

## Supporting information

### **Electrolyte Engineering on Porphyrin-based Electrode for Lithium-organic Charge Storage**

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## Experimental section

### 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 microfibre filters (Whatman, GF/D), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), propylene carbonate (PC) were purchased commercially and used as received without further purification. THF was dried over sodium/benzophenone and freshly distilled before use. Unless otherwise stated, commercially available chemicals were used as received. The compounds 5-Phenyldipyrromethane (1), 5,15-Bis(trimethylsilylethynyl)-10,20-diphenylporphyrin (2), [5,15-Bis(trimethylsilylethynyl)-10,20-diphenylporphyrinato] copper (II) (3), and [5,15-Bis(ethynyl)-10,20-diphenylporphyrinato] copper (II) (CuDEPP) were synthesized according to previous report<sup>[1]</sup> and the detail is shown in the Supporting Information.

### Material characterization:

<sup>1</sup>H and <sup>13</sup>C 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 was performed on a Bruker Aupoflex 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<sup>-1</sup> to 4000 cm<sup>-1</sup>. 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.

### **Electrochemical measurements:**

The CuDEPP electrode were prepared by mixing 40 wt % acetylene black, 10 wt % PVDF and 50 wt % CuDEPP (by mass) and the slurry was coated on stainless-steel current collectors (316L, 12 mm in diameter). Different electrolytes are used in this study, i.e. 1 M lithium hexafluorophosphate (LiPF<sub>6</sub>) in ethylene carbonate (EC): dimethyl carbonate (DMC): propylene carbonate (PC) (EC: DMC: PC = 1: 3: 1 by volume ratio), 1 M lithium hexafluorophosphate (LiPF<sub>6</sub>) in propylene carbonate (PC), 1M lithium tetrafluoroborate (LiBF<sub>4</sub>) in propylene carbonate (PC), 0.8 M lithium bis(oxalate)borate (LiBOB) in propylene carbonate (PC), and 1 M, 3 M, 6 M bis(trifluoromethylsulphonyl)imide (LiTFSI) in propylene carbonate (PC). The mass loading of active material was 1.5 mg cm<sup>-2</sup>. 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. CR-2032-coin cells were assembled in an argon-filled glove box 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.

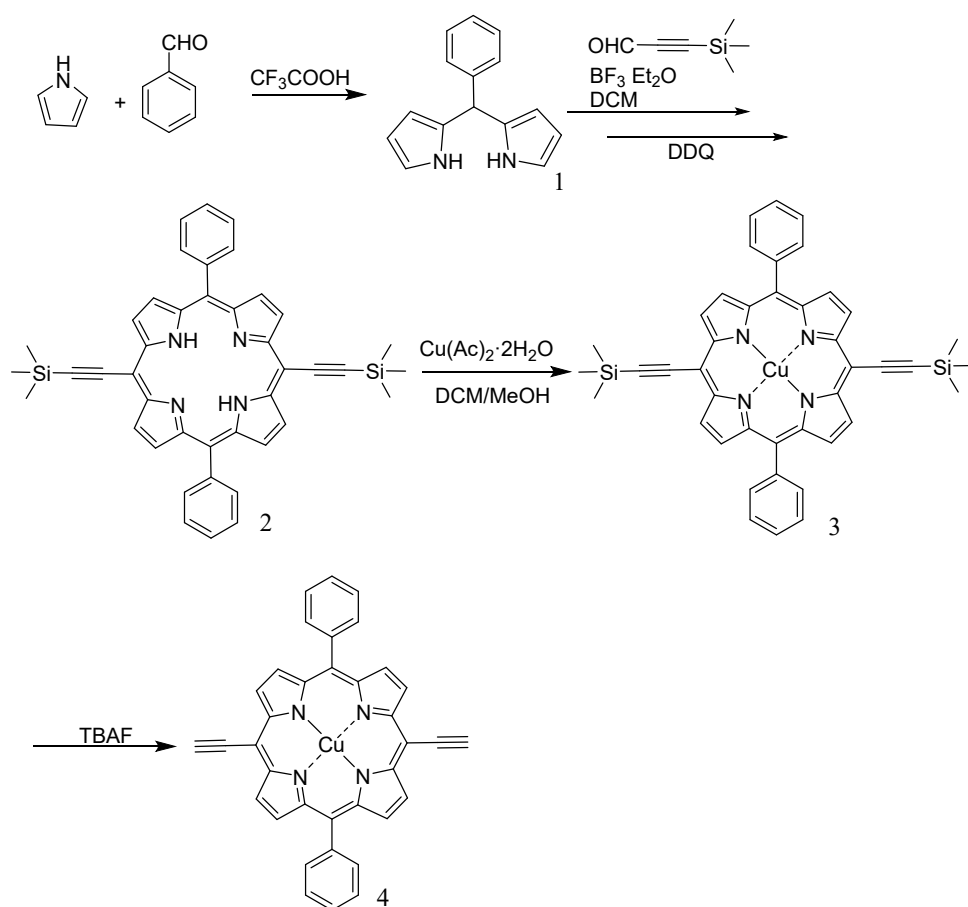
### **Synthesis of materials:**

#### **Synthesis of [5,15-bis(ethynyl)-10,20-diphenylporphinato] copper (II) (CuDEPP):**

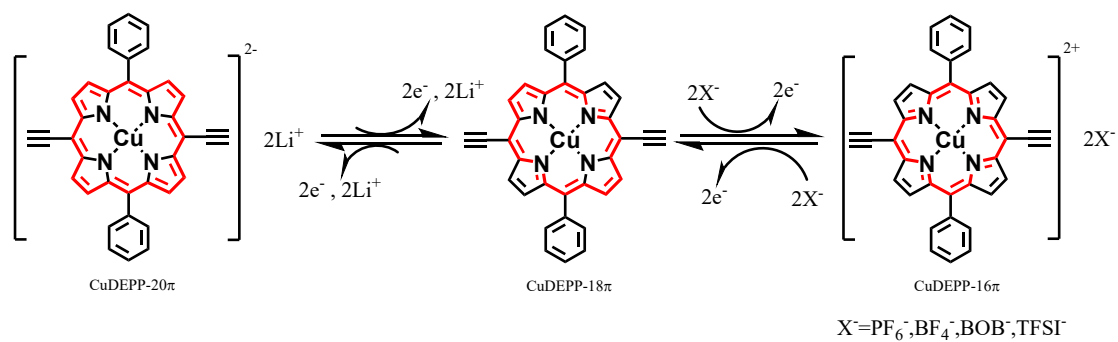
The synthesis of CuDEPP was carried out according to previous report as shown in Figure S1<sup>1</sup>. First, the compound **1** was prepared using the pyrrole (about 100 mmol) and the benzaldehyde (about 20 mmol) as precursors. After the mixture was cooled down to 0 °C and under Ar atmosphere,

0.1 mL  $\text{CF}_3\text{COOH}$  was added. Then the reaction was stirred for 30 min at room temperature. After the reaction finished, the unreacted pyrrole was removed by reduced pressure distillation. The residue was purified by column chromatography (silica gel) using DCM/petroleum ether = 1/5 as eluent and a gray yellow solid **1** was obtained (yield about 49%). Next, the compound **1** (8.18mmol) and 3-(Trimethylsilyl)-2-propynal (8.18mmol) were added to 500 mL DCM and this mixture was degassed with Ar at 0 °C. Borontrifluoride diethyletherate (0.1 mL) was added and the reaction was stirred for 10 min, following reacted at room temperature for another 20 min. Then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (8.18mmol) was added and the reaction was stirred for 1 h. After reaction finished, the solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel) using DCM/petroleum ether = 1/5 as eluent. 100 mL methanol was poured into the solution and then the DCM was dried under vacuum. After filtration, a dark purple solid **2** was obtained (yield about 34 %). Subsequently, the mixture of compound **2** (9.18 mmol) and 500 mL DCM was stirred for 5 min under ambient condition. Then 100 mL MeOH and  $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$  (45 mmol, about 5 eq.) were added. The mixture was stirred at 65°C and reflux for 72h, then was filtered through Celite and washed by DCM. The solution was directly passed through a flash column by DCM. The DCM was removed by vacuum, and the mixture was filtered and the crude product **3** was obtained. 120 mL MeOH was added to the solution, after recrystallized by DCM and MeOH, a dark purple solid **3** (yield about 58 %) was obtained. Finally, the compound **3** (10 mmol) was added to THF (500mL) in Ar, and the mixture was stirred for 10 min. The tetrabutylammonium fluoride (TBAF) (40mmol, 4 eq.) was added to the solution, and was stirred for 30 min. Then 200 mL MeOH was added. After recrystallized by DCM and MeOH, the mixture was filtered affording the final dark purple product **4** (**CuDEPP**, yield about 85

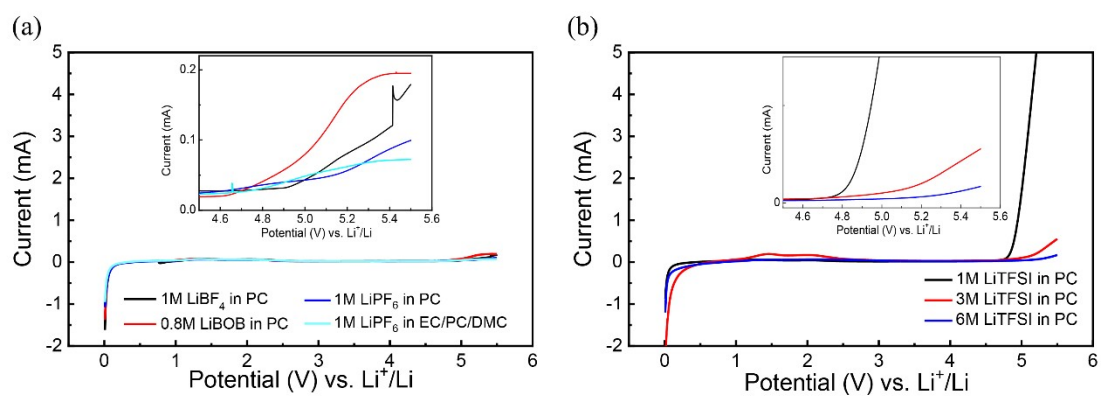
%).



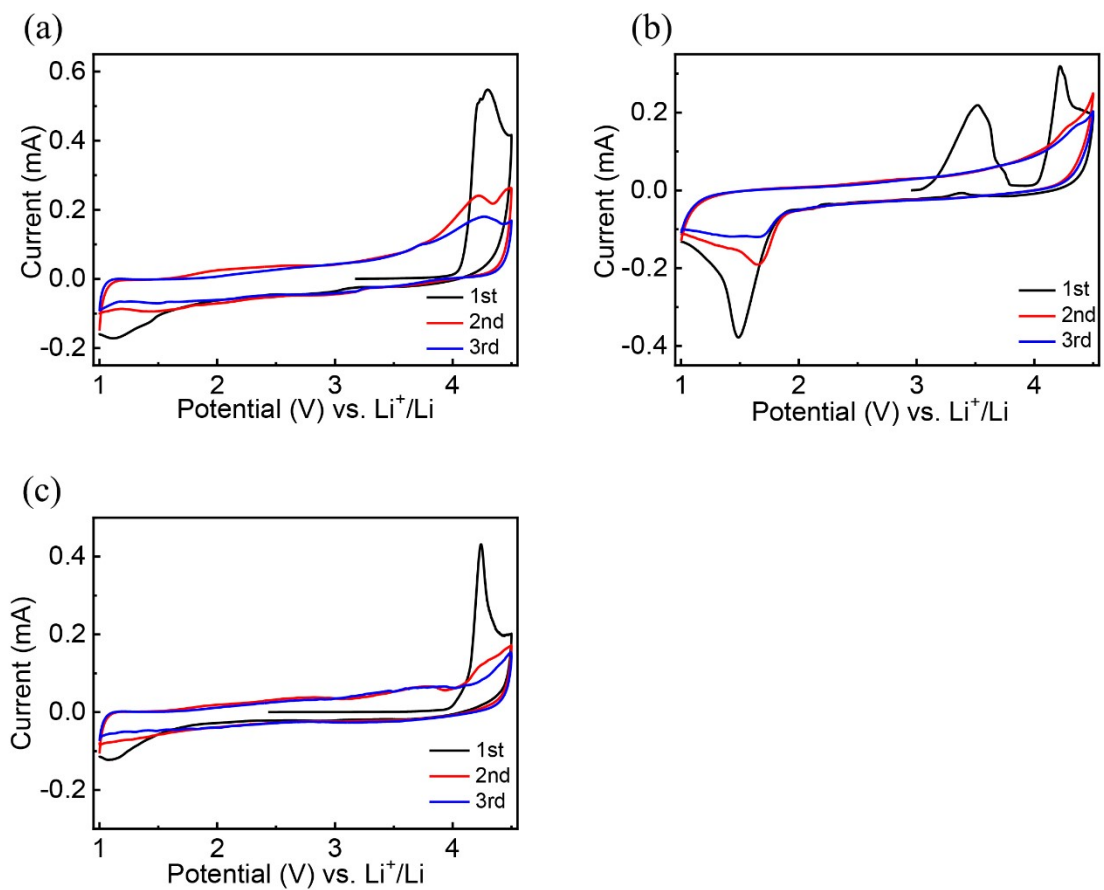
**Figure S1.** The synthetic route of CuDEPP.



**Figure S2.** The charge and discharge reaction mechanism of the CuDEPP in 4.5-1.8V (vs  $\text{Li}^+/\text{Li}$ ).

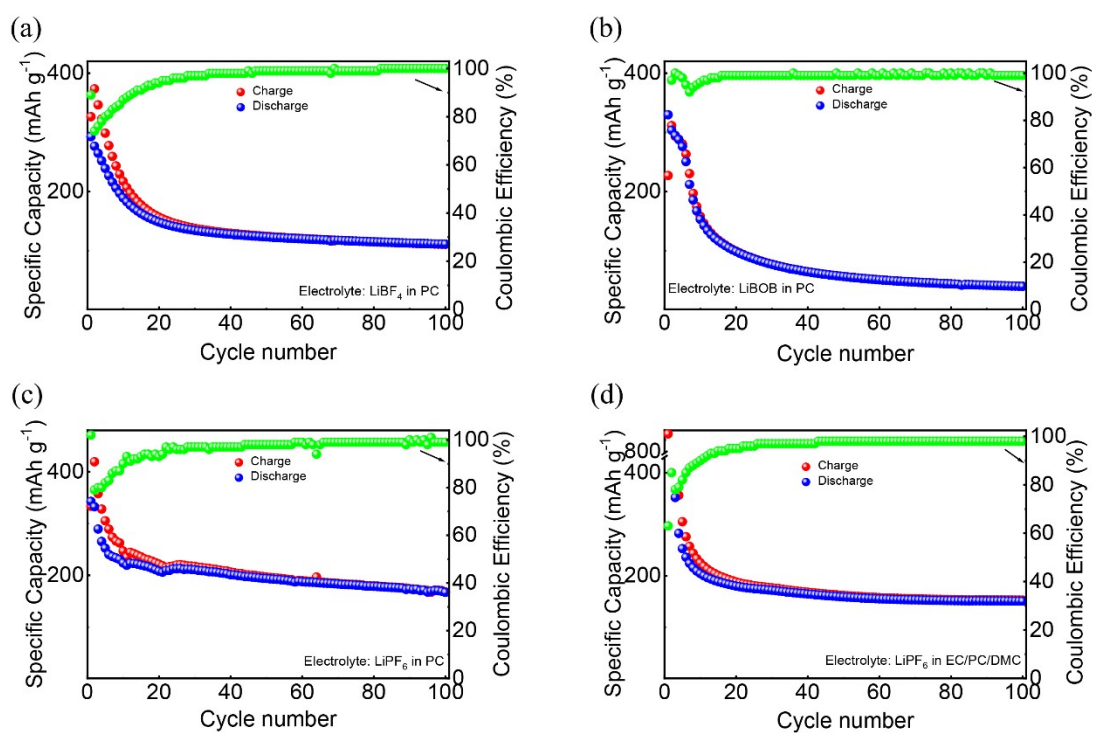


**Figure S3.** LSV curves of different electrolytes, where the cathode was stainless steel foil and the anode was Li. The scan rate was  $0.01 \text{ V s}^{-1}$  (a) Electrolyte: 1M-BF<sub>4</sub>-PC; LiPF<sub>6</sub>-PC; BOB-PC; (b) Electrolyte: 1M-TFSI-PC; 3M-TFSI-PC; 6M-TFSI-PC.

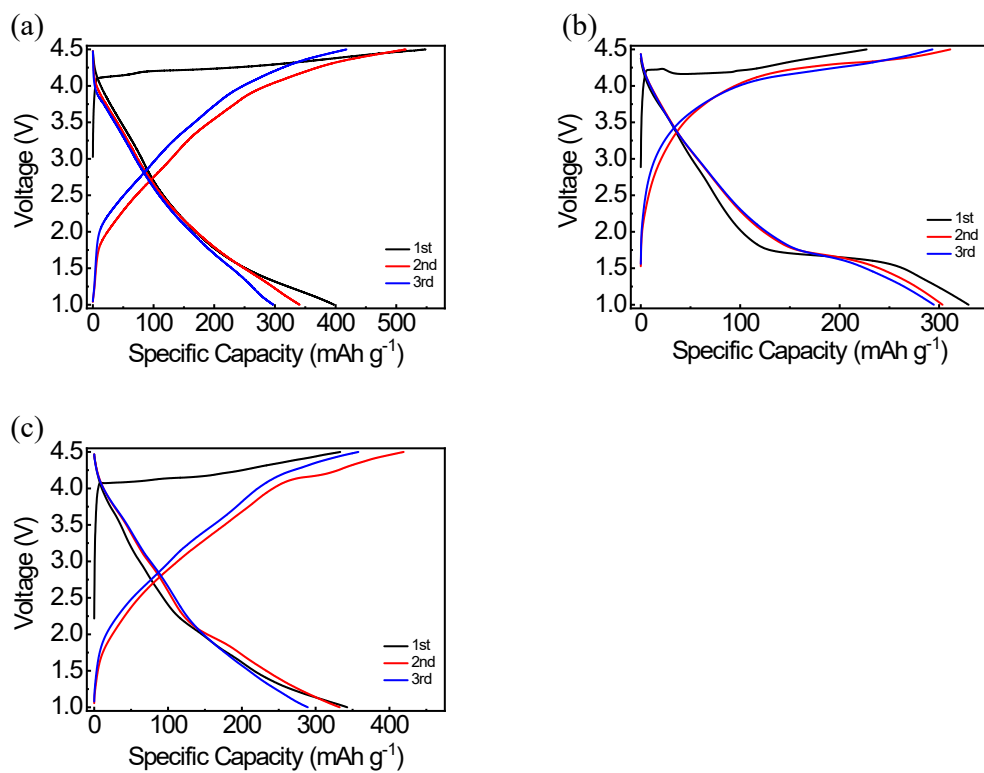


**Figure S4.** The cyclic voltammetry (CV) curves of the CuDEPP in different electrolytes in a voltage range of 1.0-4.5 V. (a) in BF<sub>4</sub>-PC. (b) in BOB-PC. (c) in PF<sub>6</sub>-PC based electrolyte.

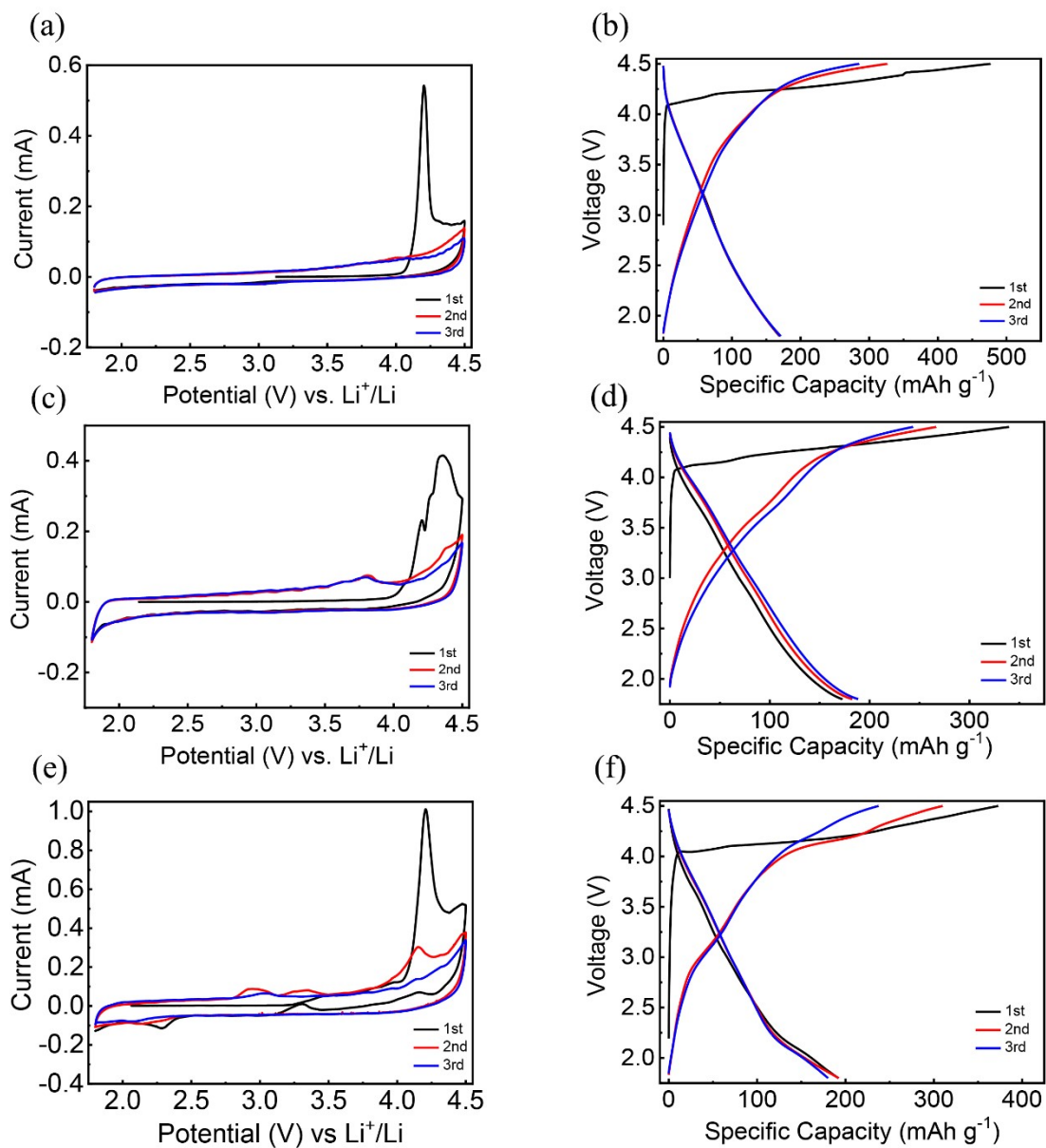




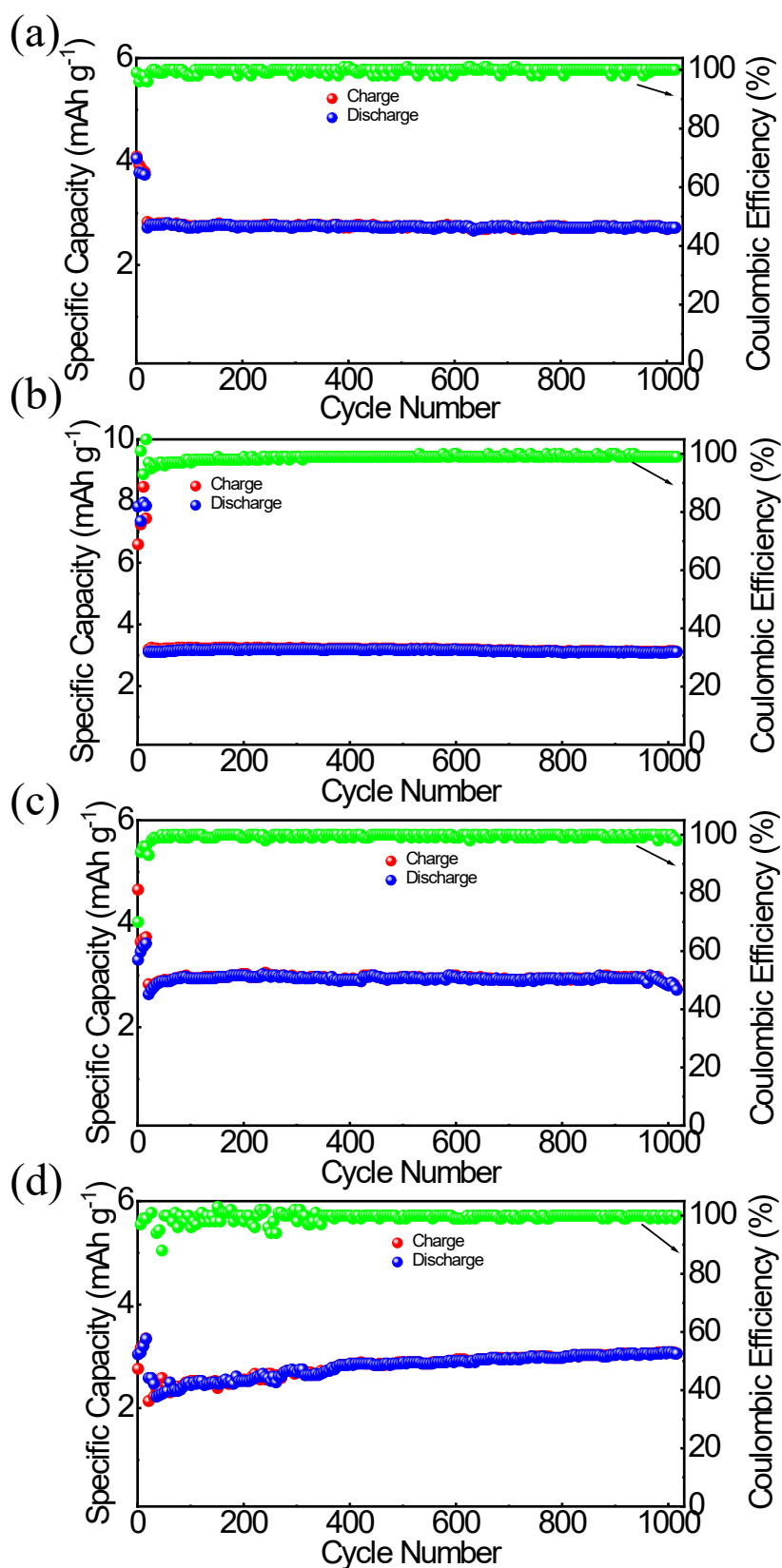
**Figure S5.** The cycling performance of CuDEPP//Li half-cell in different electrolytes, (a) BF<sub>4</sub>-PC; (b) BOB-PC; (c) PF<sub>6</sub>-PC; (d) PF<sub>6</sub>-EPD, in a voltage range of 4.5-1.0 V, at 300 mA g<sup>-1</sup>.



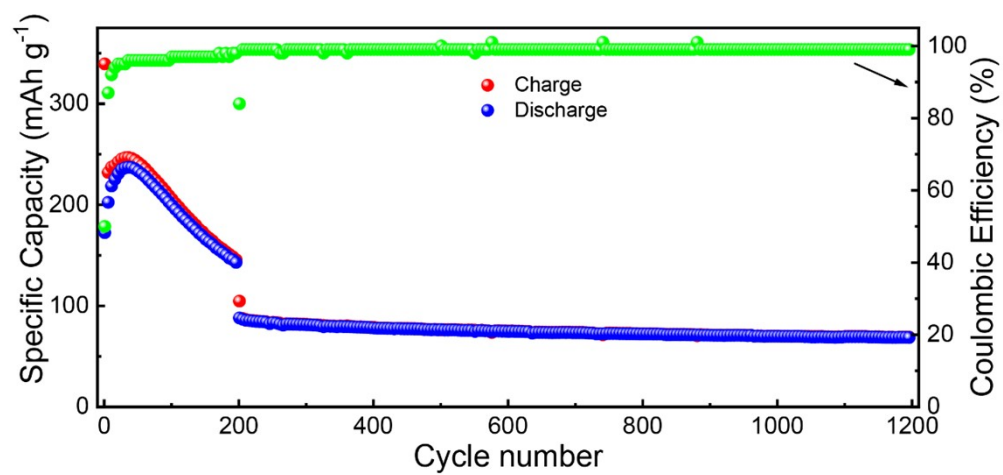
**Figure S6.** The initial charge-discharge curves of the CuDEPP in a voltage range of 1.0-4.5V. (a) BF<sub>4</sub>-PC. (b) BOB-PC. (c) PF<sub>6</sub>-PC based electrolyte.



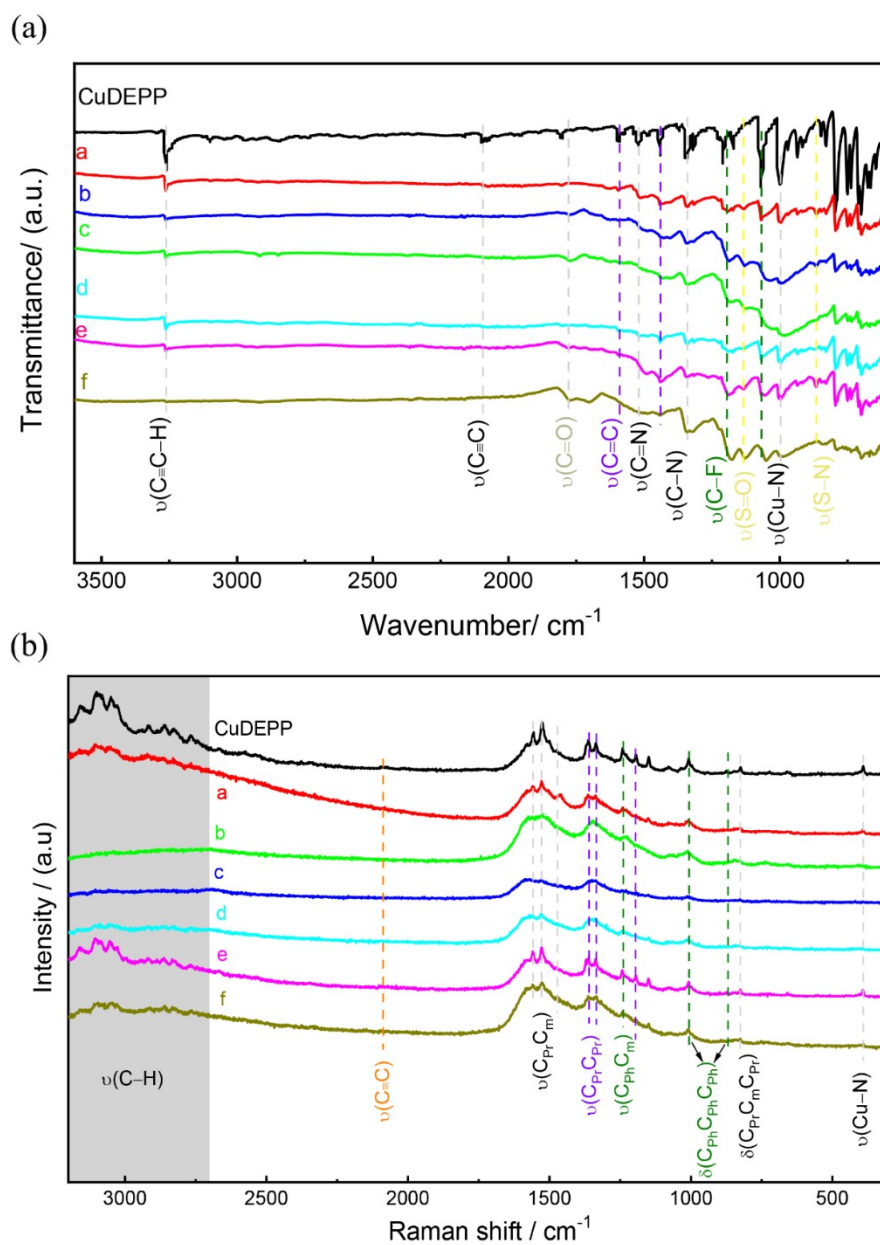
**Figure S7.** The CV and charge-discharge curves of CuDEPP in different electrolytes, the voltage range was 1.8-4.5V, the scan rate was 0.1mV s<sup>-1</sup>, and the current density was 100 mA g<sup>-1</sup>. (a, b) in BF<sub>4</sub>-PC electrolyte, (c, d) in BOB-PC electrolyte, (e, f) in PF<sub>6</sub>-PC electrolyte



**Figure S8.** The cycling performance of acetylene black in different electrolytes. (a) 1M LiBF<sub>4</sub> in PC (BF<sub>4</sub>-PC); (b) 0.8M LiBOB in PC (BOB-PC); (c) 1M LiPF<sub>6</sub> in PC (PF<sub>6</sub>-PC); (d) 1M LiPF<sub>6</sub> in EC/PC/DMC (2:2:6) (PF<sub>6</sub>-EPD).

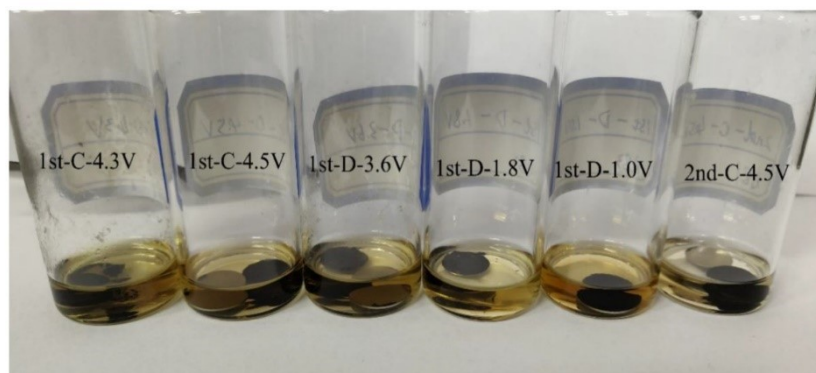


**Figure S9.** The cycle performance of CuDEPP electrode in BOB-PC electrolyte at 100 mA g<sup>-1</sup> for initial 200 times, and then it was cycled at 1000 mA g<sup>-1</sup> for 1000 times.

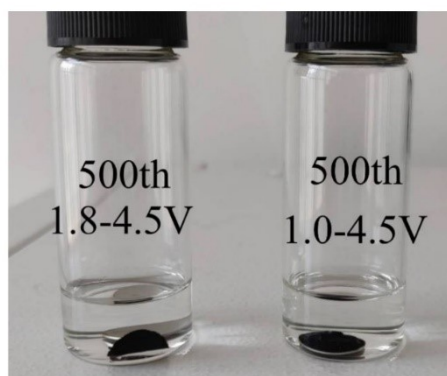


**Figure S10.** (a) IR, and (b) Raman spectra of CuDEPP at different charged states. 3M-TFSI-PC was used as the electrolyte. (a: charged to 4.3V; b: charged to 4.5V; c: discharged to 3.6V; d: discharged to 1.8V; e: discharged to 1.0V; f: recharged to 4.5 V.)

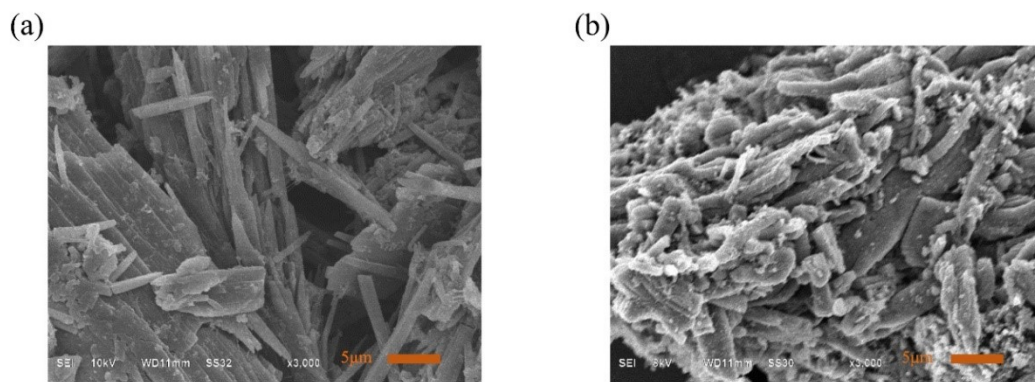
(a)



(b)

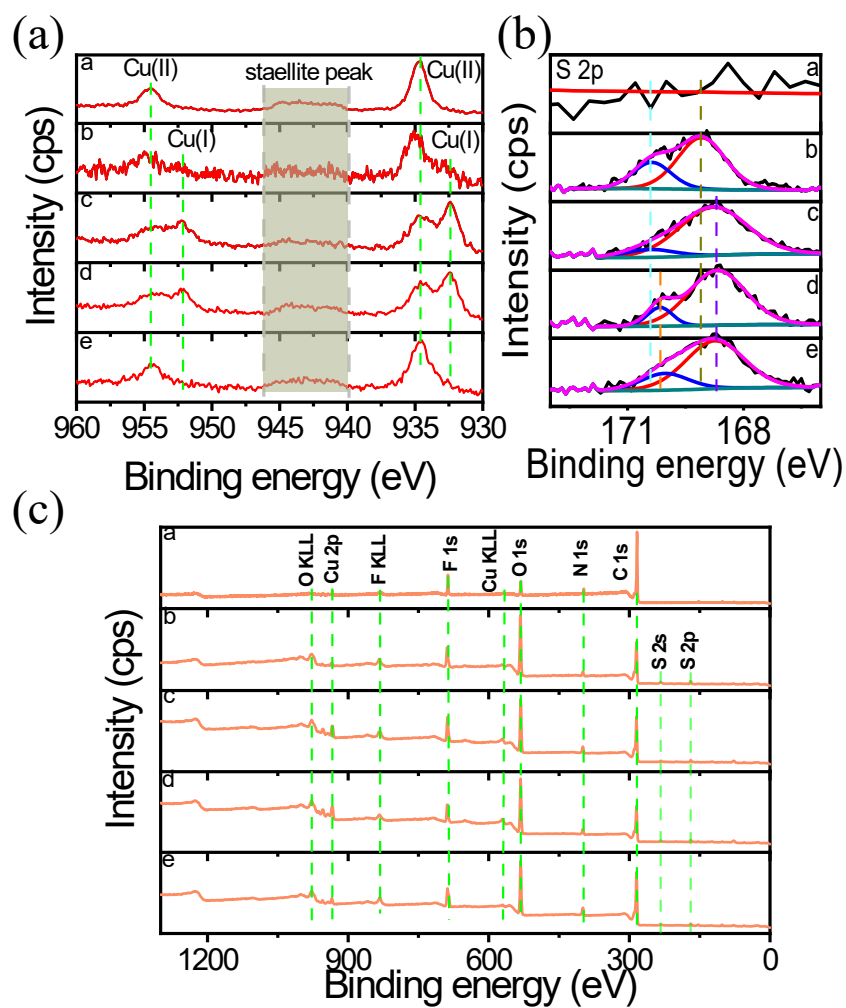


**Figure S11.** The solubility of CuDEPP in tetrahydrofuran. (a) CuDEPP electrodes were immersed for seven days at different cycled states in the 1st and 2nd cycles (b) CuDEPP electrodes were immersed in THF for 7 days after 500 cycles.



**Figure S12.** SEM of CuDEPP electrode in 3M-TFS-PC electrolyte, (a) in the 1st discharged state. (b) in the 500th discharged state.





**Figure S13.** (a) Cu2p core level peaks, and (b) S2p core level peaks, (c) full survey XP spectra of the CuDEPP cathode (a: as-prepared; b: charged to 4.5V; c: discharged to 1.8V; d: discharged to 1.0V; e: recharged to 4.5V).

## Reference

1. P. Gao, Z. Chen, Z. Zhao-Karger, J. E. Mueller, C. Jung, S. Klyatskaya, T. Diemant, O. Fuhr, T. Jacob, R. J. Behm, M. Ruben and M. Fichtner, *Angew. Chem. Int. Ed.*, 2017, **56**, 10341-10346.