

## Elementary Supporting Information

### Energy-storage covalent organic frameworks: Improving performance via engineering polysulfide chains on walls

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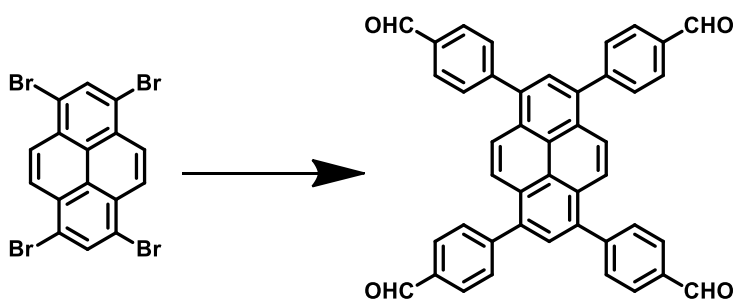
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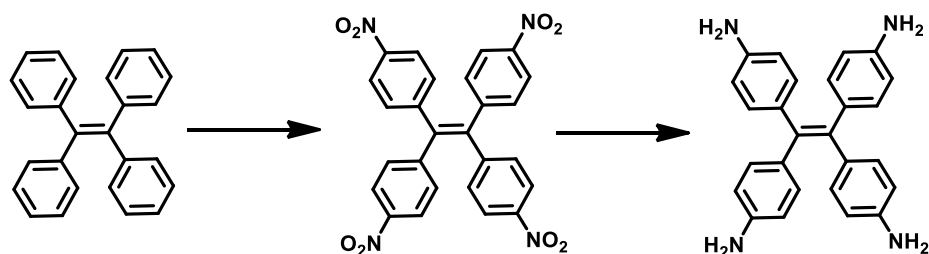
## Section A. Materials and Methods

**Materials.** *n*-Butanol (*n*-BuOH), *o*-dichlorobenzene (*o*-DCB), anhydrous acetone (99.5%), tetrahydrofuran (THF), mesitylene, dioxane, and acetic acid (AcOH) were purchased from Wako Chemicals. Sulfur with a purity of 99.99% was purchased from Macklin.

4,4',4'',4'''-(Ethene-1,1,2,2-tetrayl)tetraaniline (ETTA), 1,3,6,8-tetrakis(4-formylphenyl)pyrene (TFPPy) and model compound were prepared according to the reported methods.<sup>S1-S3</sup>



**TFPPy.** 1,3,6,8-Tetrabromopyrene (1.00 g, 1.93 mmol), 4-formylphenylboronic acid (1.74 g, 11.6 mmol), palladium tetrakis(triphenylphosphine) (0.12 g, 0.10 mmol, 5.2 mol %), and potassium carbonate (2.1 g, 15 mmol) were added into anhydrous dioxane (30 mL) and stirred for 3 days at 85 °C under nitrogen. The resulting reaction mixture was poured into a solution of ice containing concentrated hydrochloric acid, followed by filtration and washing with 2 M HCl three times. The product was extracted with CHCl<sub>3</sub> and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure after filtration. TFPPy was obtained by recrystallized from hot CHCl<sub>3</sub> in 70% yield.



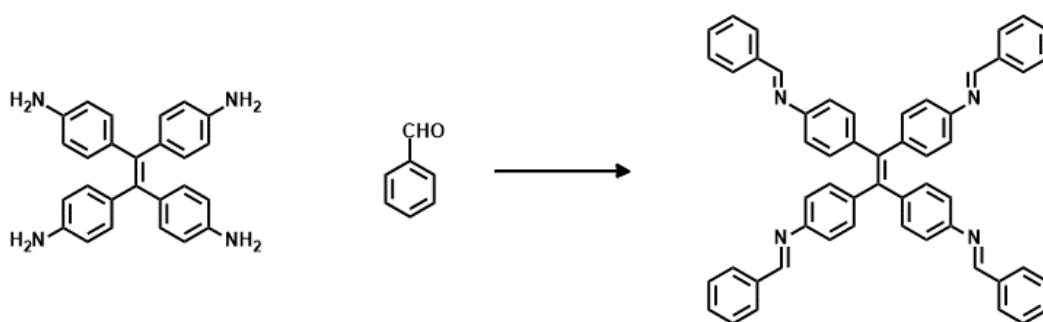
**ETTA.** 1,1,2,2-Tetraphenylethene (3g, 9 mmol) was added in small portions to a mixture of acetic acid (30 mL) and fuming nitric acid (30 mL) that was precooled by ice bath. Then the ice bath was removed and the reaction mixture was stirred at room temperature for 3 h. The light-yellow precipitation was obtained by pouring the mixture into ice water (300 g). After filtration and

recrystallization from 1, 4-dioxane, light yellow crystals were obtained as 1,1,2,2-tetrakis(4-nitrophenyl)ethane in 50% yield. Raney nickel (2 g) and hydrazine monohydrate (670 mg, 13.4 mmol) were added carefully to the solution of THF (10 mL) containing 1,1,2,2-tetrakis(4-nitrophenyl)ethene (525 mg, 1 mmol). Subsequently, the reaction mixture was heated to reflux for 2 h. After cooling, the nickel was filtered off and the filtrate was evaporated under reduced pressure to obtain a light-yellow solid in 68% yield.

**TFPPy-ETTA-COF.** A mesitylene/dioxane/6 M AcOH (5/5/1 by vol.; 1.1 mL) mixture of TFPPy (0.025 mmol, 15.5 mg) and ETTA (0.025 mmol, 9.8 mg) in a Pyrex tube (10 mL) was degassed by three freeze-pump-thaw cycles. The tube was sealed off and heated at 120 °C for 3 days. The precipitate was collected by centrifugation, and washed with anhydrous THF and acetone 3 times. The powder was dried at 120 °C under vacuum overnight to give the TFPPy-ETTA-COF in an isolated yield of 85%.

**S@TFPPy-ETTA-COF.** Sulfur and ETTA-TFPPy-COF with designated proportion were thoroughly mixed in a quartz mortar for 0.5 h to yield a yellow mixture. The mixture was sealed in a glass tube filled with nitrogen and heated firstly at 115 °C with a heating rate of 1 °C min<sup>-1</sup> and then to 155 °C with a heating rate of 0.5 °C min<sup>-1</sup> and kept at this temperature for 10 h to ensure a complete infiltration of sulfur into COF, leading to formation of S@TFPPy-ETTA-COF.

**Polysulfide@TFPPy-ETTA-COF.** The thoroughly sulfur and ETTA-TFPPy-COF mixture was put in a Pyrex tube (10 mL) that was evacuated and sealed off at room temperature. Subsequently, the tube was heated at 155 °C for 10 h and then 300 °C for 10 h, followed by cooling to room temperature, yielding polysulfide@TFPPy-ETTA-COF.



**Synthesis of model compound.** Dried benzaldehyde (53 mg, 0.5 mmol, 5 equiv.) was added to a suspension of ETTA in anhydrous 1,4-dioxane (0.5 mL) and  $\text{CHCl}_3$  (2 mL) under an argon atmosphere. The reaction mixture was heated at 70 °C for 16 h after addition of 5 beads of 3 Å molecular sieve. Upon slow cooling yellow needles formed, which were isolated by filtration and dried under reduced pressure to give the model compound in 86% yield.

## Methods

**Characterizations.** The morphology and microstructure were investigated by a JEOL model JSM-6700 field emission scanning electron microscopy (FE SEM) and a JEOL model JEM-3200 high-resolution field emission transmission electron microscope (HR-TEM) with an energy dispersive X-ray spectroscopy (EDX) detector. Nitrogen sorption measurements were carried out using a Micromeritics ASAP 3Flex analyzer at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the non-local density functional theory (NLDFT) model, the pore volume was derived from the sorption curve. X-ray diffraction (XRD) data were recorded on a Rigaku model RINT Ultima III diffract meter. A Kratos Axis Ultra DLD with 150 W Al K $\alpha$  radiation was used for X-ray photoelectron spectroscopy (XPS). Fourier transform infrared (FTIR) spectra were recorded on a JASCO model FT-IR-6100 infrared spectrometer. Thermogravimetric analysis (NETZSCH5) was performed between 35-600 °C at the speed of 10 °C min<sup>-1</sup> under the atmosphere of nitrogen.

**Structure optimizations.** The molecular structure and electronic properties of monolayer and stacked TFPPy-ETTA-COF isomers were determined using the density-functional tight-binding

(DFTB) method including Lennard-Jones (LJ) dispersion. The corresponding LJ and crystal stacking energies as well as the HOMO-LUMO energy gaps were computed. The calculations were carried out with the DFTB+ program package version 1.2.<sup>S4</sup> DFTB is an approximate density functional theory method based on the tight binding approach and utilizes an optimized minimal LCAO Slater-type all-valence basis set in combination with a two-center approximation for Hamiltonian matrix elements. The Coulombic interaction between partial atomic charges was determined using the self-consistent charge (SCC) formalism. Lennard-Jones type dispersion was employed in all calculations to describe van der Waals (vdW) and  $\pi$ -stacking interactions. The lattice dimensions were optimized simultaneously with the geometry. Standard DFTB parameters for X–Y element pair (X, Y = C, H and N) interactions were employed from the mio-0-1 set.<sup>S5</sup> The single layer model system consisted of 116 atoms. The optimized cell lattice constants are  $a = 22.41\text{Å}$  and  $b = 21.38\text{Å}$  with an angle of  $90^\circ$  between the vectors. Using the optimized monomer, several different stacking configurations: eclipsed AA, AA slip-stacked by  $0.8\text{Å}$  in the  $a$  and  $b$  directions, and staggered AB (with one layer shifted by  $\frac{1}{2}$  the  $a$  lattice vector length such that the top layer eclipses the pores of the bottom layer) were optimized. The third dimension of the lattice,  $c$  was initialized at  $4.0\text{Å}$  for all structures.

Molecular modeling and Pawley refinement were carried out using Reflex, a software package for crystal determination from XRD pattern, implemented in MS modeling ver 4.4 (Accelrys Inc.).<sup>S6</sup> Unit cell dimension was first manually determined from the observed PXRD peak positions using the coordinates. We performed Pawley refinement to optimize the lattice parameters iteratively until the  $R_{WP}$  value converges. The refinement indicates a tetragonal crystal system with a unit cell of  $a = 21.325536\text{Å}$ ,  $b = 22.358088\text{Å}$ ,  $c = 4.68645\text{Å}$ ,  $\alpha = 86.43922^\circ$ ,  $\beta = 79.56263^\circ$ , and  $\gamma = 85.34703^\circ$ . The pseudo-Voigt profile function was used for whole profile fitting and Berrar-Baldinozzi function was used for asymmetry correction during the refinement processes. The final  $R_{WP}$  and  $R_P$  values were 8.10% and 6.03%. Simulated XRD patterns were calculated for an eclipsed AA, and a staggered AB-stacking. After comparing each simulated pattern with

experimentally observed pattern, the eclipsed AA stacking mode yields a pattern that shows good agreement with the observed XRD pattern.

**Electrochemical measurements.** Cathodes were prepared by mixing the COF samples as the active material, conductive carbon black (Super P Li) and polyvinylidene fluoride binder (PVDF) (6:3:1 by weight) in *N*-methyl-2-pyrrolidinone (NMP). The obtained slurry was spread on aluminum foil using a coater, followed by removing NMP at 60 °C under vacuum. Cathode round plates with diameter of 12 mm were prepared. The electrolyte was composed of bis(trifluoromethane) sulfonimide lithium (LiTFSI, 1 M) salt in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 by volume) with LiNO<sub>3</sub> additive (0.2 M). CR2032 coin-type cells, which were composed of cathode, a separator membrane and lithium plate as anode, were assembled in an argon-filled glove box. All electrochemical performances were measured at room temperature. The galvanostatic cycling performance tests were conducted on a LAND instrument (CT2001A) at a voltage range of 1.7-2.8 V vs. Li/Li<sup>+</sup>. The cyclic voltammogram (CV) at different scan rates (0.1-0.5 mV s<sup>-1</sup>) and electrochemical impedance spectroscopy (EIS) measurements with a frequency range from 100 kHz to 0.01 Hz were performed on a CHI electrochemical workstation (Shanghai Chenhua). The specific capacity was calculated based on the weight of sulfur loaded in the cathode electrode.

**Calculation of Li ion diffusion coefficient.** According to the Randles-Sevcik Equation as show by

$$i_p = 268600n^{\frac{3}{2}}AD^{\frac{1}{2}}Cv^{\frac{1}{2}}$$

Where  $i_p$  is the peak current in A,  $n$  is the number of electrons in the reaction,  $A$  is the electrode area,  $v$  is the scanning rate and  $C$  is the Li ion concentration in the electrolyte. From the linear relationship of  $i_p$  and  $v^{0.5}$ , the lithium diffusion coefficients  $D_{A1}$  (A1 corresponds to anodic peak at 2.4 V),  $D_{C1}$  (C1 corresponds to cathodic peak at 2.3 V),  $D_{C2}$  (C2 corresponds to cathodic peak at 2.1 V), were calculated, as shown in Figure. 4C.

**Shuttle factor calculation.** Shuttle factor is described by the following equation (1), where  $I_C$  represents the charge current,  $K_S$  is shuttle constant,  $[S_{total}]$  is the total amounts of sulfur, and  $q_H$  is

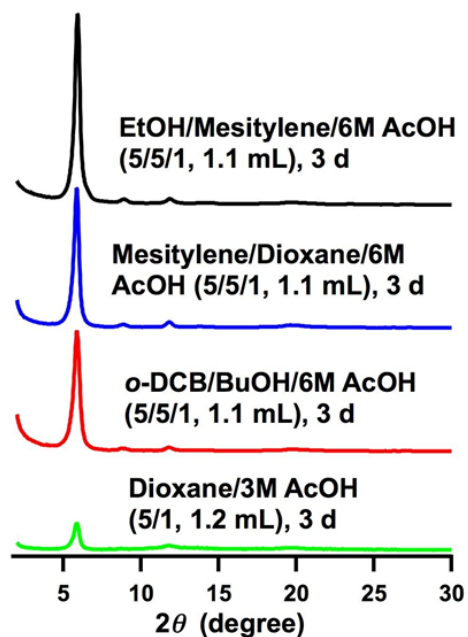
defined as specific capacity of upper plateau of charge profiles which is equal to a quarter of the theoretical capacity of sulfur  $419 \text{ mA h g}^{-1}$ .<sup>S7,S8</sup>

$$f_c = \frac{K_S q_H [S_{total}]}{I_c} \quad (1)$$

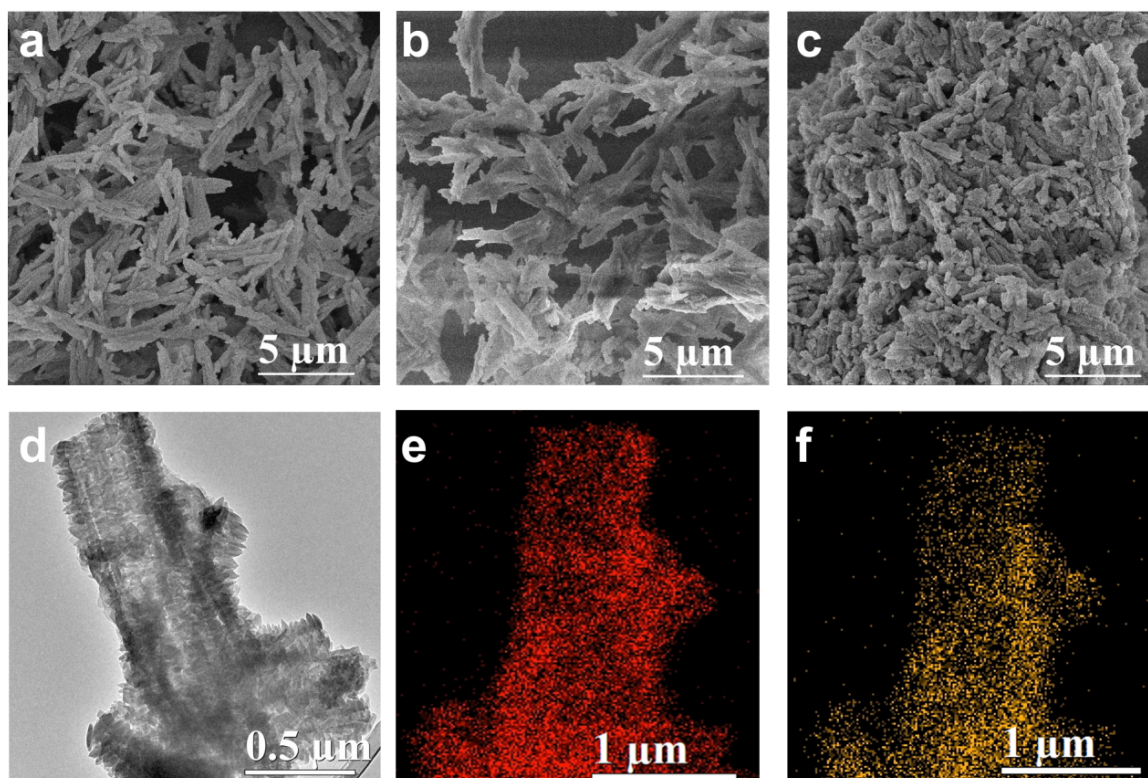
The  $K_S$  is obtained from the first derivative of capacity of upper plateau to charge current.

$$\frac{dq_H}{dI_c} = 1/K_S \quad (2)$$

## Section B. Supporting Figures

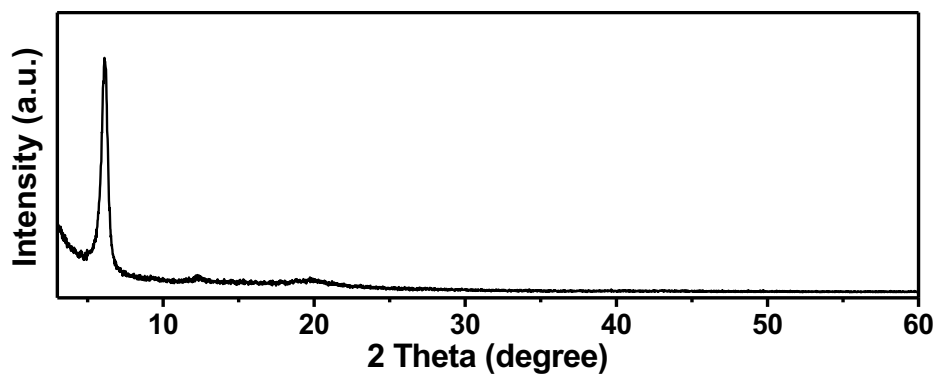


**Figure S1.** PXRD patterns of TFPPy-ETTA-COF prepared under different reaction conditions.

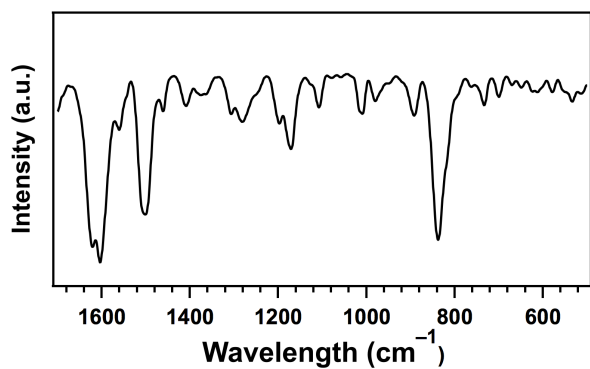


**Figure S2.** (a) FE SEM image of TFPPy-ETTA-COF. (b) SEM image of S@TFPPy-ETTA-COF. (c) FE SEM images of polysulfide@TFPPy-ETTA-COF. (d) HR TEM image of polysulfide@TFPPy-ETTA-COF. (e) The elemental mapping of carbon. (f) The elemental mapping of sulfur.

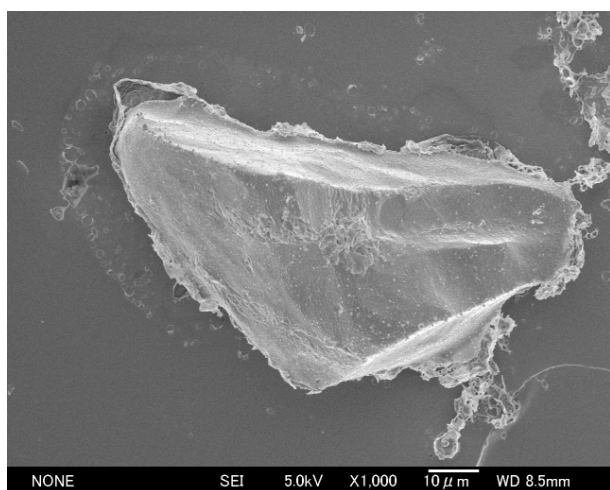




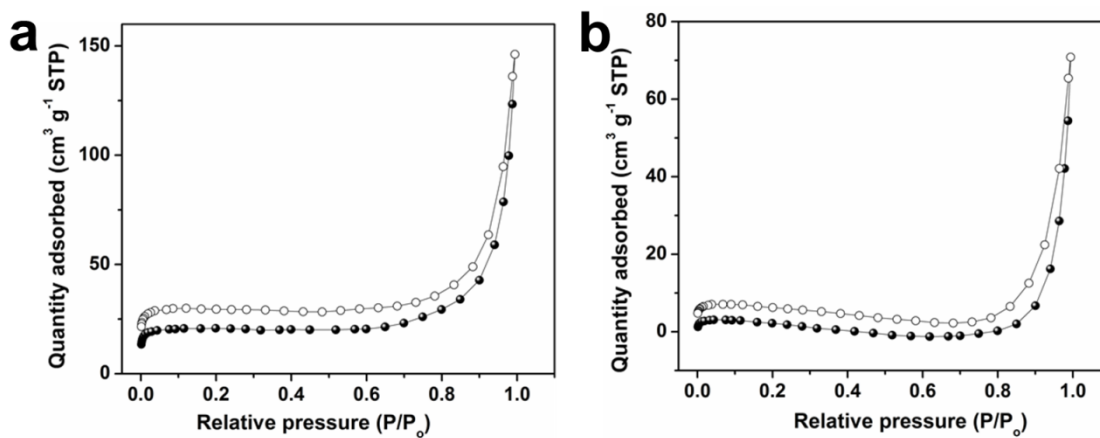
**Figure S3.** PXRD pattern of TFPPy-ETTA-COF after treatment at 430 °C in an evacuated tube.



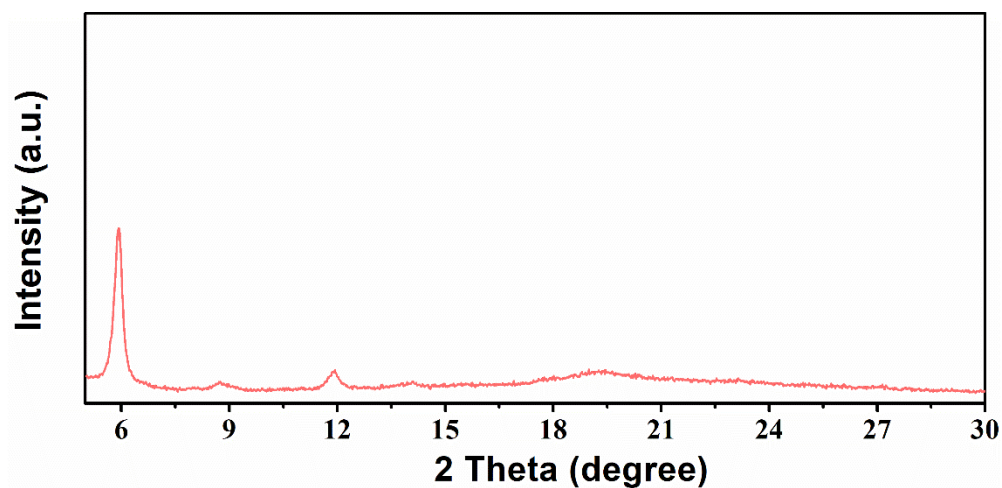
**Figure S4.** FT IR spectrum of TFPPy-ETTA-COF after treatment at 430 °C in an evacuated tube.



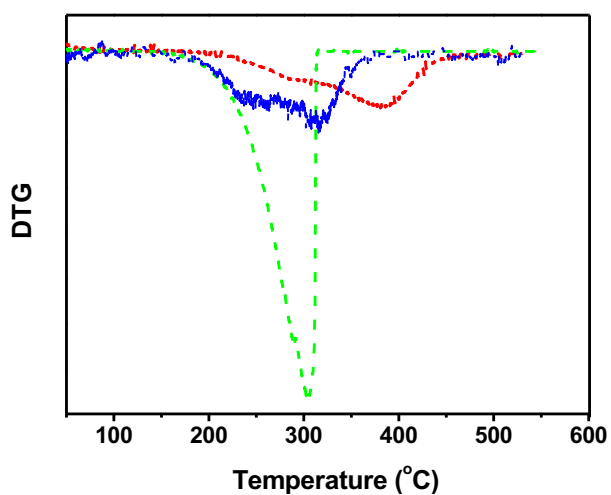
**Figure S5.** FE SEM image of bulky sulfur.



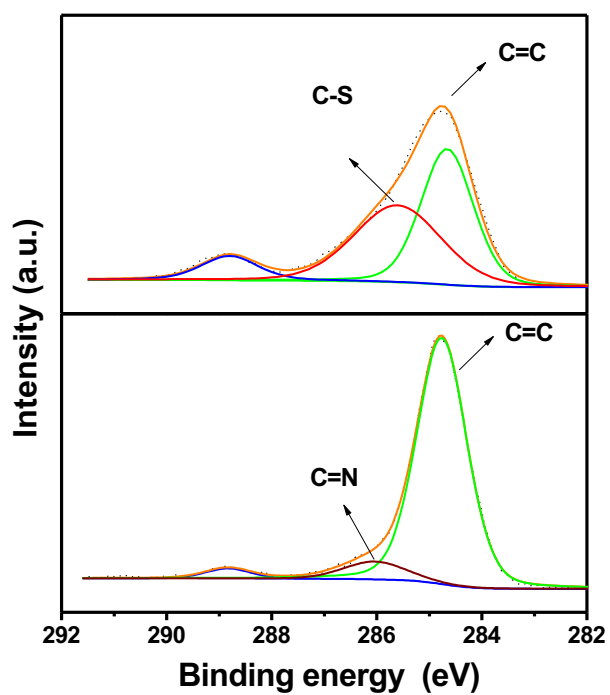
**Figure S6.** N<sub>2</sub> adsorption-desorption isotherms of (a) S@TFPPy-ETTA-COF and (b) polysulfide@TFPPy-ETTA-COF.



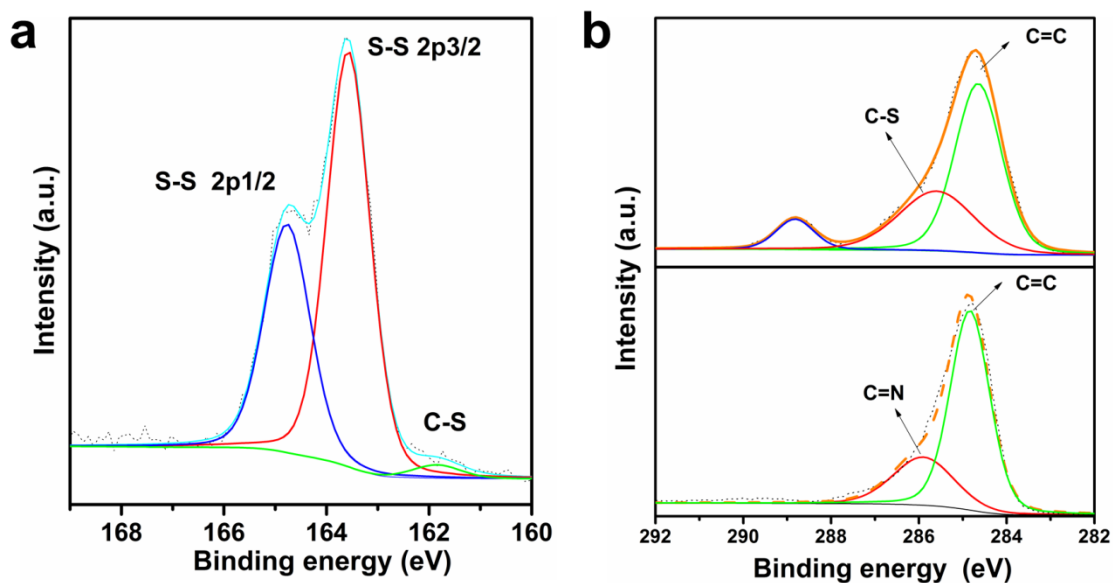
**Figure S7.** PXRD patterns of recovered polysulfide@TFPPy-ETTA-COF by washing the polysulfide@COF sample using CS<sub>2</sub> solvent to remove the elemental sulfur.



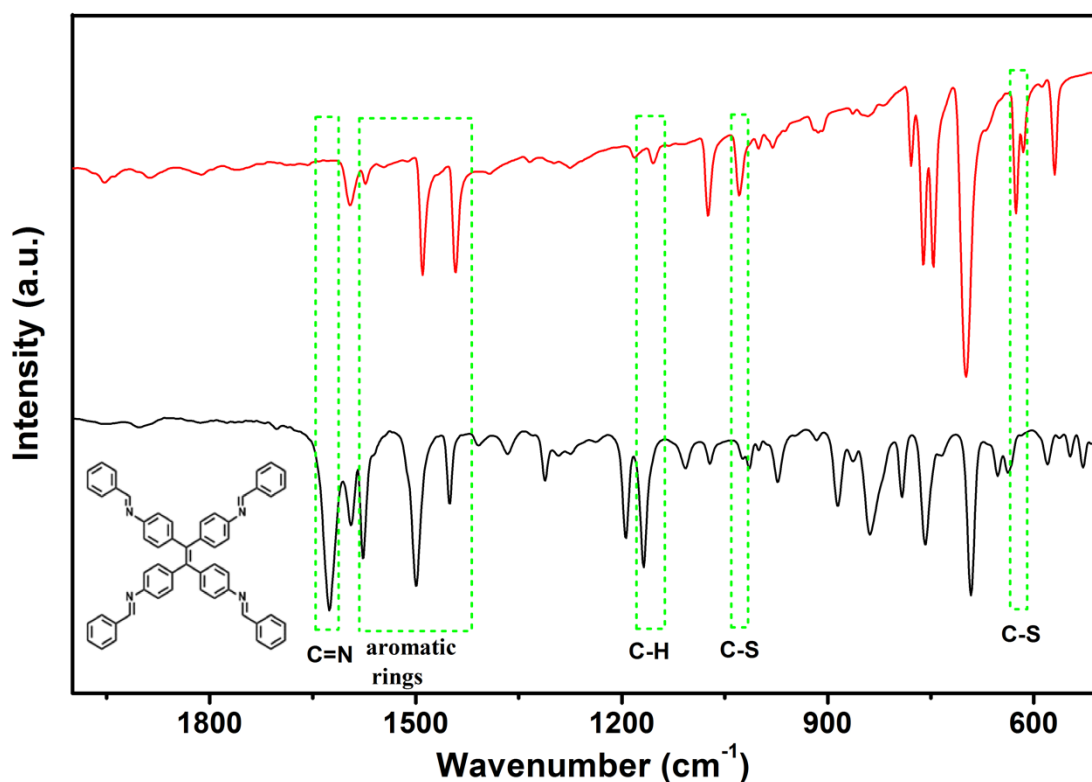
**Figure S8.** Derivative thermogravimetric analysis curves of polysulfide@TFPPy-ETTA-COF (red curve), S@TFPPy-ETTA-COF (blue curve), and sulfur (green curve).



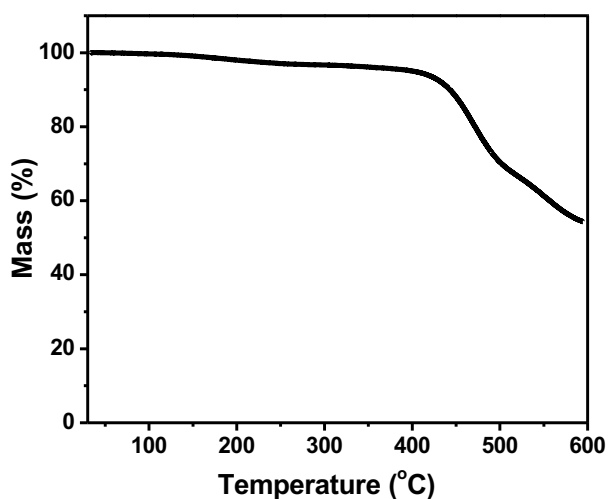
**Figure S9.** C1s XPS spectra of S@TFPPy-ETTA-COF (down) and polysulfide@TFPPy-ETTA-COF (up).



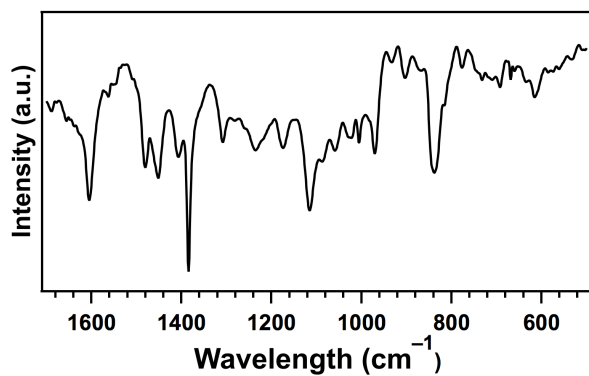
**Figure S10.** (a) The S<sub>2p</sub> XPS spectrum of polysulfide@model compound. (b) The C<sub>1s</sub> spectra of polysulfide@model compound (up) and model compound (down).



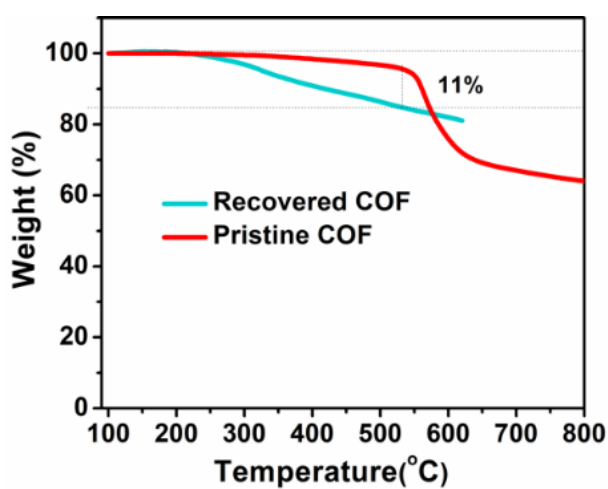
**Figure S11.** FT IR spectra of polysulfide@model compound (red curve) and model compound (black curve).



**Figure S12.** TGA curve of the model compound.



**Figure S13.** The FT IR spectra of recovered sample from polysulfide@TFPPy-ETTA-COF by washing with CS<sub>2</sub>.



**Figure S14.** TGA curves of TFPPy-ETTA-COF (red curve) and the resulting solid sample (cyan curve) upon washing polysulfide@TFPPy-ETTA-COF with CS<sub>2</sub>.

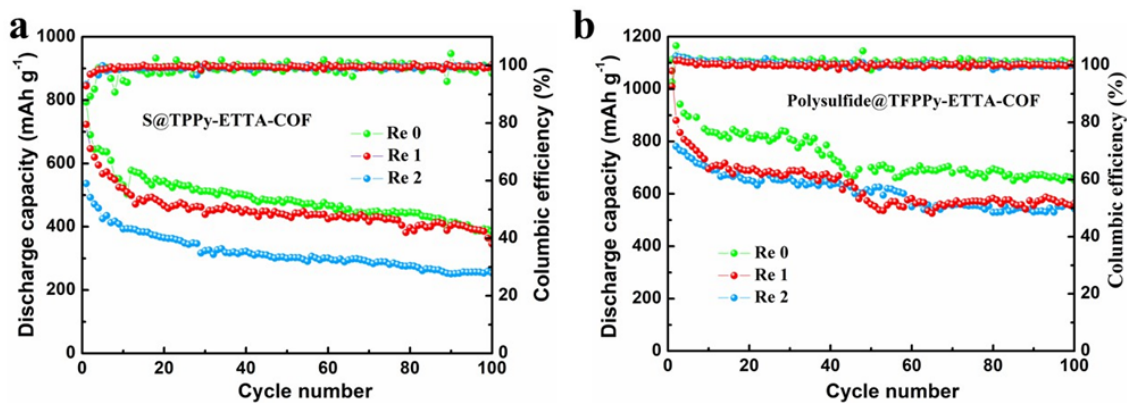


Fig. S15 Cycling performances with each 3 cells to show the reproducibility.

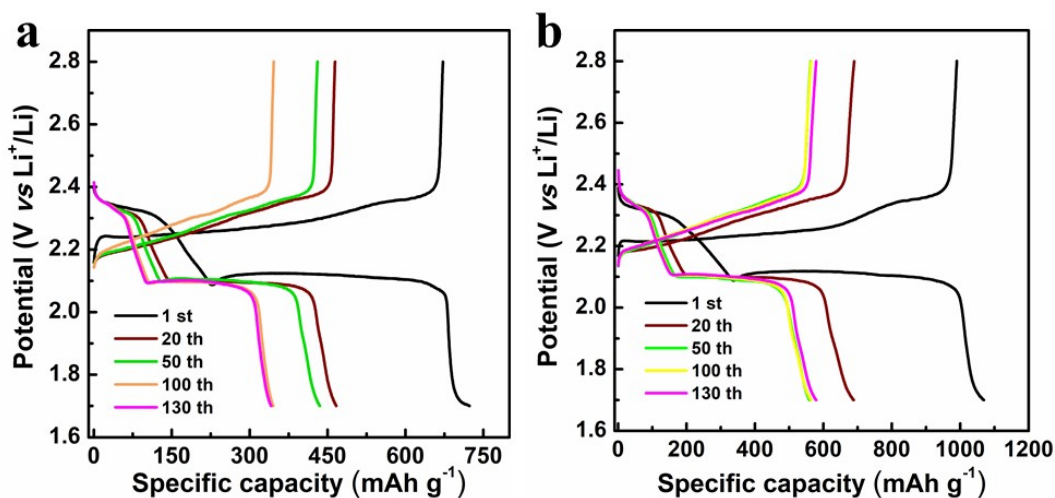


Figure S16. Galvanostatic discharge-charge curves of (a) S@TFPPy-ETTA-COF and (b) polysulfide@TFPPy-ETTA-COF with different cycles at 0.1 C.

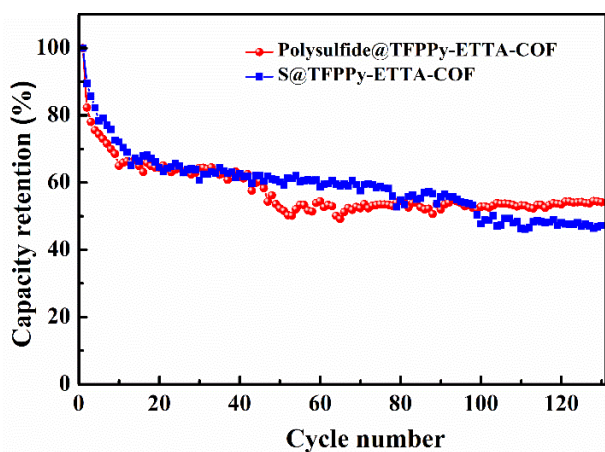


Figure S17. The capacity retention ratio at 0.1 C.

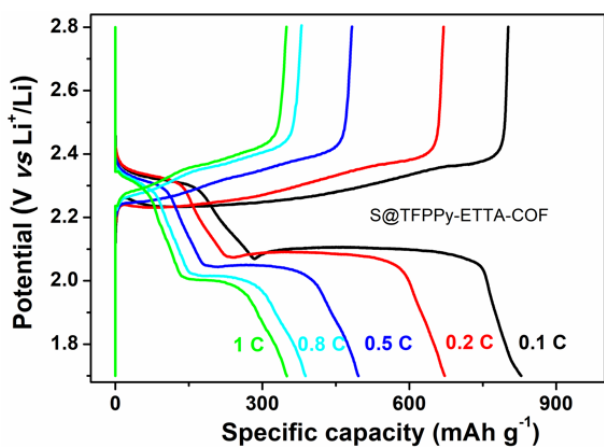


Figure S18. Galvanostatic discharge/charge curves of S@TFPPy-ETTA-COF at different rates.

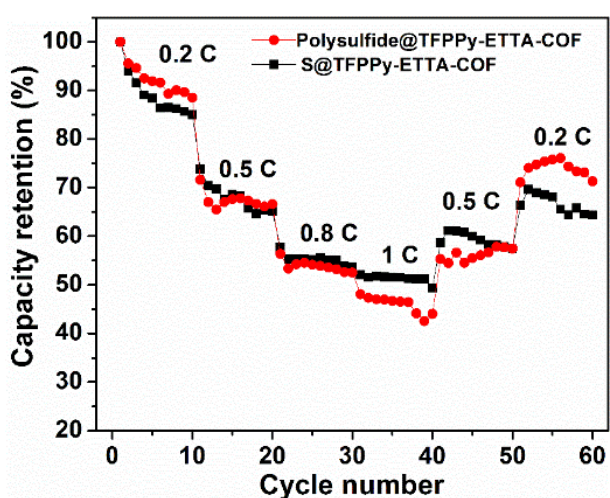


Figure S19. The capacity retention ratio at different rates upon cycling.

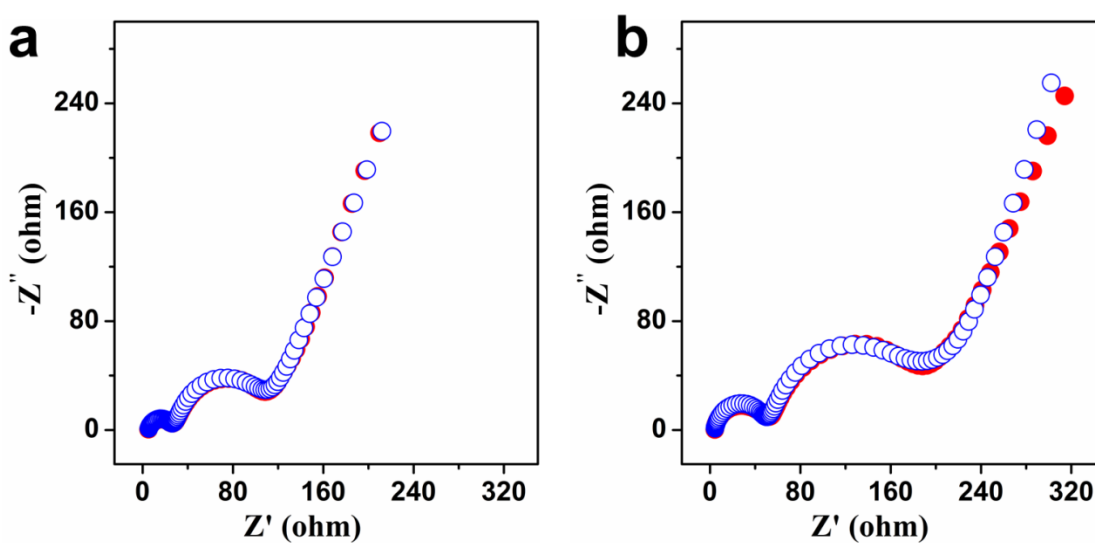
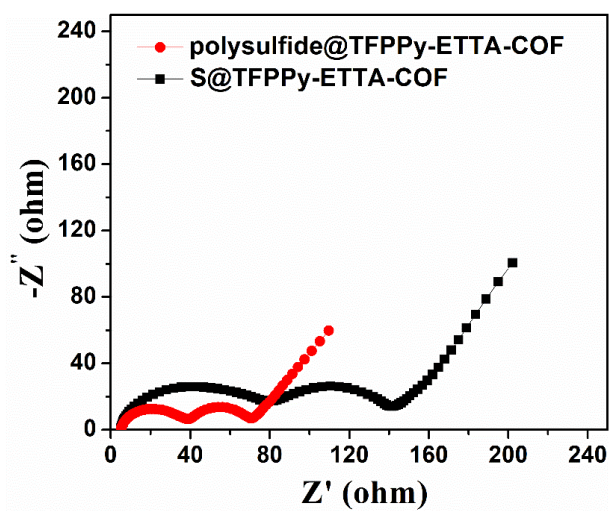


Figure S20. The experimentally measured plot (red circle) and fitted electrochemical impedance spectra (blue circle) in the form of the Nyquist plot of (a) polysulfide@TFPPy-ETTA-COF and (b) S@TFPPy-ETTA-COF.



**Figure S21.** Nyquist plots of polysulfide@TFPPy-ETTA-COF (red) and S@TFPPy-ETTA-COF (black) after 11 discharge-charge cycles at 0.1 C.



## Section C. Supporting Tables

**Table S1.** Elemental analysis of TFPPy-ETTA-COF.

Sample		C%	H%	N%
TFPPy-ETTA-COF	Calcd.	89.53	4.51	5.97
	Found	88.04	4.95	7.00

**Table S2.** The total DFTB energies, Lennard-Jones contributions (LJ), and the crystal stacking energies per monolayer as well as the corresponding HOMO-LUMO energy gap for TFPPy-ETTA-COF.

Stacking model	$c$ [Å]	Total DFTB Energy [a.u.]	LJ energy [a.u.]	Per unit crystal stacking energy [kcal.mol <sup>-1</sup> ]	HOMO-LUMO gap [eV]
Monolayer	-	-145.147886	0.6407	-	1.836
Eclipsed AA	4.52	-290.461445	1.1108	51.98	1.124
Slipped AA (0.8 Å)	4.42	-290.460303	1.1086	51.62	1.123
Staggered AB	4.77	-290.319193	1.2373	7.35	1.387

**Table S3.** Atomistic coordinates of TFPPy-ETTA-COF in the eclipsed AA-stacking model.

Atom	$x/a$	$y/b$	$z/c$
C	0.15975	0.85213	0.99704
C	0.11013	0.83729	0.90778
C	0.15741	0.90521	0.08805
C	0.05925	0.87484	0.91085
H	0.11124	0.79586	0.83643
C	0.10601	0.94194	0.09024
H	0.19563	0.917	0.15943
C	0.05601	0.92846	0.00061
H	0.02121	0.86213	0.83996
H	0.10489	0.98225	0.16421
C	0.00021	0.96684	0.99998
C	0.00014	0.03117	0.99998
C	0.94449	0.92834	0.99936
C	0.94136	0.87474	0.08923
C	0.89448	0.94166	0.90965
C	0.89055	0.83709	0.0924
H	0.97942	0.86214	0.16019
C	0.84317	0.90481	0.91185
H	0.89553	0.98195	0.83558
C	0.84091	0.85178	0.00304
H	0.88952	0.79569	0.16384
H	0.80493	0.91648	0.8404
C	0.94434	0.06955	0.00068
C	0.89435	0.05608	0.09037
C	0.94111	0.12318	0.91092
C	0.84296	0.09281	0.08824
H	0.89548	0.01578	0.16436

C	0.89024	0.16073	0.90789
H	0.97915	0.13588	0.83997
C	0.84062	0.14589	0.99721
H	0.80474	0.08104	0.15968
H	0.88912	0.20215	0.83654
C	0.05587	0.06966	0.99929
C	0.05904	0.12325	0.08916
C	0.10587	0.0563	0.90951
C	0.10986	0.16087	0.09226
H	0.02099	0.13587	0.16017
C	0.15721	0.09311	0.91168
H	0.10478	0.01603	0.83543
C	0.15949	0.14614	0.00287
H	0.11093	0.20226	0.16371
H	0.19543	0.08142	0.84018
C	0.22552	0.22534	0.92288
C	0.282	0.26008	0.93718
H	0.1947	0.23966	0.83086
C	0.32649	0.24124	0.03839
C	0.29291	0.31273	0.84841
C	0.37923	0.27519	0.05387
H	0.31891	0.19984	0.10749
C	0.34604	0.34619	0.86235
H	0.2595	0.32742	0.76582
C	0.38953	0.32906	0.96828
H	0.41222	0.26045	0.13735
H	0.35431	0.38533	0.78655
C	0.44518	0.36595	0.98793
C	0.44465	0.43221	0.99566
C	0.5001	0.33453	1

C	0.50016	0.46554	0
C	0.38993	0.46726	0.99924
C	0.55504	0.36588	0.01207
H	0.50007	0.28336	0.99999
C	0.5002	0.53245	0.00002
C	0.55564	0.43215	0.00434
C	0.38996	0.53086	0.00066
H	0.34663	0.4429	0.00187
C	0.61066	0.32894	0.03175
C	0.44471	0.56584	0.0043
C	0.55571	0.56577	0.99575
C	0.61039	0.46713	0.00076
H	0.34669	0.55527	0.99798
C	0.65416	0.34604	0.1377
C	0.62093	0.27506	0.94619
C	0.44531	0.6321	0.01206
C	0.55518	0.63204	0.98803
C	0.61043	0.53073	0.99935
H	0.65367	0.44272	0.9981
C	0.70727	0.31255	0.15166
H	0.6459	0.38519	0.2135
C	0.67366	0.24108	0.96169
H	0.58794	0.26034	0.86269
C	0.50026	0.66345	0.00006
C	0.38969	0.66905	0.03167
C	0.61084	0.66892	0.96841
H	0.65373	0.55509	0.00203
C	0.71816	0.25989	0.06289
H	0.74069	0.32722	0.23424
H	0.68122	0.19967	0.89259

C	0.34617	0.65196	0.1376
C	0.37944	0.72292	0.94606
C	0.65433	0.6518	0.86243
C	0.62114	0.72277	0.05402
C	0.77463	0.22513	0.07713
C	0.29305	0.68547	0.15151
H	0.3544	0.61282	0.21342
C	0.32672	0.75692	0.96151
H	0.41246	0.73763	0.86257
C	0.70745	0.68527	0.84843
H	0.64606	0.61266	0.78662
C	0.67389	0.75672	0.03852
H	0.58815	0.73751	0.13755
H	0.80553	0.23954	0.16894
C	0.28219	0.73812	0.06271
H	0.25962	0.67081	0.2341
H	0.31918	0.79832	0.89239
C	0.71837	0.73791	0.93723
H	0.74086	0.67059	0.76579
H	0.68147	0.79812	0.10765
N	0.21251	0.18133	0.01295
N	0.78756	0.18103	0.98723
C	0.77484	0.77267	0.92285
H	0.80558	0.75847	0.83054
C	0.22572	0.77289	0.07693
H	0.19481	0.75849	0.16874
N	0.78792	0.81655	0.0132
N	0.2128	0.81699	0.98703
H	0.50029	0.71463	0.00008
C	0.15975	0.85213	0.49704

C	0.11013	0.83729	0.40778
C	0.15741	0.90521	0.58805
C	0.05925	0.87484	0.41085
H	0.11124	0.79586	0.33643
C	0.10601	0.94194	0.59024
H	0.19563	0.917	0.65943
C	0.05601	0.92846	0.50061
H	0.02121	0.86213	0.33996
H	0.10489	0.98225	0.66421
C	0.00021	0.96684	0.49998
C	0.00014	0.03117	0.49998
C	0.94449	0.92834	0.49936
C	0.94136	0.87474	0.58923
C	0.89448	0.94166	0.40965
C	0.89055	0.83709	0.5924
H	0.97942	0.86214	0.66019
C	0.84317	0.90481	0.41185
H	0.89553	0.98195	0.33558
C	0.84091	0.85178	0.50304
H	0.88952	0.79569	0.66384
H	0.80493	0.91648	0.3404
C	0.94434	0.06955	0.50068
C	0.89435	0.05608	0.59037
C	0.94111	0.12318	0.41092
C	0.84296	0.09281	0.58824
H	0.89548	0.01578	0.66436
C	0.89024	0.16073	0.40789
H	0.97915	0.13588	0.33997
C	0.84062	0.14589	0.49721
H	0.80474	0.08104	0.65968

H	0.88912	0.20215	0.33654
C	0.05587	0.06966	0.49929
C	0.05904	0.12325	0.58916
C	0.10587	0.0563	0.40951
C	0.10986	0.16087	0.59226
H	0.02099	0.13587	0.66017
C	0.15721	0.09311	0.41168
H	0.10478	0.01603	0.33543
C	0.15949	0.14614	0.50287
H	0.11093	0.20226	0.66371
H	0.19543	0.08142	0.34018
C	0.22552	0.22534	0.42288
C	0.282	0.26008	0.43718
H	0.1947	0.23966	0.33086
C	0.32649	0.24124	0.53839
C	0.29291	0.31273	0.34841
C	0.37923	0.27519	0.55387
H	0.31891	0.19984	0.60749
C	0.34604	0.34619	0.36235
H	0.2595	0.32742	0.26582
C	0.38953	0.32906	0.46828
H	0.41222	0.26045	0.63735
H	0.35431	0.38533	0.28655
C	0.44518	0.36595	0.48793
C	0.44465	0.43221	0.49566
C	0.5001	0.33453	0.5
C	0.50016	0.46554	0.5
C	0.38993	0.46726	0.49924
C	0.55504	0.36588	0.51207
H	0.50007	0.28336	0.49999

C	0.5002	0.53245	0.50002
C	0.55564	0.43215	0.50434
C	0.38996	0.53086	0.50066
H	0.34663	0.4429	0.50187
C	0.61066	0.32894	0.53175
C	0.44471	0.56584	0.5043
C	0.55571	0.56577	0.49575
C	0.61039	0.46713	0.50076
H	0.34669	0.55527	0.49798
C	0.65416	0.34604	0.6377
C	0.62093	0.27506	0.44619
C	0.44531	0.6321	0.51206
C	0.55518	0.63204	0.48803
C	0.61043	0.53073	0.49935
H	0.65367	0.44272	0.4981
C	0.70727	0.31255	0.65166
H	0.6459	0.38519	0.7135
C	0.67366	0.24108	0.46169
H	0.58794	0.26034	0.36269
C	0.50026	0.66345	0.50006
C	0.38969	0.66905	0.53167
C	0.61084	0.66892	0.46841
H	0.65373	0.55509	0.50203
C	0.71816	0.25989	0.56289
H	0.74069	0.32722	0.73424
H	0.68122	0.19967	0.39259
C	0.34617	0.65196	0.6376
C	0.37944	0.72292	0.44606
C	0.65433	0.6518	0.36243
C	0.62114	0.72277	0.55402



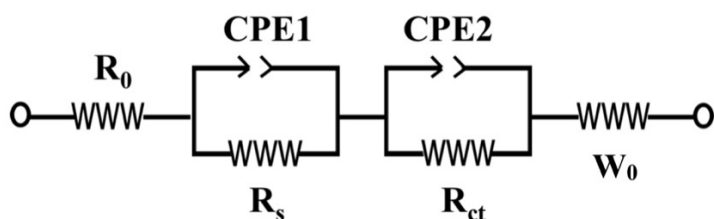
C	0.77463	0.22513	0.57713
C	0.29305	0.68547	0.65151
H	0.3544	0.61282	0.71342
C	0.32672	0.75692	0.46151
H	0.41246	0.73763	0.36257
C	0.70745	0.68527	0.34843
H	0.64606	0.61266	0.28662
C	0.67389	0.75672	0.53852
H	0.58815	0.73751	0.63755
H	0.80553	0.23954	0.66894
C	0.28219	0.73812	0.56271
H	0.25962	0.67081	0.7341
H	0.31918	0.79832	0.39239
C	0.71837	0.73791	0.43723
H	0.74086	0.67059	0.26579
H	0.68147	0.79812	0.60765
N	0.21251	0.18133	0.51295
N	0.78756	0.18103	0.48723
C	0.77484	0.77267	0.42285
H	0.80558	0.75847	0.33054
C	0.22572	0.77289	0.57693
H	0.19481	0.75849	0.66874
N	0.78792	0.81655	0.5132
N	0.2128	0.81699	0.48703
H	0.50029	0.71463	0.50008

**Table S4.** Pore parameters of TFPPy-ETTA-COF, S@TFPPy-ETTA-COF and polysulfide@TFPPy-ETTA-COF samples.

Sample	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )
TFPPy-ETTA-COF	1223	0.98
S@TFPPy-ETTA-COF	63	0.24
Polysulfide@TFPPy-ETTA-COF	11	0.11

**Table S5.** The equivalent circuit simulation and the corresponding parameters. Electrode resistances from the equivalent circuit fitting of the Nyquist plots. The EIS spectra can be explained with the following phenomena: The semicircle at high frequency associates with the lithium-ion transfer through the surface layer of the active material ( $R_s$ ), the other one at middle frequency is ascribed to the charge transfer resistances ( $R_{ct}$ ), and the inclined line is related to the Warburg impedance ( $W_0$ ). The intercept at real axis  $Z'$  associates with the combination resistance  $R_0$ , including the intrinsic resistance of active materials, the contact resistance at active/materials/current collector interface, and the ionic resistance of the electrolyte.

Sample	$R_0$ ( $\Omega$ )	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )
S@TFPPy-ETTA-COF	3.7	42.1	92.4
Polysulfide@TFPPy-ETTA-COF	4.8	18.8	56.2



## Section D. Supporting References

- S1. M. G. Rabbani, A. K. Sekizkardes, O. M. El-Kadri, B. R. Kaafarani, and H. M. El-Kader, *J. Mater. Chem.* 2012, **22**, 25409.
- S2. J. Lu, and J. Zhang, *J. Mater. Chem. A* 2014, **2**, 13831.
- S3. L. Ascher, T. Sick, J. T. Margraf, S. H. Lapidus, M. Calik, C. Hettstedt, K. Karaghiosoff, M. Döblinger, T. Clark, K. W. Chapman, F. Auras, and T. Bein, *Nat. Chem.* 2016, **8**, 310.
- S4. B. Aradi, B. Hourahine, and T. Frauenheim, *J. Phys. Chem. A* 2007, **111**, 5678.
- S5. <http://www.dftb.org>.
- S6. Accelrys, Material Studio Release Notes, Release 4.4, Accelrys Software, San Diego 2008.
- S7. A. Manthiram, Y. Fu, S. H. Chung, C. Zu, and Y. S. Su, *Chem. Rev.* 2014, **114**, 11751.
- S8. Y. V. Mikhaylik, and J. R. Akridge, *J. Electrochem. Soc.* 2004, **151**, A1969.