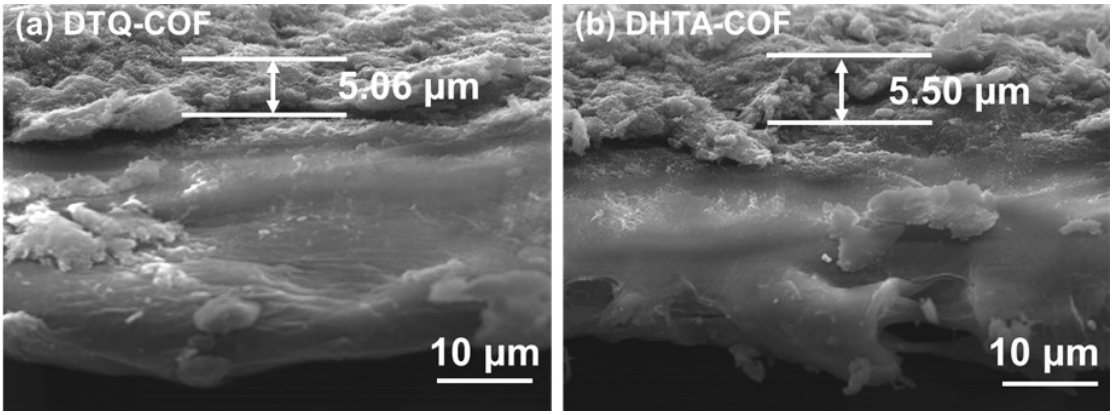

Fig. S7 The thickness of the coated (a) DTQ-COF and (b) DHTA-COF layers.

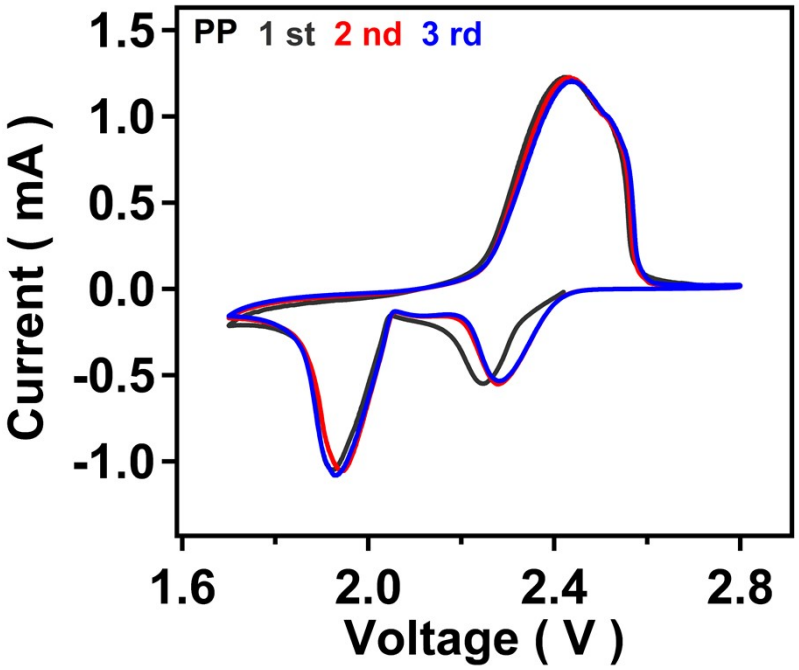

Fig. S8 CV plots of the Li-S battery with PP separator (scan rate: 0.1 mV s^{-1}).

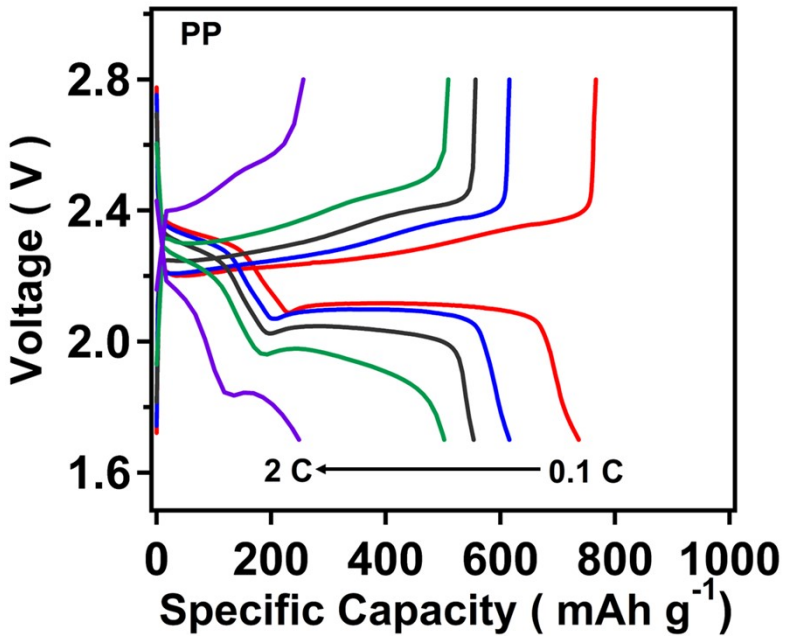

Fig. S9 Discharge-charge graphs of PP based battery at different current densities of 0.1, 0.2, 0.5, 1 and 2 C.

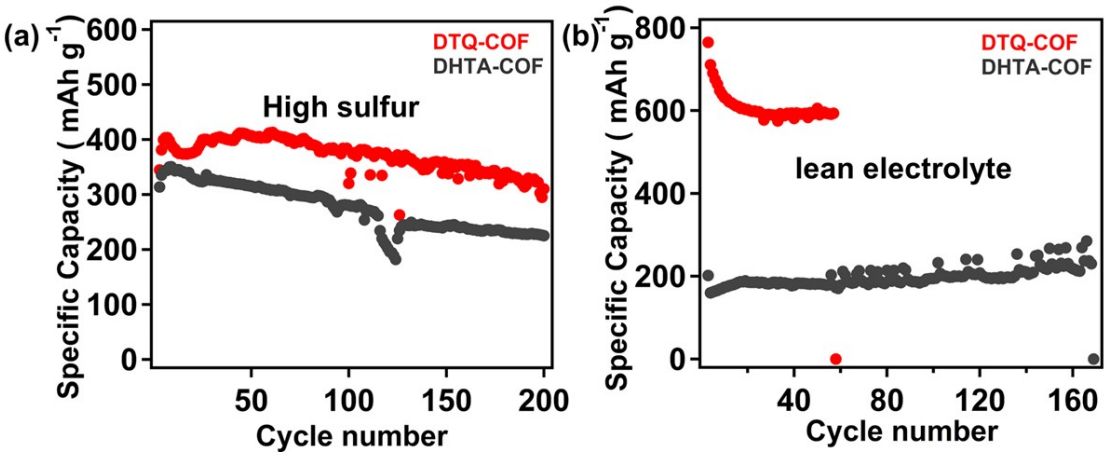

Fig. S10 The cycle performances of DTQ-COF and DHTA-COF based cells at 1 C with (a) high sulfur areal loading (3 mg/cm^2) and (b) lean electrolyte (20 μL).

Table S1 Comparison of ΔE values of Li-S batteries with different interlayers.

Interlayers	0.1 C	0.2 C	0.5 C	1 C	2 C
DTQ-COF	0.15 eV	0.17 eV	0.23 eV	0.32 eV	0.48 eV
DHTA-COF	0.15 eV	0.19 eV	0.30 eV	0.48 eV	--

Supporting references

S1. S. Cai, R. Ma, W. Ke, H. Zhang, Y. Liu, M. Jiao, Y. Tian, Y. Fang, M. Wu, Z. Zhou, *Chem. Eng. J.*, 2024, **491**, 151979.

S2. L. Liu, D. Cui, S. Zhang, W. Xie, C. Yao, N. Xu, Y. Xu, *Dalton. Trans.*, 2023, **52**, 6138-6145.