### **Supporting Information**

# Covalent Organic Framework-Based Ultrathin Crystalline Porous Film: Manipulating Uniformity of Fluoride Distribution for Stabilizing Lithium

#### **Metal Anode**

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#### **Section I. Materials and Methods**

*1.1 Materials*: Dichloromethane (DCM), *p*-toluene sulfonic acid (PTSA), benzidine (BD), were purchased from Aladdin Reagent Co., Ltd., China. 1,3,5-triformylphloroglucinol (Tp) were purchased from Yanshen Technology Co., Ltd., China. *P*-phenylenediamine (Pa) and 4,4"-diamino-*p*-terphenyl (DATP) were purchased from Tokyo Chemical Industry Co., Ltd., Japan. All the lithium salts and solvents that were prepared for electrolytes were purchased from DoDoChem. All the chemicals were used as-received without further purification. The water used throughout all experiments was purified through a Millipore system.

*1.2 Preparation of COF films*: A interfacial polymerization has been carried out to prepare a TpPa-COF film according to the earlier report (Scheme S1).<sup>S1</sup> Typically, 0.373 mmol/L of 1,3,5-triformylphloroglucinol (Tp) solution in a 25 mL of dichloromethane (DCM) was layered on the bottom of a 50 mL beaker. Then 0.56 mmol/L of *p*-phenylenediamine (Pa) solution in a 25 mL of water and was added dropwise with two equiv. of *p*-toluene sulfonic acid (PTSA) onto the top of the DCM solutions from two-fold to six-fold. The beaker was kept at room temperature for 3 days. After reaction, the formed films were transferred and soaked in water and acetone successively to remove impurities, collected by different substrates for further characterizations and then dried in vacuum at 65 °C overnight. For the preparation of the diamines including benzidine (BD), 4,4"-diamino-*p*-terphenyl (DATP) were reacted with Tp, respectively (Schemes S2,S3). The same procedure was adopted as described for TpPa-COF. Model compound of TpPa-COF, tris(*N*-salicylideneaniline), was synthesized by following the reported route (Scheme S4).<sup>S1</sup>



Scheme S1. Synthesis of TpPa-COF.



Scheme S2. Synthesis of TpBD-COF.



Scheme S3. Synthesis of TpDATP-COF.



Scheme S4. Synthesis of the model compound of TpPa-COF.

*1.3 Transferring the COF film onto lithium metal*: To cover a COF film on lithium electrode, the as-prepared TpPa-COF film was firstly transferred to a battery separator (COF@separator). After drying under vacuum, it was remained in glove box. A certain amount of 1,3-dioxolane was dipped onto the COF@separator for wetting the contact between the film and separator. Next, the COF-coated separator and lithium foil were sandwiched by two stainless steels. By pressing the COF@separator with lithium foil under given pressure, the separator could be totally peeled off after removing the stainless steels. Finally, the film was successfully transferred onto the lithium foil, dried and cut into regular-shaped pieces for battery assembly.

*1.4 Calculation of the density (based on area) of the TpPa-COF film*: In order to reduce measurement errors to calculate the ultra-low-density of the TpPa-COF film, 10 beakers (500 ml) with the same diameter were used to prepare the TpPa-COF films. The TpPa-films in 10 beakers were completely transferred and made into a bulk by vacuum suction filter; after post treatment, the weight of the bulk was measured and the area of the TpPa-COF film was determined according to the diameter of the beaker. Therefore, the density (based on area) of the TpPa-COF film can be obtained.

*1.5 Periodic DFT calculation*: Periodic DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP).<sup>S2</sup> In this work, the projector augmented wave method (PAW) was used.<sup>S3</sup> The PBE (Perdew-Burke-Ernzerhof) functional <sup>S4</sup> with the DFT-D3(BJ) dispersion correction <sup>S5,S6</sup> was applied in all calculations. A kinetic energy cutoff for the plane-wave basis set was opted at 500 eV. The electronic Brillouin zone was integrated using  $\Gamma$ -centred Monkhorst-Pack grids with the smallest allowed spacing between kpoints

(KSPACING) of 0.2 Å<sup>-1.S7</sup> All atoms in a periodic box were allowed to relax during geometry optimizations and the optimized structures were received when the forces acting on the atoms are less than 0.05 eV Å<sup>-1</sup>. For optimization criteria, an energy convergence was set at  $10^{-6}$  eV. The calculated lattice parameters of COFs triclinic primitive cell are a = 22.504 Å, b = 22.515 Å, and c = 7.229 Å. To locate the preference site for Li adsorption, the primitive cell was doubled in c axis to represent two layers of COF in one simulation cell. 12 Li atoms were added into COF channel and were found to locate near carbonyl oxygen atoms of COF. This indicates that Li prefers to locate near side-wall of COF channel. The molecular structures were visualized by using Vesta program.

1.6 Quantum cluster calculation: In this work, quantum cluster calculations were carried out with the B3LYP functional and the 6-31G+(d,p) basis set. All calculations were performed with the Gaussian 09 package. During geometry optimizations, all atoms were fully relaxed. The cluster model of TpPa-COFs used in this work was trimmed from the optimized structure of periodic DFT calculation. The adsorption energy of Li<sup>+</sup> ion in 6 different systems; (1) Li<sup>+</sup> adsorption with TFSI<sup>-</sup> anion salt, (2) Li<sup>+</sup> adsorption with DOL and TSFI<sup>-</sup>, (3) Li<sup>+</sup> ion adsorption with TpPa-COF and TSFI-, (4) Li<sup>+</sup> ion adsorption with PF<sub>6</sub>-, (5) Li<sup>+</sup> adsorption with DMC and  $PF_{6}$ , (5) Li<sup>+</sup> ion adsorption with TpPa-COF and  $PF_{6}$ , were studied to evaluate the preference of TpPa-COF with Li<sup>+</sup>. All of the systems are neutral. The interaction of Li<sup>+</sup> ion in the TpPa-COF containing systems show higher adsorption energy indicating that Li<sup>+</sup> ion prefers to adsorb with TpPa-COF than DOL or DMC solvents or PF<sub>6</sub><sup>-</sup> or TSFI<sup>-</sup> anion salts. The active site of TpPa-COF for Li<sup>+</sup> adsorption was found at the carbonyl oxygen atom. The adsorption capacity of Li on COF was studied using TpPa-COF monomer. The first three Li were placed at carbonyl oxygen atoms to study the half storage which were stabilized in between carbonyl oxygen atom and carbon atom after optimization. The latter three Li were placed near carbonyl oxygen which were stabilized between carbonyl oxygen and amine nitrogen. The highest occupied molecular orbital (HOMO) and Lowest occupied molecular orbital (LUMO) were provided. The Mulliken method was applied for charge analysis. Molecular electrostatic potential (MESP) maps were generated with the same level of theory and Gaussview 6.0 was employed for generating the picture of MESP maps which presents charge transfer direction between Li and TpPa-COF after adsorption.

1.7 Electrochemical measurements: Cycling tests for symmetric cells of pristine lithium or TpPa-COF protected lithium conducted with 1 lithium were Μ bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3- dioxolane (DOL)/1,2-dimethoxyethane (DME) (volume ratio, 1:1)) with 1wt% LiNO<sub>3</sub> electrolyte or with lithium hexafluorophosphate (LiPF<sub>6</sub>) in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v) electrolyte. Before cycling the battery in the carbonate electrolyte, the TpPa-COF protected lithium electrodes were firstly cycled in 1M DOL/DME of LiTFSI to ensure the better formation of anion-derived SEI on the film as previously reported (Nat. Energy., 2019, 4, 269). Then the battery was disassembled and the electrodes were carefully cleaned and dried. After that, the treated electrodes were reassembled in carbonate electrolyte for further cycling. For cathode fabrication, the high mas loading (3.9 mAh cm<sup>-2</sup>) NCM523 cathode was prepared by mixing the active materials with carbon black and polyvinylidene fluoride (PVDF) in a mass ratio of 94:3:3. After the slurry was coated on Al foil, the electrodes were dried at 90 °C under vacuum for 12 h and then punched into disks. For the low anode to cathode capacity ratio TpPaprotected lithium/NCM523 cells, lithium was first deposited on copper foil with the predetermined capacities (i.e, 6.5 mAh cm<sup>-2</sup>, 7.5 mAh cm<sup>-2</sup> and 11.3 mAh cm<sup>-2</sup>, which corresponds to thickness of about 30µm, 36µm and 50µm, respectively) in 1M LiTFSI DOL/DME (1:1), whose surface was thoroughly cleaned with DOL solvent and dried. Then the same TpPa-COF film transfer process was applied to achieve the LiTpPa-LiF@Li anode, as described previously. All the electrochemical properties were tested by assembled 2032-coin cells and polypropylene separator (Celgard 2500). All Galvanostatic charge-discharge measurements were carried out on a battery testing instrument (Land CT2001A, Wuhan China) at different current densities. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were measured by a CHI 660E electrochemical workstation. CV curves of asymmetric cells (TpPa film@Cu/Li cell) were recorded over the voltage range of 0.01-3V for Li<sup>+</sup> redox tests and -0.25-2.5V for Li plating/stripping tests. For CV tests of symmetric cells,

the lithium metal was used as the counter electrode and pristine lithium or TpPa protected lithium were used as the working electrodes, the voltage range was -0.2V-0.2V. EIS was measured in a frequency range of 100 kHz to 0.1 Hz at open circuit potential and an amplitude of 5 mV. The fitting parameters of the equivalent circuit were analyzed by the ZSimpWin software.

1.8 Characterization: Powder X-ray diffraction (PXRD) data was measured by a Bruker D8 Advance with Cu-Ka X-ray radiation ( $\lambda = 0.154056$  nm), using an operation voltage and current of 40 kV and 40 mA. Fourier transform infrared (FT IR) spectra were collected on a Thermofisher Nicolet 6700 spectrometer. Raman spectra were collected on a Renishaw In Via Qontor microscopic Raman spectrometer. <sup>1</sup>H NMR and <sup>19</sup>F NMR experiments were conducted on a Bruker AV-3-HD-500 instrument. Solid-state <sup>13</sup>C NMR spectra were acquired using an Agilent 600 MHz NMR spectrometer. Elemental analyses (EA) including C, H, N were conducted on a VARIO EL-III Elemental analyzer. N2 adsorption-desorption isotherms were measured at 77 K on a Micromeritcs TriStar II 3020 volumetric adsorption analyzer after degassed in a vacuum at 120 °C overnight. Atomic Force Microscope (AFM) was performed on a NT-MDT NTEGRA Spectra II microscope. Field-emission scanning electron microscopy (FE SEM) images were acquired from a Zeiss Gemini SEM500, equipped with an Aztec X-Max Extreme energy dispersive spectrometer (EDS). High-resolution Transmission Electron Microscope (HR TEM) images were collected from a JEM-2010F transmission electron microscope. Thermogravimetric analyses (TGA) were carried out on a TA Instrument 5550 thermogravimetric analyzer under N<sub>2</sub> atmosphere at a heating rate of 10 °C min<sup>-1</sup> with a temperature range from 100 to 800 °C. XPS measurements were carried out with a Thermo Scientific K-Alpha+ spectrometer under vacuum.

## Section II. Tables and Figures

Sample (formula)		C (wt.%)	H (wt.%)	N (wt.%)
TpPa-COF	calculated	67.92	3.77	13.20
$(C_{36}H_{24}N_6O_6)_n$	found	66.70	4.19	12.89

 Table S1. Element analysis of the as-synthesized TpPa-COF film.

Strategy	Full cell	Cathode	Cycling	Electrolyte	Electrolyte	Li metal	Reference
	type	loading	stability		amount	thickness	
"Polyurea" Thin	Li/LFP	0.75	200	1M LiPF <sub>6</sub> in	71 μL/ 250 μm		Adv. Mater.
Film	N/P:68	mAh/cm <sup>2</sup>	cycles	EC/DEC/DMC (1:1:1	mAh		2019, 31,
				vol)			1806541
Alloy films/LiCl	Li/LTO	0.5	1500	1 M LiTFSI in	80 µL/	250 μm	Nat. Energy
	N/P:103	mAh/cm <sup>2</sup>	cycles	DOL/DME (1	mAh		2017, 2, 17119
				:1 vol)			
Fluorinated	Li/NCM811	1.5	300	1 M LiFSI/DME-TFEO	40 μL/ 50 μm		Nat. Energy
solvents	N/P:6.8	mAh/cm <sup>2</sup>	cycles	(1:9 by weight)	mAh		2019, 4(9):
							796-805.
Concentrated	Li/NCM	1.7	300	2 M LiTFSI /2 M	41 μL/ 250 μm		Nat.Energy,
dual-salt/ether	N/P:30	mAh/cm <sup>2</sup>	cycles	LiDFOB in DME,	mAh	mAh	
electrolyte							739.
Sn alloy	Li/NCA	3	100	1 M LiPF <sub>6</sub> in EC/DMC	25 μL/	45 μm	Nat. Energy,
interphase	N/P:3	mAh/cm <sup>2</sup>	cycles	(1:1) with 10 v% FEC	mAh		2018, 3(4):
				and 1 vol% VC			310.
				additives			
Lithiophilic LiC <sub>6</sub>	Li/LFP	1.2	140	1M LiPF <sub>6</sub> in EC/DEC	36 µL/	50 µm	Adv. Mater.
layers	N/P:8.6	mAh/cm <sup>2</sup>	cycles	(1:1: vol)	mAh		2019, 31,
							1807131
Electrolyte	Li/NCM	1	250	1 M LiPF <sub>6</sub> in EC/DEC	80 µL/	50 µm	Nature
additive	N/P:6.8	mAh/cm <sup>2</sup>	cycles	with sustained-released	mAh		Commun.
				LiNO <sub>3</sub> additive			2018, 9, 3656.
Electrolyte	Li/NCM	1.5	168	0.6M LiTFSI and 0.4M	67 μL/	120 µm	Nat. Energy,
additive	N/P:10.3	mAh/cm <sup>2</sup>	cycles	LiBOB in EC/EMC	mAh		2017, 2, 17012
				with 0.05M LiPF <sub>6</sub>			
Single-ion-	Li/NCM	2	160	1 M LiPF <sub>6</sub> in EC/DEC	32 µL/	42 μm	Joule 2019, 3,
conductive	N/P:4	mAh/cm <sup>2</sup>	cycles	with 10 wt % FEC	mAh		1-16
network				additive			
This work	Li/NCM	3.9	152	1 M LiPF <sub>6</sub> in EC/DMC	12 μL/	50 µm	This work
	N/P:2.8	mAh/cm <sup>2</sup>	cycles	(no additive was used)	mAh		

**Table S2.** Summary of the state-of-art Li-metal battery performances.



**Figure S1.** Photographs for showing the interfacial growth of TpPa-COF film at different reaction times.



**Figure S2.** Illustration of synthesis of the representative TpPa-COF-film coated lithium metal anode. (a) The brightly yellow film was transferred onto a polypropylene separator and the composite film dried under vacuum. (b) After the surface of lithium metal was wetted with a certain amount of DOL solution, the composite film was compressed with the wetted lithium metal under pressure for at least 10 min, and then the polypropylene separator was peeled off. (c) The as-prepared COF-coated lithium metal was dried and cut into regularly shaped pieces by doctor blade for the further cell assembling. (d) the cross-section FE SEM image of the TpPa-COF coated lithium (e) and the corresponding EDS profile.



**Figure S3.** (a) Photographs of the TpDATP-, TpBD- and TpPa-COF films synthesized at the solution interface. (b) According to the EIS results, TpPa films demonstrate a lower interfacial resistance when coated on lithium metal. Thus, TpPa films facilitate the faster Li<sup>+</sup> transport than TpBD- and TpDATP-COF films.



**Figure S4.** Structural illustration (a), SEM image (b) and coulombic efficiency at 1mAh cm<sup>-2</sup> and 1 mA cm<sup>-2</sup> (c) of the TpBD-COF film.



**Figure S5.** (a) Voltage profiles of lithium deposition/dissolution on the symmetric TpBDprotected lithium cell, measured at a current density of 2 mA cm<sup>-2</sup> and at a deposition capacity of 1 mAh cm<sup>-2</sup>. The magnified voltage profiles from 0 to 5 h (b) and from 250 to 255 h (c), respectively.



**Figure S6.** Structural illustration (a), SEM image (b) and coulombic efficiency at 1mAh cm<sup>-2</sup> and 1 mA cm<sup>-2</sup> (c) of the TpDATP-COF film.



**Figure S7.** (a) Voltage profiles of lithium deposition/dissolution on the symmetric TpDATPprotected lithium cell, measured at a current density of 2 mA cm<sup>-2</sup> and at a deposition capacity of 1 mAh cm<sup>-2</sup>. The magnified voltage profiles from 0 to 5 h (b) and from 200 to 205 h (c), respectively.



**Figure S8.** FT IR spectra of *p*-phenylenediamine (Pa), 1,3,5-triformylphloroglucinol (Tp) and TpPa COF film. Both N–H bands of Pa (3100-3400 cm<sup>-1</sup>) and C=O bands of Tp (1644 cm<sup>-1</sup>) disappear in the spectrum of TpPa-COF and there are newly emerging characteristic bands ascribed to C=C at 1574 cm<sup>-1</sup> and C-N at 1259 cm<sup>-1</sup>, demonstrating the formation of keto-enamine linkage in the TpPa-COF film.



Figure S9. Solid-state CP/MAS <sup>13</sup>C NMR of TpPa-COF film.



**Figure S10.** Raman spectra of *p*-phenylenediamine (Pa), 1,3,5-triformylphloroglucinol (Tp) and TpPa-COF film.



**Figure S11.** TGA curves of the TpPa-COF film before and after cycling in the lithium symmetric cell.



Figure S12. FE SEM (a) and TEM (b) images of the TpPa COF film.



**Figure S13**. HR TEM image (left) of the TpPa COF film with the corresponding FFT pattern (right).



**Figure S14.** PXRD patterns of TpPa-COF before (red) and after (black) cycling in the lithium symmetric cell. The characteristic diffraction peaks at  $2\theta = 4.7^{\circ}$  and  $26.7^{\circ}$  correspond to the (100) and (001) planes as reported.<sup>S1</sup>



Figure S15. N<sub>2</sub> adsorption/desorption isotherm of the TpPa-COF film at 77K.



**Figure S16.** AFM images and height profiles of the different TpPa-COF films synthesized by varying the monomer concentrations from one-fold (a), two-fold (b) to six-fold (c), respectively, under otherwise identical conditions.



**Figure S17.** Density functional theory (DFT) calculation for the model cluster of TpPa-COF, i.e. tris(*N*-salicylideneaniline), including the free energy of the two-step lithiation reaction (a) and the HOMO and LUMO orbitals and energy levels of the different lithiated clusters (b), respectively.



**Figure S18.** Discharge-charge profiles of the TpPa-COF film over 10 cycles at the current density of 0.1 mA cm<sup>-2</sup>. (b) CV curves of the TpPa-COF@Cu/Li-metal half-cell, of which the TpPa-COF film is *ca*. 80 nm thick.



**Figure S19.** FT IR spectra of the TpPa-COF film before and after lithiation. As observed, upon lithiation of TpPa-COF, the C=O peak at 1609 cm<sup>-1</sup> is attenuated and merged with the strong C=C band and the C-O peak at 1195 cm<sup>-1</sup> is largely increased.



**Figure S20.** Raman spectra of the TpPa-COF film before and after lithiation. After cycling, the lithiated TpPa-COF gave the slightly weakened C=O peak and the remarkably increased C-C peak at 1440 cm<sup>-1</sup>, signifying the lithiation sites at the carbonyl groups and the adjacent  $\alpha$ -C atom as earlier reported.



**Figure S21.** Calculation of adsorption energy for the model cluster of TpPa-COF. Irrespective of LiTFSI with DOL (a) or LiPF<sub>6</sub> with DMC (b), Li<sup>+</sup> ion is preferable to adsorption on the TpPa-COF skeleton rather than anions and solvents. (c) The proposed mechanism of adsorption of electrolytes onto the TpPa-COF through the formation of electric double layer (EDL).



**Figure S22.** <sup>1</sup>H NMR spectrum of the model compound of TpPa-COF, namely tris(*N*-salicylideneaniline).



**Figure S23.** (a) Photographs of the DOL solution of LiTFSI at different concentrations in the presence of 5 mg mL<sup>-1</sup> tris(N-salicylideneaniline). (b) Zeta potential profiles of the MC-TpPa/DOL solution with or without addition of LiTFSI.



**Figure S24.** <sup>19</sup>F NMR spectra of the electrolyte (400  $\mu$ L) before and after the immersion of (~1.5mg) TpPa-COF film. The amount of electrolyte before absorption experiment was normalized to 100% by comparing the peak area of TFSI anions (-71.8 and -73.3 ppm in <sup>19</sup>F NMR spectra) with a given amount of an internal reference (Trifluorotoluene, -113.2 ppm in the <sup>19</sup>F NMR spectra). Surprisingly, after 1.5 mg TpPa film with negligible volume was immersed in electrolyte for 24 h, only 71% salts in the electrolyte was retained and its 29% was absorbed by the film.



**Figure S25.** EIS profiles of the TpPa-COF-protected Li metal over the few cycles in the presence of LiTFSI in DOL/DME electrolyte. The decreasing resistances of the symmetric cell indicated the lithiation process could be completed after few cycles.



**Figure S26.** (a) XPS survey of the TpPa-COF film before and after cycling. (b) The N 1s XPS profile of the as-prepared TpPa-COF film coated on lithium and its XPS depth profiles. (c) The effect of etching depth on the relative C/N ratio, which is defined as a comparison of the C/N ratio measured on lithium with the as-prepared TpPa-COF film. (d) The abundance comparison of the N1s and F1s atoms at different etching points, which shows the concurrent decline of N and F contents with an increase of etching depth.



**Figure S27.** Top view (a) and side view (b) of C (red), F (blue), O (green) and N (purple) element mapping for the pre-cycled COF film on the lithium metal. (c) HR TEM image (left) and FFT pattern (right) of the TpPa-COF film after the lithium symmetric cell test. The FFT pattern demonstrates the typical crystal lattice of LiF (0.20 nm),<sup>S8</sup> with the crystalline characteristic of TpPa-COF.



Figure S28. Young's modulus of the LiTpPa-LiF hybrid interphase over 15 cycles.



**Figure S29.** EIS profiles (a) and comparison of interfacial resistance (b) of the TpPa@Li, of which the different thick TpPa-COF films treated by pre-cycling were used, respectively.



**Figure S30.** Voltage profiles of the TpPa@Li at the deposition capacity of 1 mAh cm<sup>-2</sup> and at the current density of 1 mA cm<sup>-2</sup>, of which the different thick TpPa-COF films treated by precycling were used, respectively. As shown here, the 80-nm film has the lowest overpotential, which is conducive to realize the smooth lithium deposition. Also, as the film thickness would not affect the growth of LiF-rich SEI species, the electrochemical performances have been studied in detail for the 80-nm TpPa-COF film.



**Figure S31.** Chronoamperometric responses under a polarization of 20 mV before and after polarization for the symmetric Li/Li cells with (a) or without (b) TpPa-COF film protection. The lithium transference number is determined by using the known Bruce-Evans formula as follows.

$$t_{Li+} = \frac{I_{SS}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{SS} R_{SS})}$$

Sample	$\Delta V(\mathrm{mV})$	$I_0(mA)$	$I_{SS}(mA)$	$R_0(\Omega)$	$R_{SS}(\Omega)$	$t_{Li^+}$
TpPa@Li	20	0.124	0.1035	53.44	50.27	0.79
Pristine Li	20	0.075	0.0487	138.2	105.1	0.41



Figure S32. CV curves of Cu/Li cells with/without the TpPa-COF film coated copper at a sweep rate of  $0.2 \text{ mV s}^{-1}$ .



**Figure S33.** CEs for the electrodeposition on the TpPa-COF protected Cu foil and pristine Cu foil at a deposition capacity of 1 mAh cm<sup>-2</sup> with a current density of 1 mA cm<sup>-2</sup> (a) and 2 mA cm<sup>-2</sup> (b). (c,d) The corresponding voltage profiles for (a) and (b) after given cycles.



**Figure S34.** Top-view and cross-sectional SEM images of the pristine Li after Li deposition/dissolution for 100 cycles at a current density of 2 mA cm<sup>-2</sup> and at a capacity of 1 mAh cm<sup>-2</sup> with LiTFSI in DOL/DME electrolyte with 1wt% LiNO<sub>3</sub>.



**Figure S35.** Top-view and cross-sectional SEM images of the TpPa-protected Li after Li deposition/dissolution (left) for 20 cycles and (right) for 100 cycles at a current density of 2 mA cm<sup>-2</sup> and at a capacity of 1 mAh cm<sup>-2</sup> with LiTFSI in DOL/DME electrolyte with 1wt% LiNO<sub>3</sub>.



**Figure S36.** Voltage profiles of Li deposition/dissolution on the symmetric TpPa-protected lithium cells and pristine lithium cells with LiTFSI in DOL/DME electrolyte with 1 wt% LiNO<sub>3</sub> at different deposition capacities/current densities: (a) 1 mAh cm<sup>-2</sup>/2 mA cm<sup>-2</sup>, (b) 1 mAh cm<sup>-2</sup>/3 mA cm<sup>-2</sup>, (c) 1 mAh cm<sup>-2</sup>/5 mA cm<sup>-2</sup>, and (d) 1 mAh cm<sup>-2</sup>/10 mA cm<sup>-2</sup>.



**Figure S37.** EDS mapping of the LiTpPa-LiF hybrid interphase after cycling shown from top view (a) and side view (b).



**Figure S38.** Li deposition/dissolution profiles of LiTpPa -LiF@Li at current densities from 1 to 10 mA cm<sup>-2</sup> at a deposition capacity of 5 mAh cm<sup>-2</sup> with 1M LiPF<sub>6</sub> in EC/DMC electrolyte.



**Figure S39.** Voltage profiles of Li deposition/dissolution on the symmetric TpPa-COF protected lithium cells and pristine lithium cells with LiPF<sub>6</sub> in EC/DMC electrolyte under different deposition capacities/current densities: (a) 1 mAh cm<sup>-2</sup>/0.5 mA cm<sup>-2</sup>, (b) 1 mAh cm<sup>-2</sup>/2 mA cm<sup>-2</sup>, (c) 1 mAh cm<sup>-2</sup>/3 mA cm<sup>-2</sup>, (d) 3 mAh cm<sup>-2</sup>/3 mA cm<sup>-2</sup>, (e) 5 mAh cm<sup>-2</sup>/5 mA cm<sup>-2</sup>.



**Figure S40.** EIS profiles of pristine Li (a) and TpPa-COF protected Li (b) after given cycles with LiPF<sub>6</sub> in EC/DMC electrolyte at 1 mAh cm<sup>-2</sup>, 2 mA cm<sup>-2</sup>. The interfacial resistance of pristine lithium metal before cycling is as large as  $\approx$ 320  $\Omega$ , which could be attributed to the formation of the passivation layers. During repeated cycling, the collapse of the passivation layers and the growth of Li dendrite could induce loose and porous deposition morphology, which in turn made the resistance dramatically drop to  $\approx$ 60  $\Omega$  after 12 cycles and  $\approx$ 40  $\Omega$  after 32 cycles. In contrast, the TpPa-COF protected Li electrodes show stable interfacial resistance of  $\approx$ 75  $\Omega$  before cycling,  $\approx$ 80  $\Omega$  after 12 cycles, and  $\approx$ 52  $\Omega$  after 32 cycles. The stable and low interfacial resistance proved that this uniform and stable TpPa-COF protective film successfully enabled smooth and dense lithium deposition.



**Figure S41.** Top-view and cross-sectional FE SEM images of pristine Li after Li deposition/dissolution for 20 cycles (left) and 50 cycles (right) at a current density of 1 mA cm<sup>-2</sup> and at a capacity of 1 mAh cm<sup>-2</sup> with LiPF<sub>6</sub> in EC/DMC electrolyte.



**Figure S42.** Top-view and cross-sectional SEM images of TpPa-protected Li after Li deposition/dissolution for 20 cycles (left) and 50 cycles (right) at a current density of 1 mA cm<sup>-2</sup> and at a capacity of 1 mAh cm<sup>-2</sup>with LiPF<sub>6</sub> in EC/DMC electrolyte.



**Figure S43.** Electrochemical performance and its voltage profiles of the full cells with 3.9 mAh cm<sup>-2</sup> NCM 523 as cathode and 450  $\mu$ m Li foil as anode (a) or TpPa-protected 450  $\mu$ m Li foil as anode (b) at 0.5 C.



**Figure S44.** Electrochemical performance and its voltage profiles of the full cells with TpPaprotected 450  $\mu$ m Li foil as anode and 3.9 mAh cm<sup>-2</sup> NCM 523 as cathode at 0.8 C.



**Figure S45.** Electrochemical performance and its voltage profiles of the full cells with 55  $\mu$ m TpPa-protected thin Li foil as anode and 3.9 mAh cm<sup>-2</sup> NCM 523 as cathode at a current density of 1 mA cm<sup>-2</sup>.



**Figure S46.** FE SEM images of the pristine 55 µm lithium anode (a) and the TpPa-protected 55 µm lithium anode (b) in the full cells after 50 cycles, respectively.

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