Electronic Supplementary Material (ESI) for Dalton Transactions.

Precise lithiophilic sites by diyne-linked phthalocyanine polymer for suppressing metallic lithium dendrite

Yu Gu[a], Chunhua Li[a], Yingbin Wang[a], Wenxin Lu[b], Hong Shang[a,]*, Bing Sun[a,]*

[a] School of Science, China University of Geosciences (Beijing), Beijing, 100084, China

[b] College of Chemical and Biological Engineering, Shandong University of Science and Technology, Qingdao, 266590, China

Corresponding Author: shanghong@cugb.edu.cn; sunbing@cugb.edu.cn

Experimental details:

Synthesis of 2(3),9(10),16(17),23(24)-tetraiodophthalocyanine $H_2Pc(I)_4$

In a typical experiment, 4-iodophthalonitrile (1.0 g, 4.0 mmol) and DBU (0.4 mL) in n-pentanol (8.0 mL) was heated to reflux under nitrogen for 4 h. After being cooled to room temperature, the volatiles were removed under reduced pressure and the residue was purified by a silica gel column using CH_2Cl_2/hexane (V/V, 6/1) as eluent. Repeated chromatography followed by recrystallization from CH_2Cl_2 and CH_3OH gave a purified product $H_2Pc(I)_4$ (450 mg, 44%) as green powder.

Synthesis of 4,4',4'',4'''-(phthalocyanine-2(3),9(10),16(17),23(24)-tetrayl)tetrakis(2-methylbut-3-yn-2-ol) $H_2Pc(etynol)_4$

A mixture of $H_2Pc(I)_4$ (172 mg, 0.17 mmol), methyl butynol (366 μL),$Pd(PPh_3)_2Cl_2$ (1.5 mg, 0.002 mmol) and CuI (0.15 mg, 0.0008 mmol) in THF (2 mL) and Et_3N (4 ml) were stirred under room temperature in nitrogen atmosphere for 24 h. Then, the volatiles were removed under reduced pressure and the residue was purified by a silica gel column using THF/hexane (V/V, 6/1) as eluent. Repeated chromatography followed by recrystallization from THF and hexane gave a purified product $H_2Pc(etynol)_4$ (45.9 mg, 32%) as green powder.

Synthesis of 2(3),9(10),16(17),23(24)-tetraethynylphthalocyanine $H_2Pc(ethynyl)_4$

A mixture of $H_2Pc(etynol)_4$ (132 mg, 0.16 mmol) and NaOH (74mg, 1.85 mmol) in THF (3 mL) and toluene (3 ml) was heated at 90 °C under nitrogen atmosphere for 12 h with a TLC monitoring. After being cooled to room temperature, the volatiles were removed under reduced pressure and the residue was purified by a silica gel column using THF as eluent. Repeated chromatography followed by recrystallization from THF and hexane gave a purified product $H_2Pc(ethynyl)_4$ (29.3 mg, 30%) as green powder.

Characterization: Raman spectra were measured on Renishaw-2000 Raman spectrometer with a resolution of 2 cm^{-1} from Ar laser, the excitation wavelength is 473 nm. XPS was performed on a Thermo Scientific ESCALab 250Xi instrument using 200 W monochromatic Al Kα radiation. XRD was measured using an empirical diffractometer and copper Kα radiation at a voltage of 40 kV, the output power is 1.6

kW. SEM measurements were performed on a Hitachi S-4800 field emission scanning electron microscope. TEM and HRTEM measurements were performed on a JEM-2100F electron microscope.

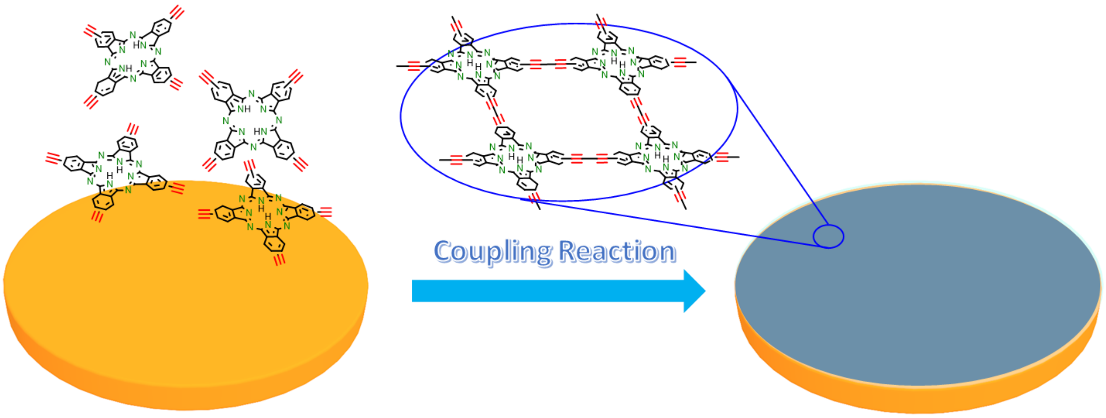
Theoretical Calculation: The first-principle calculations were conducted in DMol^3 module. Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation function was used in the dispersion correction. An all-electron double numerical basis set (DND basis set) was used during calculation. The k-points for Brillioun zone were selected as the gamma point, which is effective considering the large cell sizes of each dimension. A 2×2×1 supercell of a single-layer with a 1.5 nm vacuum layer distance was constructed to interact with Li polysulfides in each periodic system. The binding energy of Li and the substrate was defined as follows:

$$E_{\mathrm{ads}} = E_{\mathrm{Li\text{-}substrate}} - E_{\mathrm{substrate}} - E_{\mathrm{Li}}$$

where $E_{\mathrm{Li\text{-}substrate}}$, $E_{\mathrm{substrate}}$, and E_{Li} are the total energies of PcEP bound with a Li atom, the PcEP substrate, and the single Li atom, respectively. Furthermore, the electron density difference (ρ_{dif}) was calculated similarly as following:

$$\rho_{\mathrm{dif}} = \rho_{\mathrm{Li\text{-}substrate}} - \rho_{\mathrm{substrate}} - \rho_{\mathrm{Li}}$$

where the arithmetic between each cube file was processed on the modified Multiwfn (version 3.5) package sentences.



Scheme S1. In situ growth of PcEP on the copper foil surface.

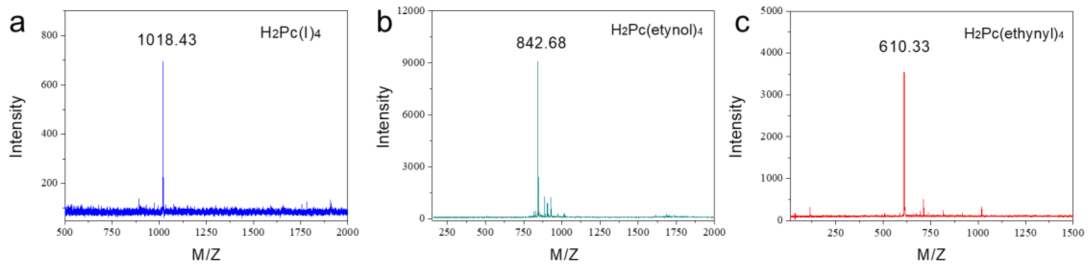


Figure S1. MS spectra of the phthalocyanines. (a) 2(3),9(10),16(17),23(24)-tetraiodophthalocyanine $H_2Pc(I)_4$; (b) 4,4',4'',4'''-(phthalocyanine-2(3),9(10),16(17),23(24)-tetrayl)tetrakis(2-methylbut-3-yn-2-ol) $H_2Pc(etynol)_4$; (c) 2(3),9(10),16(17),23(24)-tetraethynylphthalocyanine $H_2Pc(ethynyl)_4$.

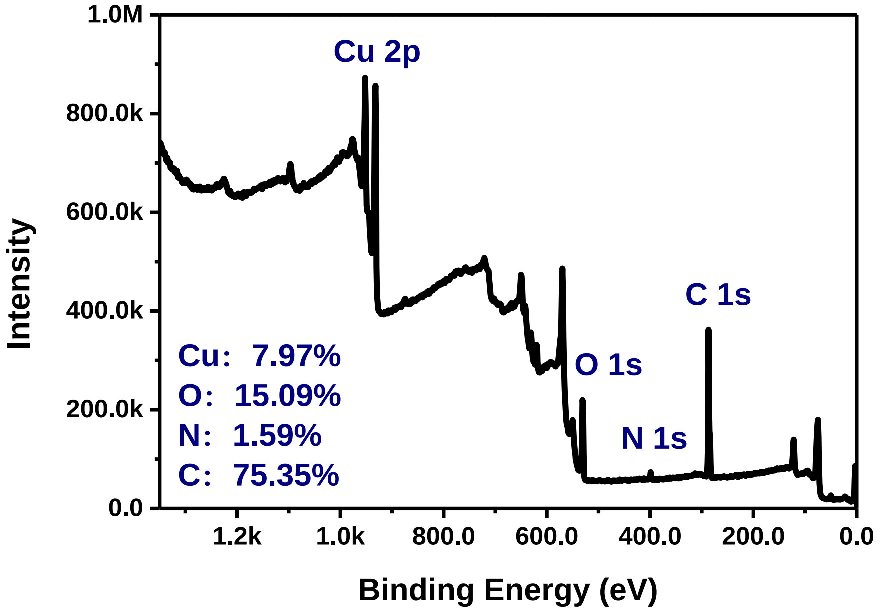


Figure S2. XPS survey spectrum of PcEP@Cu.

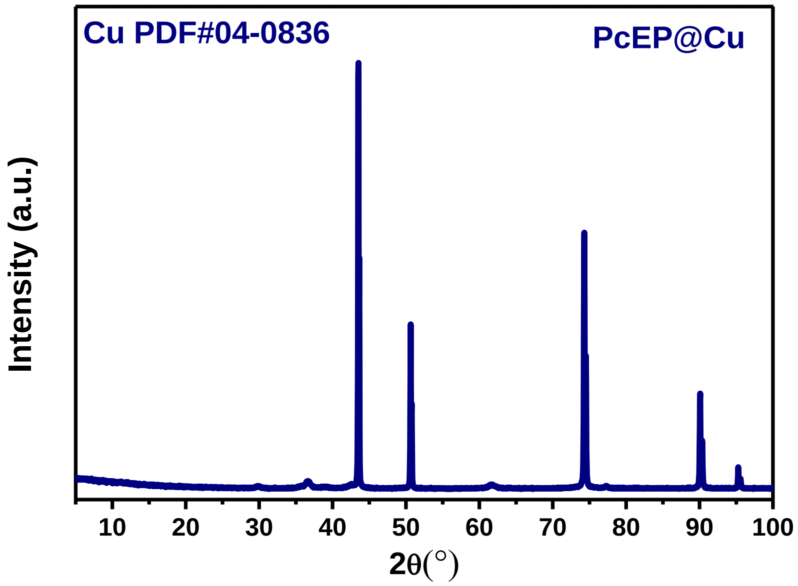


Figure S3. XRD patterns of PcEP@Cu.

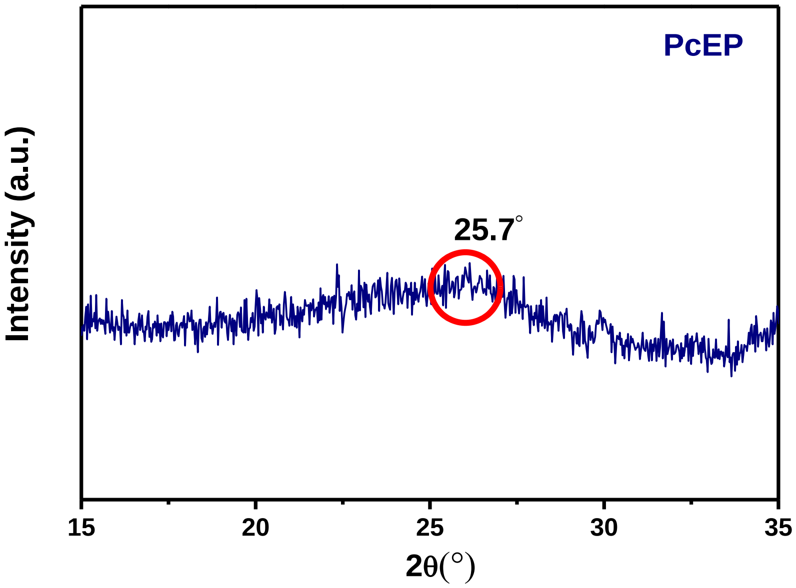


Figure S4. XRD patterns of PcEP.

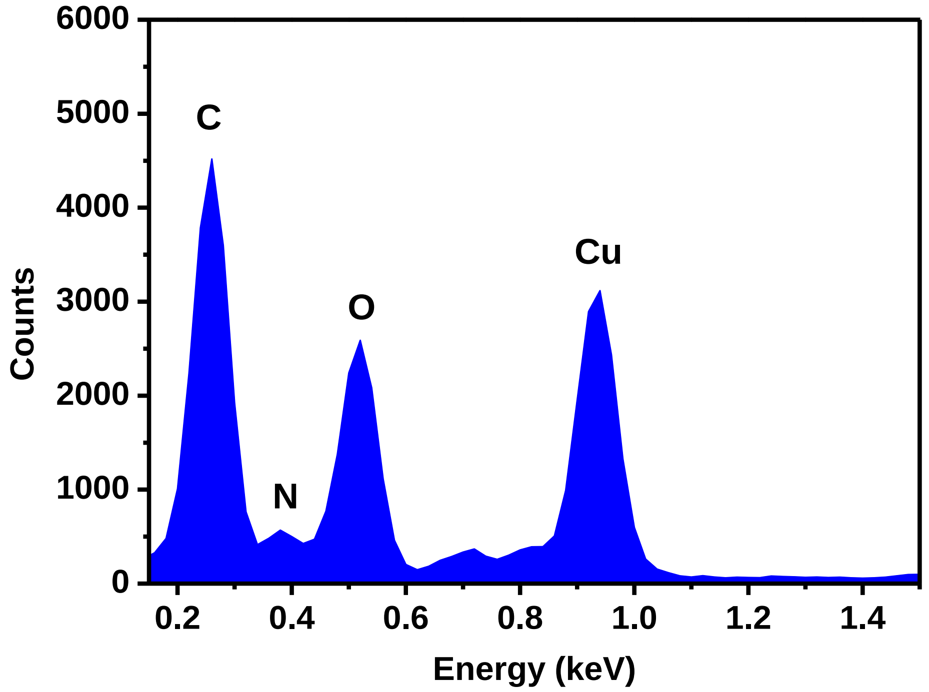


Figure S5. The EDS spectra plot of the PcEP film.

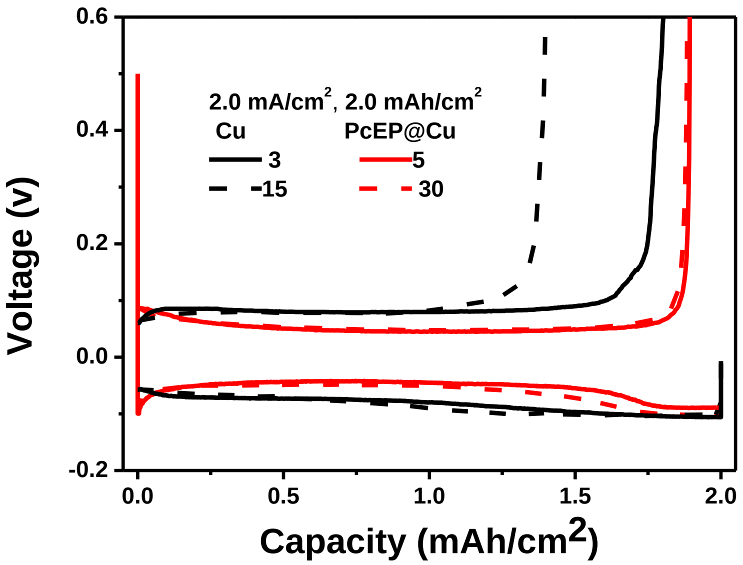


Figure S6. The charge/discharge voltage profiles at the current density of 2.0 mA cm^{-2} with a capacity of 2.0 mAh cm^{-2}.

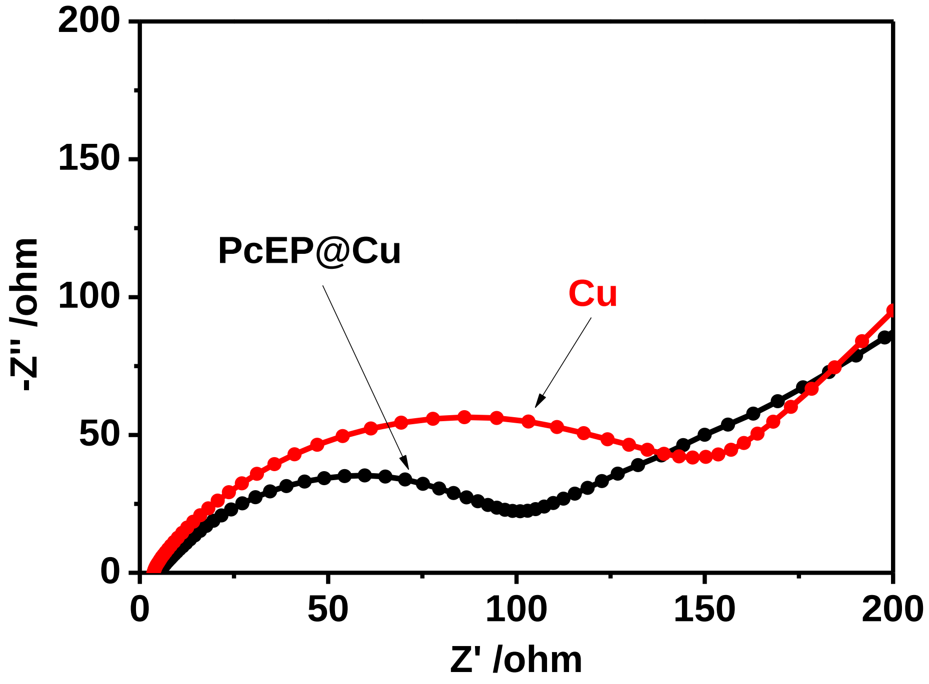


Figure S7. Impedance variations during cycling at a current density of 1.0 mA cm^{-2} with a capacity of 1.0 mAh cm^{-2} after 10 cycles.

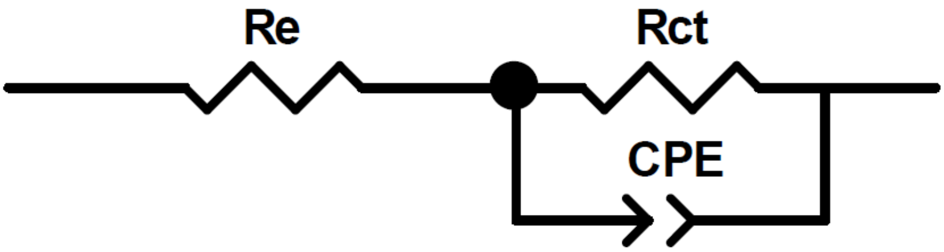


Figure S8. The equivalent electrical circuit for simulating the impedance spectra.

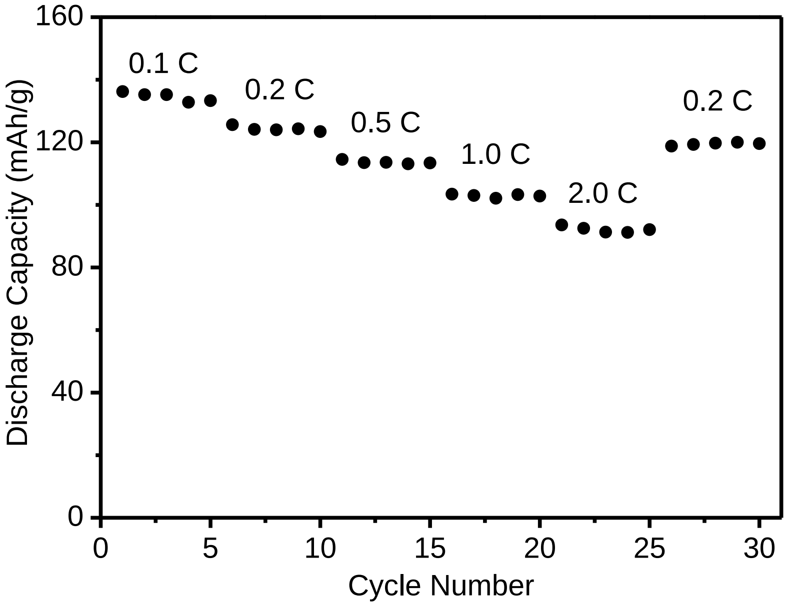


Figure S9. The rate capability of the full cell for PcEP@Cu|Li||LFP at various current rates from 0.1 to 2.0 C.

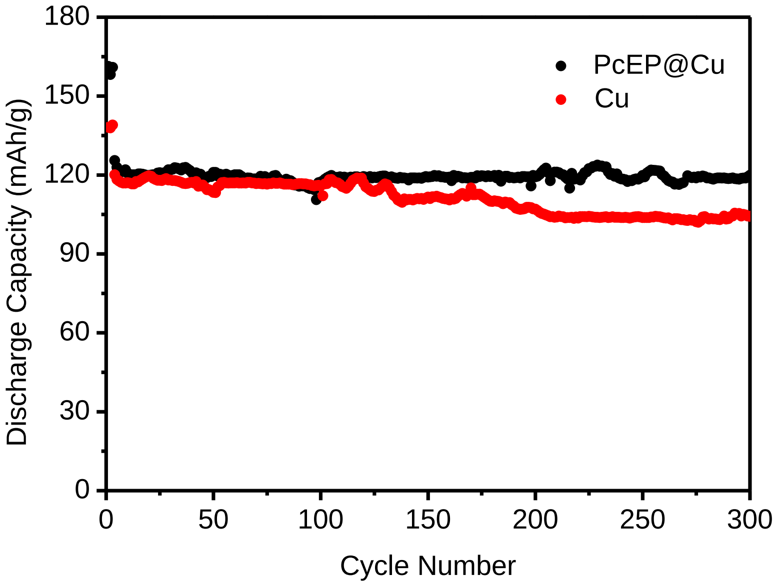


Figure S10. Long-term cycling behavior of the full cells for PcEP@Cu|Li||LFP and Cu|Li||LFP at the rate of 1 C.

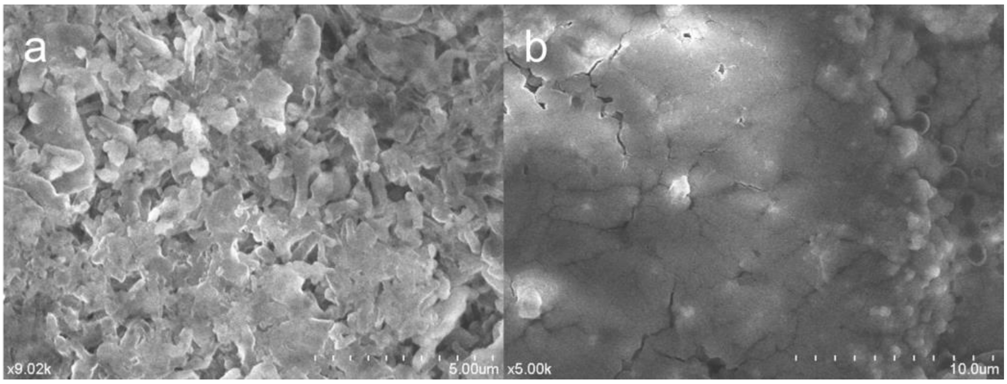


Figure S11. SEM images of continuous deposited Li on (a) Cu and (b) PcEP@Cu electrodes.