

Electronic Supplementary Information

A coupled polymeric porphyrin complex as a novel cathode for highly stable lithium organic batteries

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Experimental section

1.1 Materials:

All reagents and solvents were obtained from Alfa Aesar and Chemical Great-wall. Polyvinylidene fluoride (PVDF), acetylene black, and N-methyl-2-pyrrolidone (NMP), Glass microfiber filters (Whatman, GF/D) were purchased commercially and used as received without further purification. THF was dried over sodium/benzophenone and freshly distilled before use. The compounds dipyrromethane (**1**) and 2,6-dioctoxybenzaldehyde (**2**) were synthesized according to the previous literatures.¹⁻³

1.2 Structural characterization:

¹H and ¹³C NMR spectra were recorded with a Bruker Avance 400 instrument. UV-vis spectra of porphyrins were measured on a Perkin–Elmer Cary 60 spectrometer. Mass spectrometry (MS) data were performed on a Bruker Aupoffflex III MALDI-TOF Analyzer using CCA as matrix. The morphology of samples was carried out using field emission scanning electron microscope (FESEM, Hitachi S-4800). The attenuated total reflectance-fourier transformation infrared (ATR-FTIR) spectroscopy was obtained on a Thermo Fisher Nicolet IS50 ATR-FTIR spectrometer from 600 cm⁻¹

to 4000 cm^{-1} . X-ray photoelectron Spectroscopy was recorded on a Escalab250Xi (Thermo Scientific), using monochromatized Al $K\alpha$ radiation (1486 eV). The pass energy for survey spectra was 100 eV, for detail spectra the energy was 30 eV. The binding energies of all spectra were calibrated with respect to the C1s peak of ubiquitous carbon at a binding energy of 284.8 eV.

1.3 Electrochemical measurements:

The Pre and PPre electrode were prepared by mixing 40 wt % acetylene black, 10 wt % PVDF and 50 wt % **Pre** (or **PPre**) and the slurry was coated onto a stainless steel current collector (12 mm in diameter). 1 M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC): dimethyl carbonate (DMC): propylene carbonate (PC) was used as electrolyte (EC : DMC : PC = 1 : 3 : 1 by volume ratio). The mass loading of active material was around 1.5 mg cm^{-2} . All capacities were calculated based on active material of electrode. Electrochemical redox potentials were obtained by cyclic voltammetry (CV) using a three-electrode configuration. The CV and Electrochemical impedance spectroscopy (EIS) were conducted on an electrochemical workstation (CHI600E) and the frequency range for EIS study was between 100 KHz and 0.01 Hz. The working electrode was a glassy carbon electrode, the auxiliary electrode was a Pt electrode, and Ag/AgCl electrode was used as a reference electrode. Tetrabutylammonium hexafluorophosphate (TBAP, 0.1 M) was used as a supporting electrolyte in dry CHCl_3 . The scan rate was 30 mV s^{-1} . CR-2032 coin cells were assembled in an argon-filled glove box (MIKROUNA) with oxygen and water concentration lower than 0.1 ppm. The galvanostatic charge/discharge tests of coin-type cells (CR2032) were performed with a Neware battery testing system at 298K (Neware, Shenzhen, China).

1.4 Synthesis of 5,15-bis(2,6-dioctoxyphenyl)porphyrin (3)

Compound **3** was synthesized according to literature procedure.³ Dipyrrromethane (1.52 g, 10mmol) was dissolved in a 500ml two-neck flask with

DCM (300 ml), and then 2,6-dioctoxybenzaldehyde (3.77 g, 10 mmol) was added. After degassed with dinitrogen for 5 min, trifluoroacetic acid (0.5 ml, 6.8 mmol) was slowly dropped in and stirred. After stirred for 5 h at room temperature, the solvent was added with DDQ (3.58 g, 15.7 mmol) and stirred for another 1 h and Et₃N (10 ml) was added. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel) using DCM/petroleum ether = 1/1 as eluent. The product was recrystallized from MeOH/CH₂Cl₂ to give the purple solid (1.32g, 26 %). ¹H NMR (CDCl₃, 400 MHz) δ_H 10.16 (s, 2H), 9.28 (d, *J* = 4.4 Hz, 4H), 8.99 (d, *J* = 4.4 Hz, 4H), 7.75 (t, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 4H), 3.87 (t, *J* = 6.4 Hz, 8H), 0.95–0.84 (m, 16H), 0.68–0.64 (m, 8H), 0.60–0.55 (m, 28H), 0.47–0.44 (m, 8H), -3.00 (s, 2H). ¹³C NMR (CDCl₃, 400 MHz) δ_C 160.1, 147.6, 144.9, 130.8, 130.4, 130.0, 120.0, 111.5, 105.3, 103.9, 68.7, 31.3, 28.6, 25.3, 22.3, 13.8. UV-vis (CHCl₃, nm) 409, 503, 536, 576. MALDI-TOF-MS calcd for C₆₄H₈₆N₄O₄: 975.392; found 975.711.

1.5 Synthesis of 5,15-dibromo-10,20-bis(2,6-dioctoxyphenyl)porphyrin (4)

Compound **3** (800 mg, 0.82 mmol) was dissolved by chloroform (300 ml) in a three-neck flask and degassed with dinitrogen at 0 °C, and a solution of chloroform (50 ml) dissolved with NBS (0.3 g, 1.68 mmol) was added, the mixture was stirred for 6 h and then quenched with acetone (10 ml). The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel) using DCM/petroleum ether = 1/3 as eluent. The product was recrystallized from MeOH/CH₂Cl₂ and get the title product as a purple solid (787 mg 85%). ¹H NMR (CDCl₃, 400 MHz) δ_H 9.53 (d, *J* = 4.8 Hz, 4H), 8.81 (d, *J* = 4.6 Hz, 4H), 7.73 (t, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 4H), 3.87 (t, *J* = 6.4 Hz, 8H), 0.97–0.91 (m, 8H), 0.84–0.83 (m, 8H), 0.63–0.48 (m, 36H), 0.46–0.37 (m, 8H), -2.57 (s, 2H). ¹³C NMR (CDCl₃, 400 MHz) δ_C 160.0, 151.5, 149.8, 132.9, 130.3, 120.0, 114.2, 105.1, 102.3, 68.7, 31.3, 28.6, 25.4, 22.2, 13.9. UV-vis (CHCl₃, nm) 423, 521, 553, 602, 659. MALDI-TOF-MS calcd for C₆₄H₈₄Br₂N₄O₄: 1133.486; found 1133.756.

1.6 Synthesis of [5,15-dibromo-10,20-bis(2,6-di-octoxyphenyl)porphinato] zinc(II) (5)

To a solution of compound **4** (1.13 g, 1 mmol) in 300 ml DCM and a solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (1.84 g, 10 mmol) with MeOH (50 ml) was added, the solution was stirred at room temperature for 4h and then the mixture was extracted with DCM (2×100 mL) and washed with water. Then the solvent was dried over with anhydrous MgSO_4 and removed under reduce pressure and passed through a short column chromatography on silica gel (petroleum ether: DCM = 1:1) to give the product (1.16 g, 95 %). ^1H NMR (CDCl_3 , 400 MHz) δ_{H} 9.64 (d, $J = 4.0$ Hz, 4H), 8.90 (d, $J = 4.0$ Hz, 4H), 7.72 (t, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 4H), 3.86 (t, $J = 6.4$ Hz, 8H), 0.97–0.92 (m, 8H), 0.85–0.76 (m, 8H), 0.62–0.55 (m, 8H), 0.53–0.42 (m, 28H), 0.39–0.32 (m, 8H). ^{13}C NMR (CDCl_3 , 400 MHz) δ_{C} 159.9, 151.4, 149.7, 132.8, 130.0, 120.7, 114.8, 105.2, 103.9, 68.6, 31.3, 28.6, 25.2, 22.3, 13.8. UV-vis (CHCl_3 , nm) 423, 553, 595. MALDI-TOF-MS calcd for $\text{C}_{64}\text{H}_{82}\text{Br}_2\text{N}_4\text{O}_4\text{Zn}$ 1196.548, found 1196.554.

1.6 Synthesis of [5,15-bis(2,6-di-octoxyphenyl)-10,20-bis(trimethylsilylethynyl)porphinato] zinc(II) (**6)**

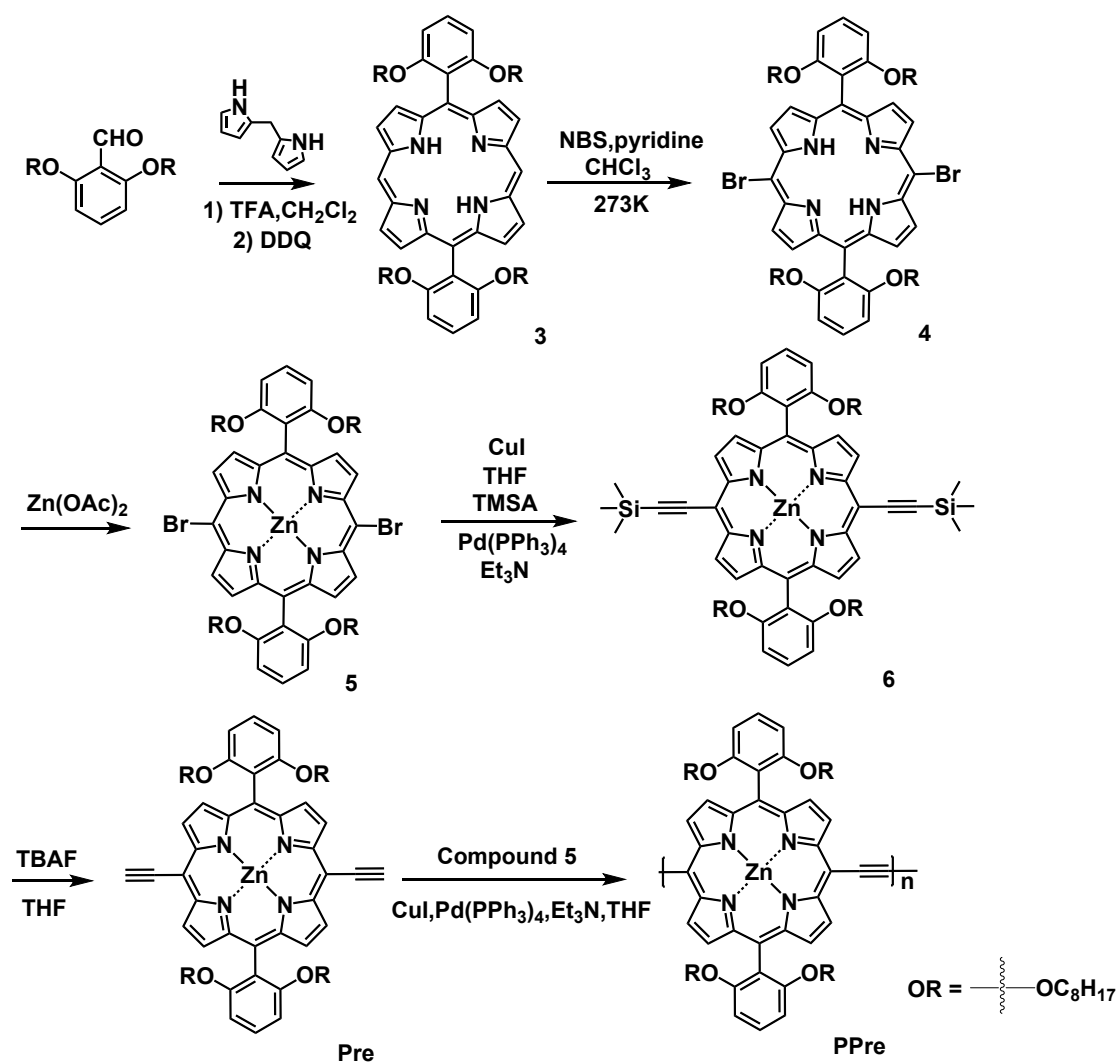
Compound **5** (600 mg, 0.5 mmol) was dissolved with dry THF (50 ml) in a three-neck flask, and (trimethylsilyl)acetylene (200 mg, 2 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (17.5 mg 0.025 mmol), CuI (5 mg 0.025 mg), and Et_3N (10 ml) was added. After stirring for 3 days under dinitrogen, the solvents were removed under reduced pressure and the residue was purified by column chromatography (silica gel) using DCM/petroleum ether = 1/3 as eluent and give the title product (400 mg, 65%) as a purple solid. ^1H NMR (CDCl_3 , 400 MHz) δ_{H} 9.62 (d, $J = 4.4$ Hz, 4H), 8.86 (d, $J = 4.8$ Hz, 4H), 7.73 (t, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.4$ Hz, 4H), 3.85 (t, $J = 6.4$ Hz, 8H), 1.00–0.93 (m, 8H), 0.87–0.80 (m, 8H), 0.66–0.49 (m, 54H), 0.45–0.37 (m, 8H). ^{13}C NMR (CDCl_3 , 400 MHz) δ_{C} 159.9, 151.8, 150.7, 131.9, 130.9, 129.9, 120.9, 115.2, 108.1, 105.3, 100.3, 100.1, 68.7, 31.3, 28.6, 28.5, 25.2, 22.2, 13.9, 0.41. UV-vis (CHCl_3 , nm) 437, 573, 619. MALDI-TOF-MS calcd for $\text{C}_{74}\text{H}_{100}\text{N}_4\text{O}_4\text{Si}_2\text{Zn}$ 1231.161; found 1231.169.

1.7 Synthesis of [5,15-bis(2,6-di-octoxyphenyl)-10,20-bis(ethynyl)porphinato]zinc(II) (Pre)

Compound **6** (200 mg, 0.16 mmol) was dissolved in dry THF (100 ml) and MeOH (30 ml), then added with tetrabutylammonium fluoride (1.1 mL, 1.1 mmol), the mixture was stirred for 0.5 h at room temperature under dinitrogen and then concentrated and extracted with CH₂Cl₂/H₂O. The product was recrystallized from MeOH/CH₂Cl₂ and give the title product as a purple solid (159 mg, 92%). ¹H NMR (CDCl₃, 400 MHz) δ_H 9.66 (d, *J* = 4.4 Hz, 4H), 8.91 (d, *J* = 4.4 Hz, 4H), 7.74 (t, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 4H), 4.11 (s, 2H), 3.86 (t, *J* = 6.4 Hz, 8H), 1.01–0.94 (m, 8H), 0.88–0.78 (m, 8H), 0.65–0.57 (m, 8H), 0.58–0.44 (m, 28H), 0.43–0.35 (m, 8H). ¹³C NMR (CDCl₃, 400 MHz) δ_C 159.9, 152.0, 150.9, 132.1, 130.9, 129.9, 120.7, 115.2, 105.2, 98.8, 86.4, 82.8, 68.6, 31.3, 28.6, 25.2, 22.2, 13.7. MALDI-TOF-MS calcd for C₆₈H₈₄N₄O₄Zn 1086.799, found 1086.391.

1.8 Synthesis of the polymer (PPre)

To a degassed solution of monomer **4** (43.0 mg, 36 μmol), Pre (42.4 mg, 39 μmol) in anhydrous tetrahydrofuran (3 mL) and triethylamine (0.75 mL), and the mixture was deoxygenated with argon for 5 min before Pd(PPh₃)₄ (2.10 mg, 1.8 μmol) and CuI (1.02 mg, 5.4 μmol) were added. The mixture was stirred at 40 °C (while for PPre₁₅ and PPre₂₅ the temperature were 60 °C and 80 °C, respectively) for 48 h in nitrogen atmosphere, then it was precipitated in methanol and filtered. The polymer was extracted with acetone, hexane and dichloromethane. The polymer was dissolved in tetrahydrofuran and filtered, the solvent was evaporated and the polymer was precipitated in acetone. The polymer was collected by filtering over a 0.45 μm PTFE membrane filter and dried in a vacuum oven to yield Polymer (55 mg, 65 %) as a green film.



Scheme S1. Synthetic procedures and structural of pre-polymerized porphyrin (**Pre**) and polymerized porphyrin (**PPre**).

Table S1 Molecular weights of **PPre** polymers

Polyme r	Temperature/ °C	M _n ^a /kDa	M _w /kDa	Dp ^b	PDI
PPre ₉	40	9.7	14.2	9	1.46
PPre ₁₅	60	15.4	20.3	15	1.31
PPre ₂₅	80	25.9	37.5	25	1.44

^aDetermined by GPC in CHCl₃ based on polystyrene standards. ^bThe degree of polymerization (Dp) is obtained by dividing the molar mass of **Pre**.

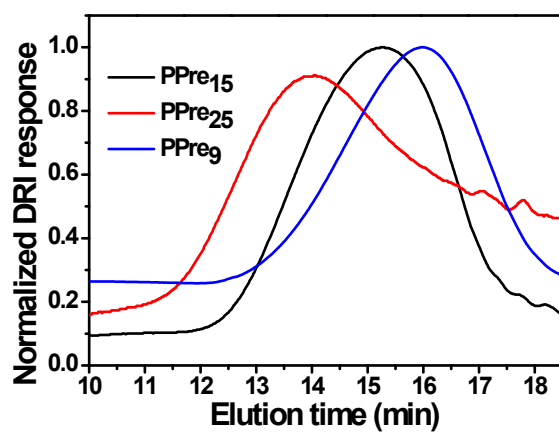


Fig. S1. GPC curves of PPre₉, PPre₁₅, and PPre₂₅.

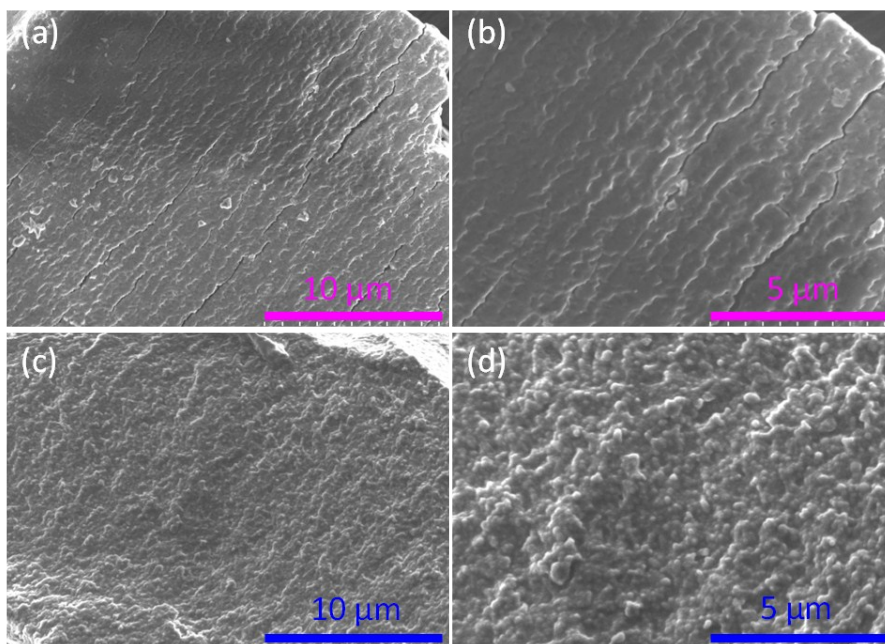


Fig. S2. SEM images of the **Pre** (a, b) and the **PPre₁₅** (c, d).

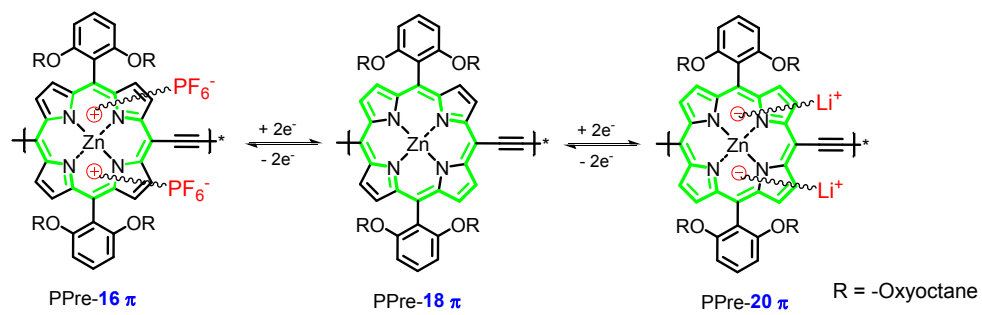


Fig. S3. The reaction mechanism of PPre molecule.

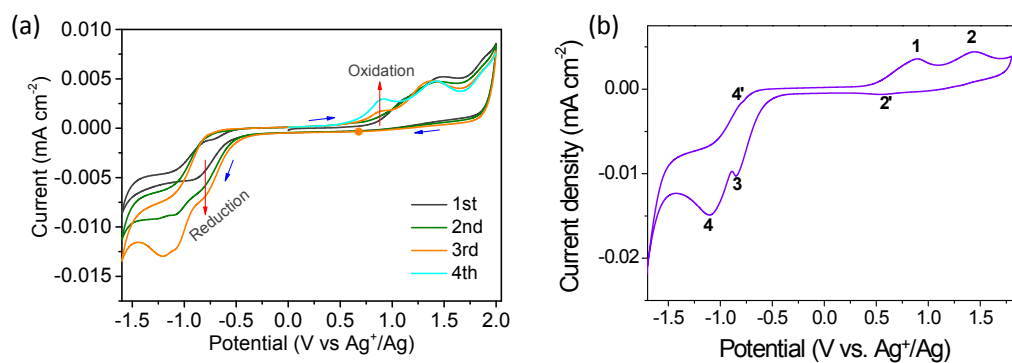


Fig. S4. The CV curves of the (a) Pre, and (b) PPre15 in chloroform at a scan rate of 30 mV s^{-1} , where glass carbon was used as a working electrode, Ag/AgCl and Pt were used as a reference electrode and counter electrode, respectively.

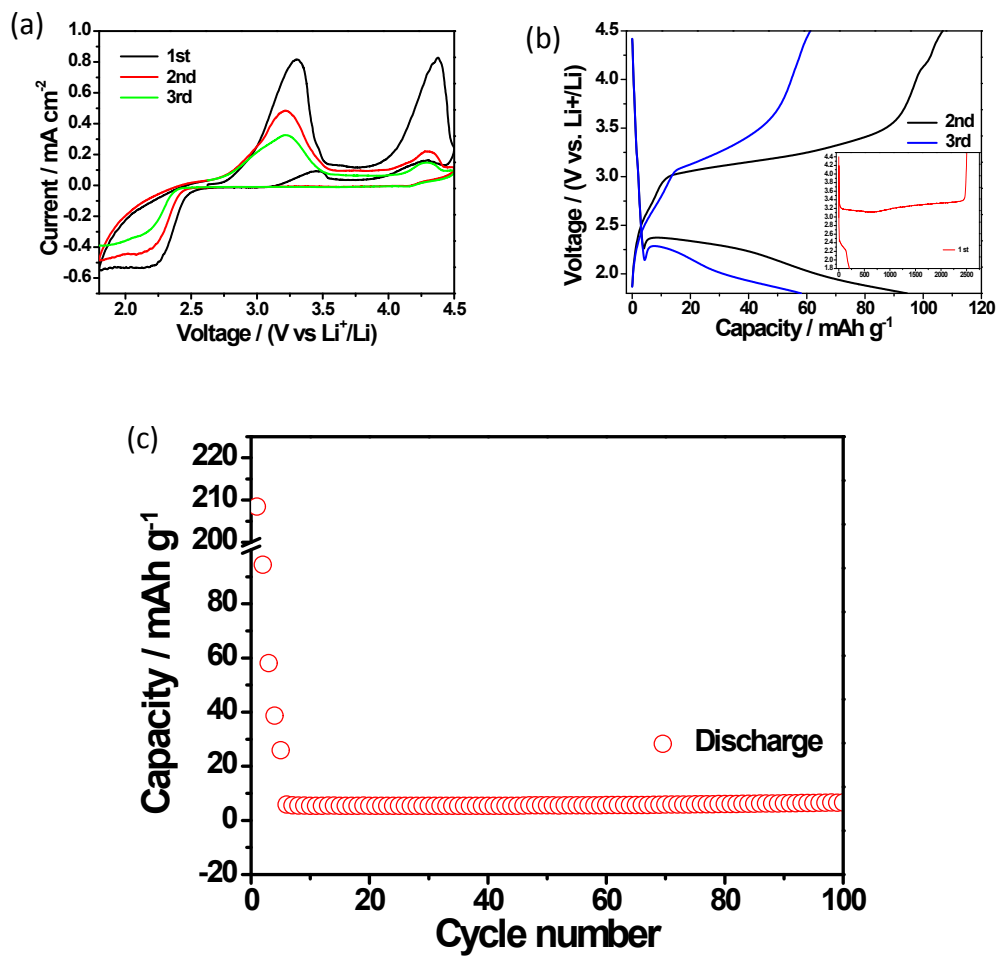


Fig. S5. (a) Cyclic voltammogram and (b) initial charge/discharge curves of acetylene black, (c) Cycling performance of acetylene black electrode at a current density of 0.5 A g⁻¹.

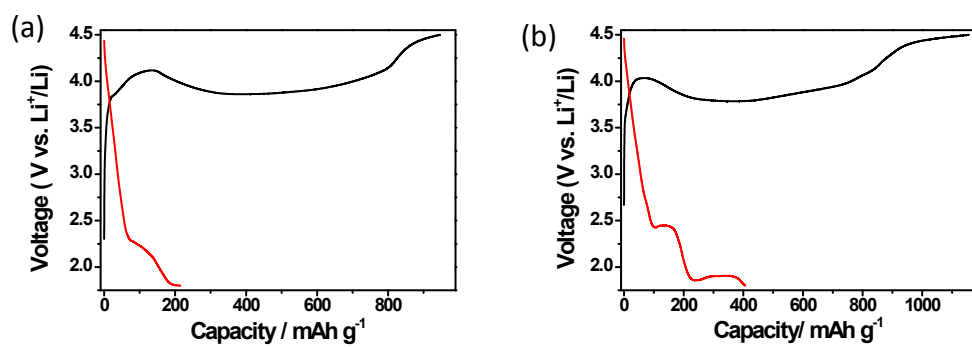


Fig. S6. Charge and discharge curve of **Pre** (a) and **PPre₁₅** (b) in the first cycle at a current density of 200 mA g⁻¹.

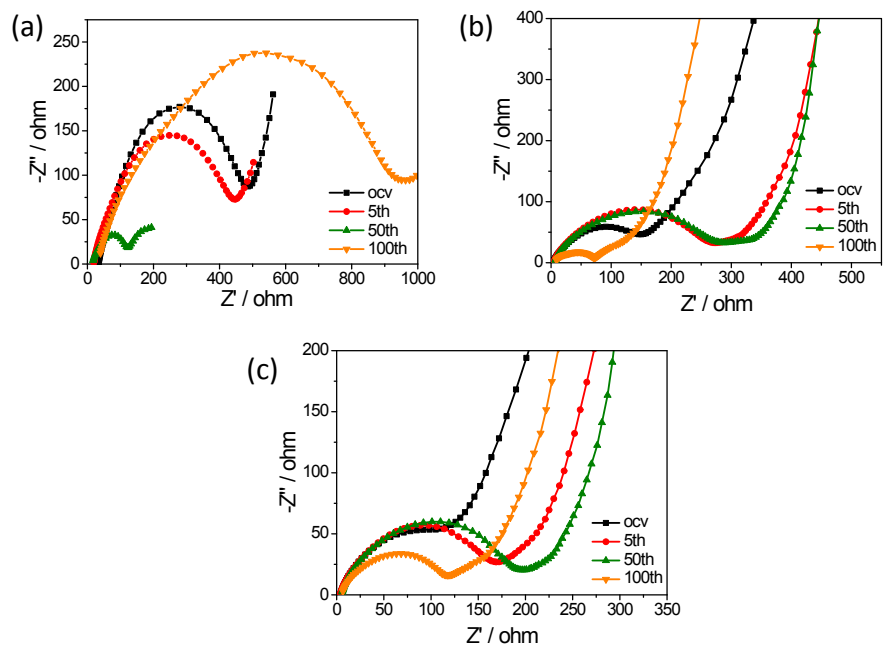


Fig. S7. Electrochemical impedance spectroscopy of (a) Pre, (b) PPre15, and (c) PPre25 in different cycles.

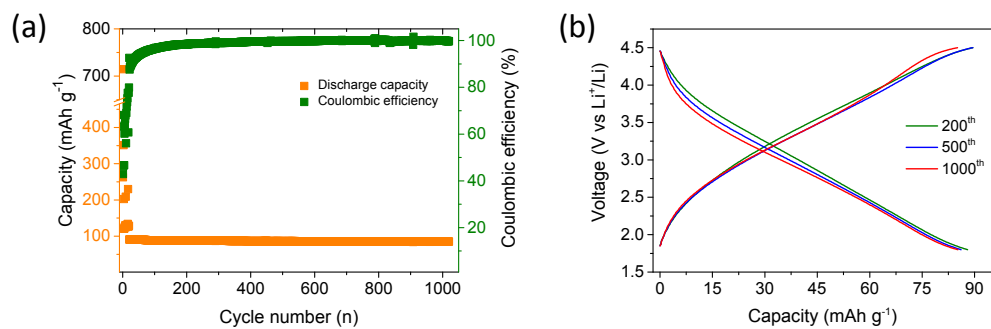


Fig. S8. Cycling performance of PPre15 cathode at a high current density of 1000 mA g⁻¹ in a voltage range of 4.5-1.8 V. The electrode was initially cycled at 200 mA g⁻¹ for 20 times. Selected curves of PPre15 were cycled at the 200th, 500th, and 1000th.

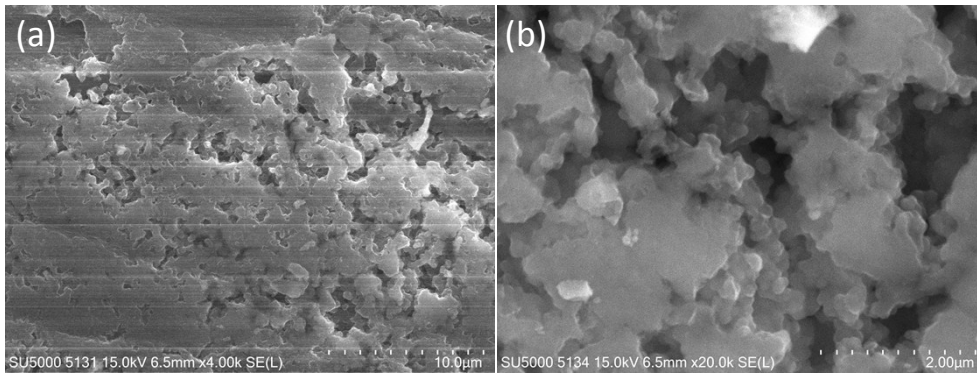


Fig. S9. The morphology of PPre15 after 2000 charge and discharge cycles.

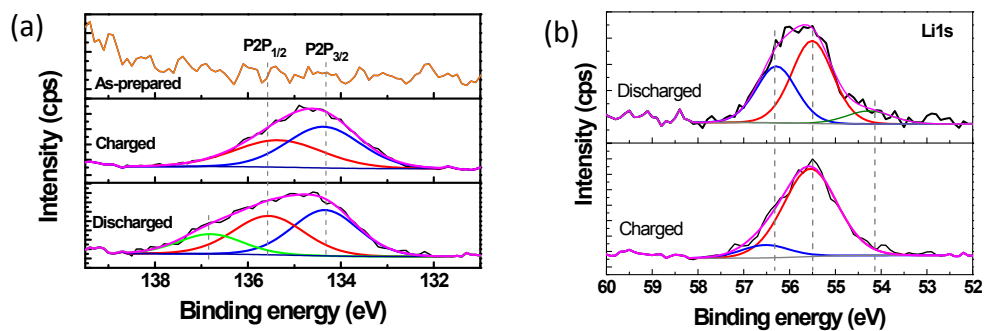


Fig. S10. XPS spectra of P_{2p} and Li_{1s} core level of PPre₁₅ at the pristine, discharged and charged states.

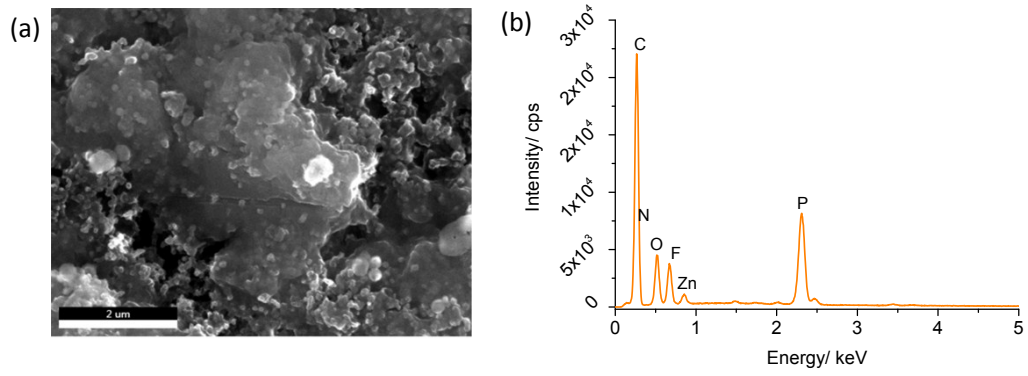


Fig. S11. (a) SEM image and (b) the EDX spectrum of the PPre15 in the first charged state.

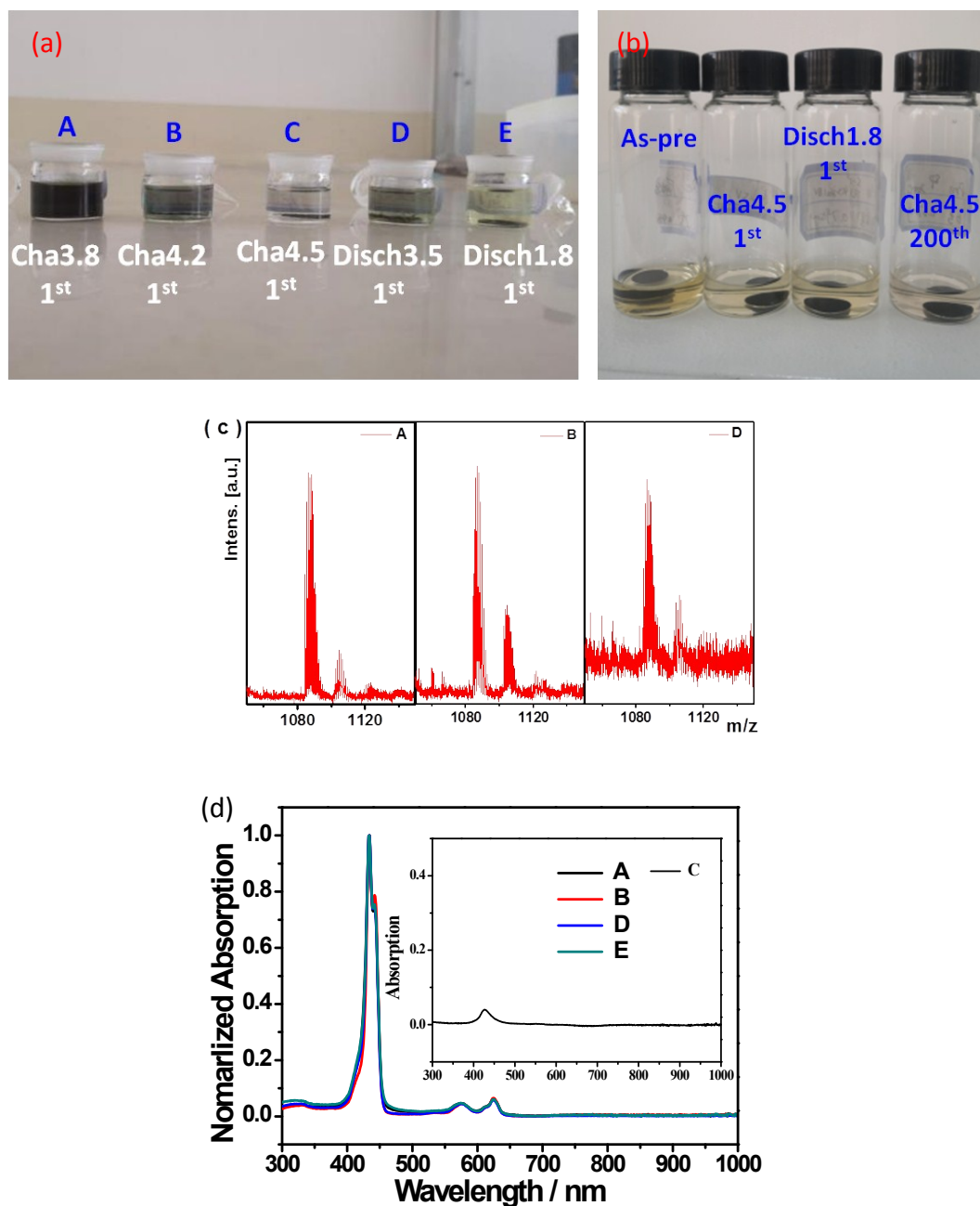


Fig. S12. (a) The solubility of **Pre** at different cycled states in THF, A, B, C, D, E represent states of charged to 3.8V, 4.2V, 4.5V and discharged to 3.5V and 1.8V in the first cycle, respectively, (b) The solubility of **Pre** at different charged and discharged states in the electrolyte (LiPF₆ in EC:PC:DMC=2:2:6), (c) The MS spectra of **Pre** at A, B, D states, (d) the UV-Vis absorption properties of **Pre** at different states in THF.

Reference

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