Support information

A functionalized metal organic framework-laden nanoporous polymer electrolytes for exceptionally stable lithium electrodeposition

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1. Materials

The materials used in the experiments are listed as follows: Poly(ethylene oxide) (PEO, M_w=100000), lithium bis(trifluoromethane sulphonyl)imide (LiTFSI), lithium iron phosphate ($LiFePO_4$), conductive carbon black (Super C65), 1-methyl-2-pyrrolidinone (NMP), poly(vinylidene fluoride) (PVDF), zirconium(Ⅳ) chloride ($ZrCl_4$), 1,4-benzenedicarboxylic acid (BDC), 2-amino-benzenedicarboxylic acid (H_2N-H_2BDC), 2-nitro-benzenedicarboxylic acid (O_2N-H_2BDC), *N,N*-Dimethylformamide (DMF), hydrochloric acid (HCl), anhydrous ethanol (EtOH) were purchased from Sigma-Aldrich, Adamas or Aladdin. DMF were freshly distilled from CaH_2 before using.

2. Synthesis and analytical methods

2.1 Preparation of SPE and electrodes

Synthesis of nanostructured MOFs fillers:

$ZrCl_4$ (0.250g, 1.08mmol) and H_2N-H_2BDC (0.271g, 1.5mmol) were dissolved in 30 mL anhydrous DMF by ultrasonic stirring at room temperature. HCl (2mol/L) was added into the mixed solution as the modulator.[1] Then, the above mixture was transferred into a 50 mL Teflon liner and was heated at 120 °C for 24h. After reaction was completed, the mixture was cooled to room temperature for filtration. The products were washed for three times by DMF and EtOH respectively. Finally, gray white precipitation (UIO-66-NH_2) was obtained. To remove excess solvent, the obtained nanocrystals were heated at 120 °C under vacuum for 12h. Similar procedure was used to prepare nanocrystal filler containing nitro group (UIO-66-NO_2).

Preparation of MOFs-PEO electrolytes:

First, PEO and LiTFSI were vacuum dried at 60 °C and 100 °C for 12 hours, respectively, and then transferred to the glove box before using. The powder of UIO-66-NH_2 with 10 wt% of PEO and LiTFSI with the molar ratio of $[O]/[Li^+] = 18:1$ were mixed in a mortar, and heated at 100 °C with grinding until UIO-66-NH_2 and PEO were uniformly mixed. By pressing the resultant mixture for 30 min at 100 °C under 10 MPa of pressure, a uniform composite electrolyte membrane with a thickness of approximately 0.1 cm was prepared (UIO-66-NH_2@P). The same method was used to prepare pure PEO and UIO-66-NO_2@P.

Preparation of $LiFePO_4$ cathode:

To prepare the cathode, LFP/Super C65 (90/5 wt%) was firstly mixed and ground for 30 minutes until a uniform powder was formed. Then, PVDF (5 wt%) was placed in NMP and vigorously stirred for 4h. Finally, the slurry of LFP/Super C65/PVDF and NMP was vigorously stirred overnight. The uniform slurry was coated on aluminum foil and dried under vacuum at 80 °C for 8 hours. Solid-state lithium batteries were assembled with coin cells (LIR 2032) in an Ar-filled glove box ($O_2 \leq 0.01$ ppm, $H_2O \leq 0.01$ ppm).

2.2 Characterization methods

The X-ray diffraction (XRD) measurements were performed by a RigakuTTRII-18KW instrument. Fourier transform infrared (FT-IR) spectra was tested by Nicoletis10 instrument with a scan range of 400-4000 cm^{-1}. The nitrogen sorption isotherm was measured by Quadrasorb-evo analyzer at 77K. The samples were activated at 120 °C for 12 hours under vacuum (10^{-5} bar) prior to the gas sorption analysis. Surface areas were calculated from the nitrogen adsorption data. The pore size distributions were calculated from the nitrogen adsorption branch with the nonlocal density functional theory (NLDFT). Scanning electron microscope (SEM) measurement was performed on Nova Nano SEM 450 instrument. A transmission electron microscope (TEM, JEM-

2100) was used to study the microstructure of the materials. The thermal stability of the samples was evaluated by thermogravimetric analysis (TGA) with a thermal analysis instrument (Mettler Toledo TGA/1600LF) over the temperature range from 0 °C to 800 °C at a temperature increase of 10 K/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) was tested with a TA Instruments Q2000 and heated two cycles from -80 °C to 120 °C at a heating rate 10 °C/min under nitrogen atmosphere. The rheology was tested by a HAAKE MARS III rheometer with 20 mm parallel plate in a convection oven. The oscillatory shear experiments were carried out with strain $\gamma = 1\%$ and angular frequency $\omega = 1$ rad/s at room temperature (25 °C) and 60°C for 6000 s. The X-ray photoelectron spectrometer (XPS) analysis was used to study the SEI surface after cycling by tested on K-Alpha$^+$ instrument.

2.3 Electrochemical measurements

The electrochemical stability window was determined by stainless-steel/SPE/Li cells using cyclic voltammetry (CV), which was conducted from -0.2 V to 5 V at a scan rate of 0.5 mV s^{-1} by the electrochemical workstation (Bio-logic VMP-300 and CHI 760E). The ionic conductivities (σ) were measured by the electrochemical workstation with the frequency range from 0.01 Hz to 1 MHz and at an amplitude of 5 mV. AC impedance measurements were performed on symmetric cells with two stainless steel electrodes. The sample was heated at desired temperatures for an hour before each measurement.

The ionic conductivity σ was calculated based on the following equation:

$$\sigma = \frac{L}{RA} \tag{1}$$

Where L represents the thickness of the electrolyte, R is the bulk resistance of the electrolyte, and A is the contact area between the electrolyte and the electrode.

The temperature dependence of ionic conductivity can be described by the

Arrhenius behavior. The Arrhenius equation is:

$$\sigma = \frac{A}{T} exp[-\frac{E_a}{kT}] \qquad (2)$$

Where A refers to the pre-exponential factor, E_a is the activation energy for conductivity, and k is boltzmann constant.

The lithium ion transference number (t_{Li}^{+}) was determined in a Li/SPE/Li cell. t_{Li}^{+} was calculated according to the following equation:

$$t_{Li}^{+} = \frac{I_S R_{b^0}\left[\Delta V - I_0 R_{I^0}\right]}{I_0 R_{b^S}\left[\Delta V - I_s R_{I^s}\right]} \qquad (3)$$

Where ΔV is the applied DC polarization voltage (10 mV), I_0 and I_S are the initial and stable currents during polarization, and R_{b^0} and R_{I^0} are the bulk resistance and interface resistance of the solid electrolyte before polarization, R_{b^S} and R_{I^S} are the bulk resistance and interface resistance of the solid electrolyte after polarization.

Lithium dendrite growth was monitored by LAND cycle test system using symmetric Li/SPE/Li cells with the current densities of 0.1 mA cm^{-2} and 0.2 mA cm^{-2} at 60 °C, respectively. The cells were subjected to a charge-discharge cycling at 0.1C with a Li/LFP setup. Excessive lithium with a thickness of 450 μm was used (N/P ratio of 56.04) , and the tests were carried out at different charge-discharge rates at 60 °C on the LAND cycle test system.

3. Experimental details for structure characterization

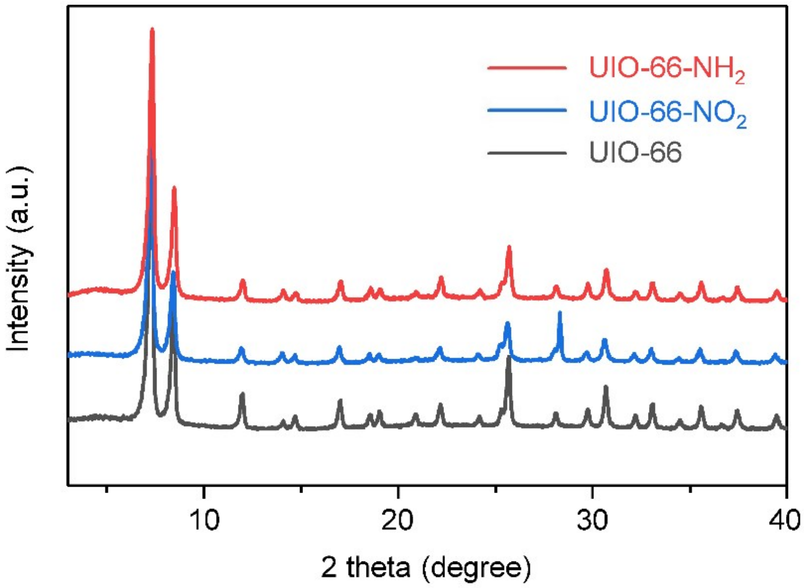


Figure S1. XRD patterns of UIO-66-NH$_2$, UIO-66-NO$_2$, and UIO-66.

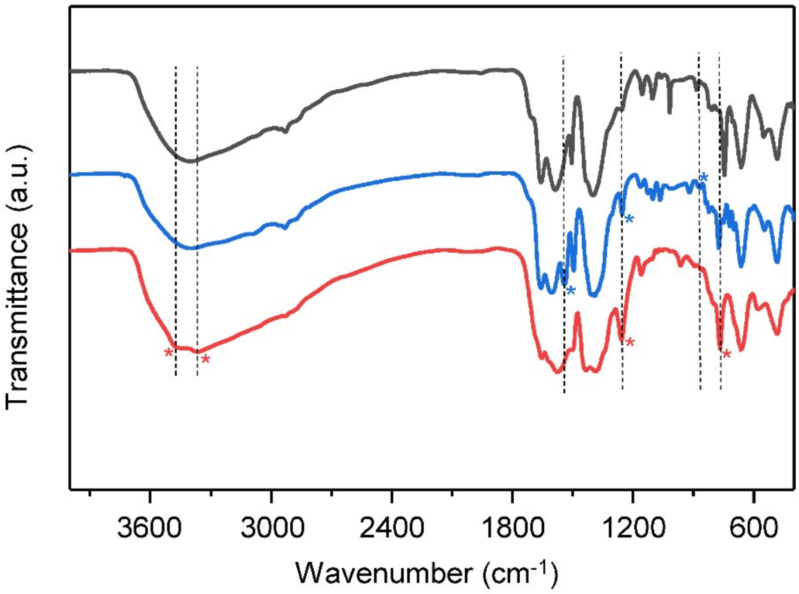


Figure S2. The FT-IR of UIO-66-NH$_2$ (red), UIO-66-NO$_2$ (blue), and UIO-66 (black).

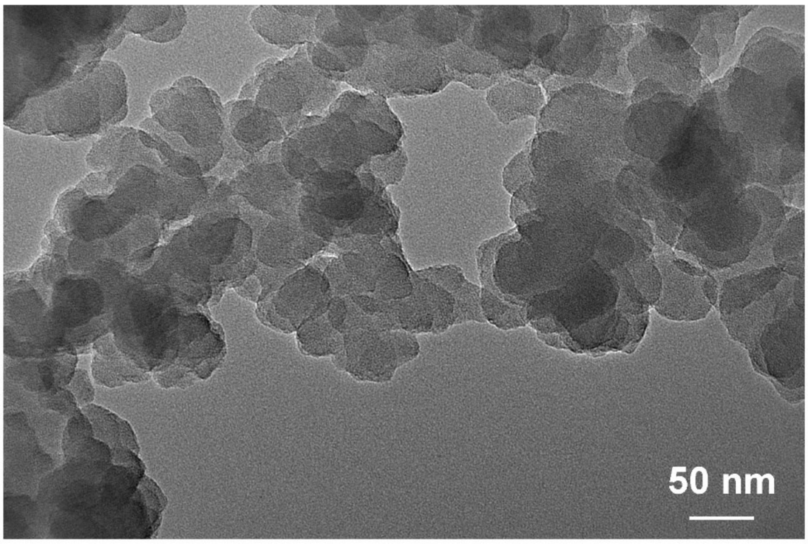


Figure S3. TEM image of nanostructured UIO-66-NH_2.

4. Experimental details for physicochemical characterization

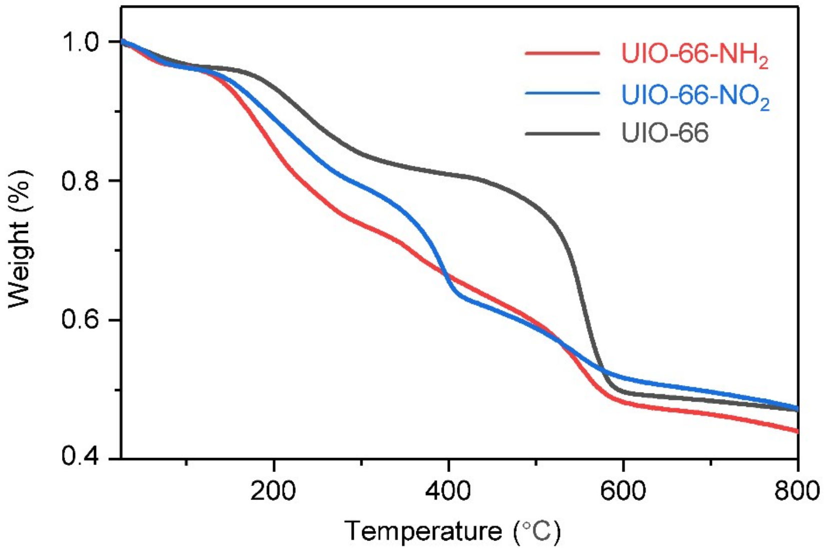


Figure S4. TGA curves of UIO-66-NH$_2$, UIO-66-NO$_2$, and UIO-66 at 25 °C to 800 °C, where the weight loss before around 100 °C correspond to H_2O, and the solvent of DMF was lost from 100 °C to 300°C in nanopores of the MOFs. The decomposition temperature of MOFs started at around 300 °C.[2]

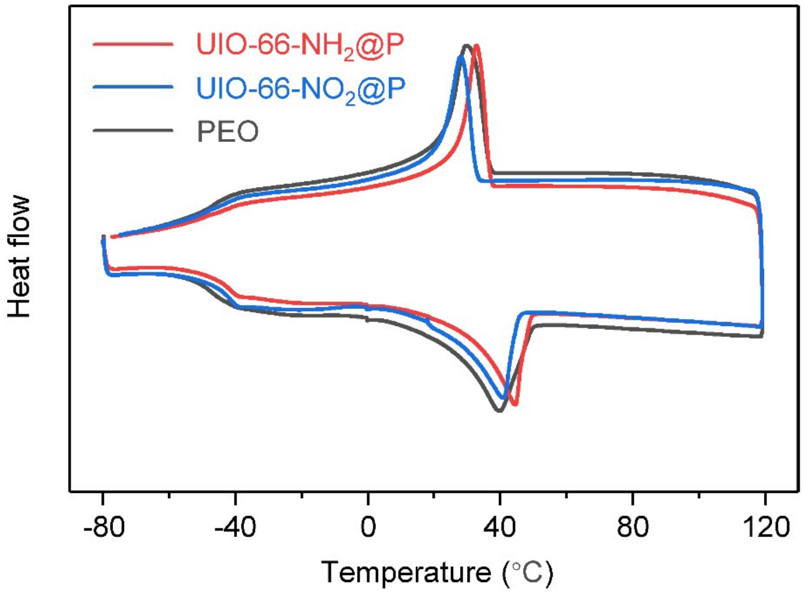


Figure S5. DSC curves of UIO-66-NH_2@P, UIO-66-NO_2@P, and PEO from -80 °C to 120 °C.

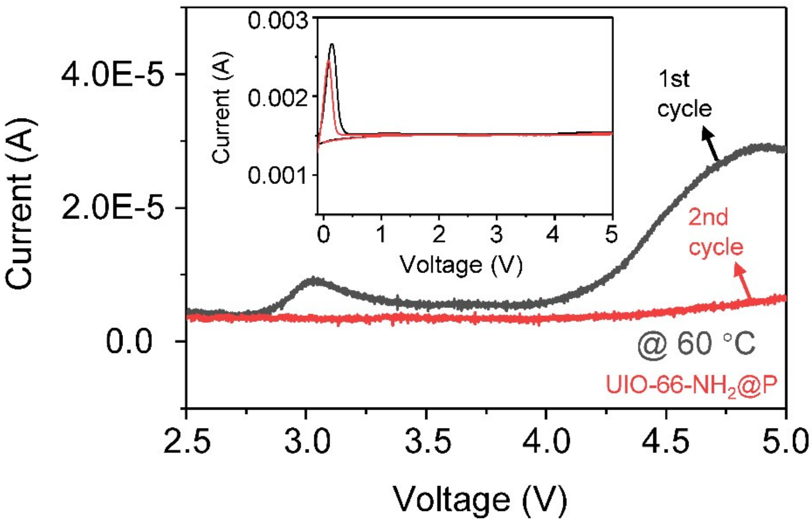


Figure S6. CV curves of UIO-66-NH_2@P at 0.5 mV s^{-1}. (Black: 1st cycle of UIO-66-NH_2@P; Red: 2nd cycle of UIO-66-NH_2@P).

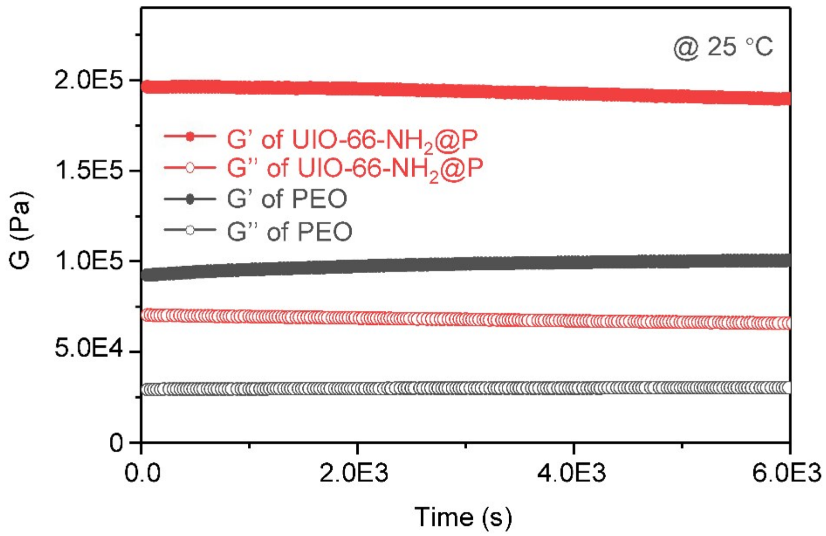


Figure S7. Rheological curves of UIO-66-NH$_2$@P and PEO at room temperature (ω = 1 rad s^{-1}, strain γ= 1%).

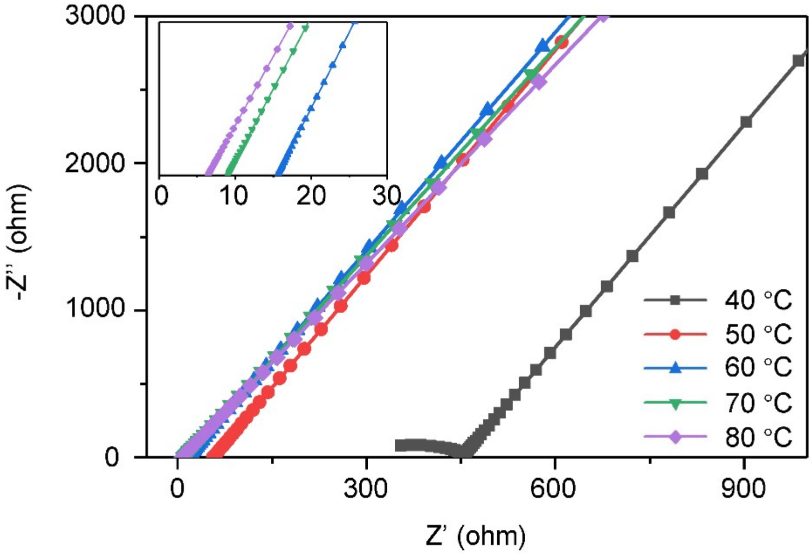


Figure S8. EIS curves of UIO-66-NH_2@P from 40 ℃ to 80 ℃.

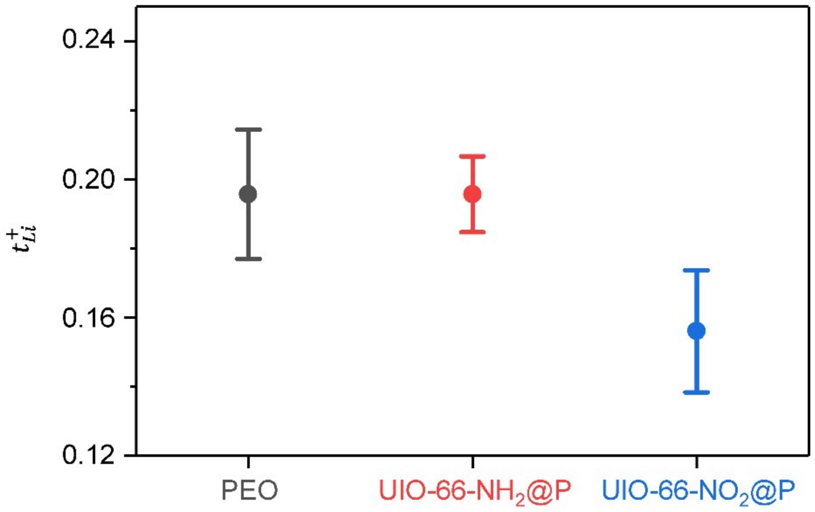
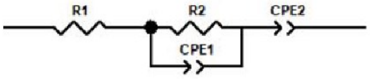


Figure S9. Measurement of lithium transference numbers of UIO-66-NH$_2$@P, UIO-66-NO$_2$@P and PEO.



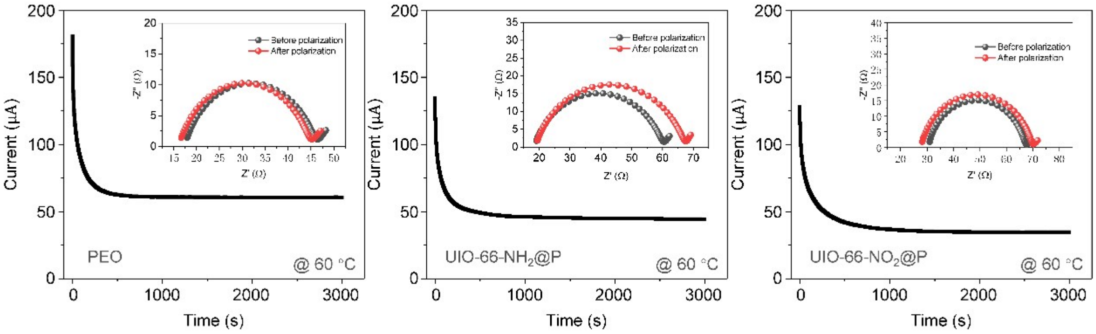


Figure S10. Potentiostatic polarization current as a function of measuring time at 60 °C for PEO, UIO-66-NH$_2$@P and UIO-66-NO$_2$@P. Inset: AC impedance spectra of the solid-state battery before and after polarization.

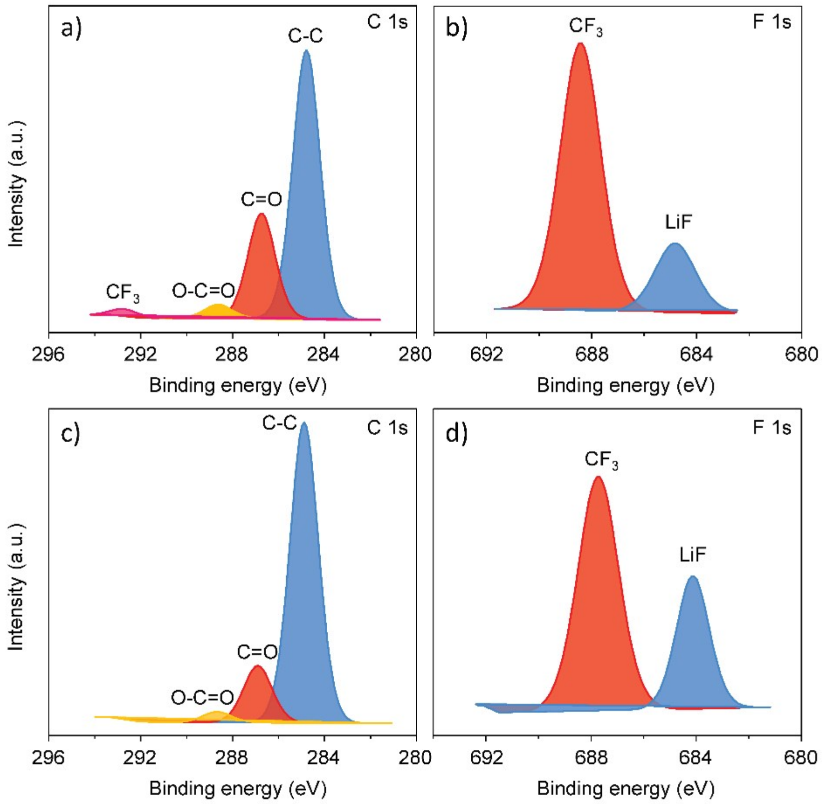


Figure S11. XPS characterization of lithium metal surface after plating/stripping test. a,b) XPS spectra of C 1s and F 1s for lithium metal retrieved from solid electrolyte of PEO after cycling for 100h; c,d) XPS spectra of C 1s and F 1s for lithium metal retrieved from solid electrolyte of UIO-66-NH$_2$@P after cycling for 100h.

5. Experimental details for electrochemical characterization

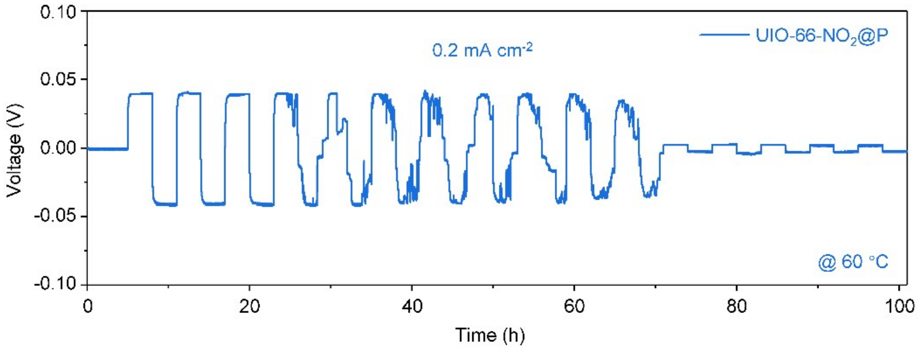


Figure S12. Voltage profiles of the Li/ UIO-66-NO_2@P/Li cell at 0.2 mA cm^{-2} and 60 °C. The time for each cycle is 3 h.

References

1. M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chemical Communications*, 2013, **49**.
2. M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino and K. P. Lillerud, *Chem. Mater.*, 2010, **22**, 6632.

Author Contributions

X.L. and M.C. conceived the idea. Q.X., J.R.L. and Z.W. conducted experiments of synthesis, characterization and electrochemical tests. Q.X., J.L. and M.C. analyzed related results. X.L., J.L. and M.C. wrote the paper.