Supporting Information

Cu-mediated bipolar-type extended π -conjugated microporous polymers for lithium-ion battery cathode with high energy density and fast-charging capability

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TABLE OF CONTENTS

1. Material Synthesis	3-4
2. Materials Characterization and Electrochemical Measurements	5-7
3. Supplementary Equations (S1-S9)	8-11
4. Computational Details	12-13
5. Supplementary Figures (S1-S23)	13-23
6. Supplementary Tables (S1-S6)	24-27
7. Supplementary References	28-30

Material Synthesis

Synthesis of 5,10,15,20-tetrakis(4-pyrrolyl)-porphyrin (PP) monomer

2 g 4-(1H-Pyrrol-1-yl) benzaldehyde (TT) was dissolved in the mixture of nitrobenzene (60 mL) and acetic acid (90 mL). After heating the oil bath to 120 °C, 0.8 mL of pyrrole was added and stirred at 120 °C for 1 h. The mixture was then cooled to room temperature and vacuum filtered. The crude product was washed with methanol using a water bath and the Soxhlet extractor. Finally, the sample was dried in vacuum oven at 60 °C for 24 h. The product as a powder with purple color.



Scheme S1. Synthetic procedure and structural of PP.

Synthesis of PPCMP

The PP monomer and chloroform were placed in 50 mL flask and stirred for 30 min. The FeCl₃ was then dissolved in nitromethane and added into the monomer solution, followed by stirring for 24 h. Afterward, the mixture was purified by a water bath and Soxhlet extractor with methanol and chloroform after filtering. Finally, the sample was dried in a vacuum oven at 100 °C for 24 h.



Scheme S2. Synthetic procedure and structural of PPCMP.

Synthesis of PPCMP-Cu

PPCMP (0.2 mmol), $CuCl_2$ (1 mmol) and DMF (20 mL) were mixed in 100 mL Pyrex tube. The tube was then placed in a 120 °C oil bath and stirred for 24 h. After the reaction, the crude product was purified by washing with methanol and water. The product was then dried in a vacuum oven at 100 °C for 24 h.



Scheme S3. Synthetic procedure and structural of PPCMP-Cu.

Materials Characterization and Electrochemical Measurements

Materials Characterization

The structure of the PP and PPCMP were tested using a nuclear magnetic resonance spectrometer (¹H NMR, AVANCE NEO) and solid-state nuclear magnetic resonance spectrometer (¹³C NMR, AVANCE 400, Bruker), respectively. The structures of PPCMP, PPCMP-Cu-1, PPCMP-Cu, and PPCMP-Cu-10 were characterized by Fourier transform infrared (FT-IR, Nicolet IS5, Thermo Fisher), and X-ray diffraction (XRD, D8 Advance, Bruker) using Cu K α radiation (2 θ = 5-60°). The thermostability of PPCMP and PPCMP-Cu was confirmed by thermal gravimetric analysis (TGA, TGA 550, Discovery) from room temperature to 900 °C in nitrogen (N₂) with the temperature rate of 10 °C min⁻¹. The surface area and pore properties were measured by Brunauer-Emmett-Teller (BET) method (ASAP 2460, Micromeritics Instrument Corporation) and calculated based on the non-local density functional theory (NLDFT). The metal content of PPCMP-Cu-1, PPCMP-Cu, and PPCMP-Cu-10 were determined by inductively coupled plasma (ICP) analysis (ICP, Leeman Prodigy-ICP). The morphologies of PPCMP and PPCMP-Cu were obtained by scanning electron microscope (SEM, GeminSEM 560G560) and transmission electron microscope (TEM, Talos F200S, FEI). The energy dispersive spectrometer (EDS) of PPCMP-Cu was obtained using GeminSEM 560G560 (SEM) and JEM-2100 (TEM). The surface elements changes were recorded by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher) under high vacuum (1*10⁻⁹ Torr), and all binding

energy were calibrated to the C1s peak at 284.8 eV. In addition, all samples for *ex-situ* tests were prepared by immersing the electrodes into dimethyl carbonate (DMC) at different voltages. The electrical conductivities of PPCMP and PPCMP-Cu were measured by current-voltage (I-V) curves based on the semiconductor tester (Keithley, 4200A-SCS).

Electrochemical Measurements

Electrochemical lithium-storage properties of PPCMP and PPCMP-Cu were evaluated using CR2032 coin-type test cells which assembled in the argon-filled glove box (the concentration of oxygen and water was below 1 ppm). The working electrode was fabricated by slurry with appropriate viscosity consisting of 50 wt% active materials, 30 wt% Ketjen black and 20 wt% PVDF binder dissolved in NMP. More proportion of conductive agents and binders is owing to the low electrical conductivity and improved the mechanical stability.^{1,2} The slurry was cast onto aluminum foil, dried in a 60 °C oven for 30 min, and then further dried in a vacuum at 100 °C for 12 h. The loading mass of PPCMP and PPCMP-Cu on the electrode was around 0.3–0.35 mg cm⁻². The high mass loading was improved to $\sim 1.0 \text{ mg cm}^{-2}$ to further study the electrochemical performance of PPCMP-Cu. A pure lithium foil was used as the counter electrode, and the electrolyte consisted of 1 mol L^{-1} LiPF₆ in a 3:7 v/v mixture of EC/DMC. The electrolyte addition is 60 µL. The size and active material areal loading of cathode (PPCMP and PPCMP-Cu), separator (Polypropylene), and anode (Li metal) are 1.13 cm⁻² with 0.3–0.35 mg cm⁻², 2.01 cm⁻² with 1.5 mg cm⁻², 1.54 cm⁻² with 21.6 mg

cm⁻², respectively. The separator used was Celgard 2500. Galvanostatic charge/discharge cycles were performed in a potential range of 1.2-4.4 V vs. Li/Li⁺ on the Neware instrument. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed using a Gamry Interface 1000E electrochemical workstation, with the EIS frequency range spanning from 10^6 to 10^{-1} Hz.

EXAFS Test

Data reduction, data analysis, and EXAFS fitting were performed and analyzed with the Athena and Artemis programs of the Demeter data analysis packages³ that utilizes the FEFF6 program⁴ to fit the EXAFS data. The energy calibration of the sample was conducted through standard and Cu foil, which as a reference was simultaneously measured. A linear function was subtracted from the pre-edge region, then the edge jump was normalized using Athena software. The $\chi(k)$ data were isolated by subtracting a smooth, third-order polynomial approximating the absorption background of an isolated atom. The k³-weighted $\chi(k)$ data were Fourier transformed after applying a Hanning window function ($\Delta k = 1.0$). For EXAFS modeling, the global amplitude EXAFS (CN, R, σ^2 and ΔE_0) were obtained by nonlinear fitting, with least-squares refinement, of the EXAFS equation to the Fourier-transformed data in R-space, using Artemis software, EXAFS of the Cu foil are fitted and the obtained amplitude reduction factor S_0^2 value (0.736) was set in the EXAFS analysis to determine the coordination numbers (CNs) in sample.

Supplementary Equations

Calculations of theoretical capacity

Theoretical capacity C_t (mAh g⁻¹) was calculated using the following equation S1:

$$C_t = \frac{nF}{3600(M_w/1000)}$$
 S1

Where n and M_w is the number of charge carrier and the molecular weight of the active material, respectively, F is the Faraday constant (96485 C mol⁻¹).

In the PPCMP-Cu the molecular weight of a repeating unit ($C_{60}H_{32}N_8Cu$) is calculated to be $M_w = 928.58$ g mol⁻¹. The number of electrons (n) involved in the repeating unit is 10. Therefore, the theoretical capacity is calculated using the equation of $C_t = 286.2$ mAh g⁻¹.

Tap density and electrolyte uptake

The tap density for the electrode was tested by using the following equation S2: ⁵

$$\rho = \frac{m}{V} = \frac{m}{S \times H}$$
 S2

Where m, V, S, and H are the mass, volume, area and thickness of the active material layer, respectively.

The electrolyte uptake for the electrode was tested based on the literature by using the following equation S3:⁶

$$EU\% = \frac{m_2 - m_1}{m_1} \times 100\%$$
 S3

in which m_1 and m_2 present the dry weight and the weight of immersing in the electrolyte followed by removing the electrolyte on the surface, respectively."

Capacity Contribution Distribution

The capacity contribution is generally classified as two types (pseudo-capacitance and diffusion capacitance), this classification follows the relationship between the peak current (i) and scan rate (v) is fitted by equation S4:⁷

$$logi = blogv + loga$$
 S4

in which a and b are defined as constants. The type of capacity contribution can be reflected by the value of b. If the value of b is close to 0.5, the capacity storage behaviors are mainly based on the diffusion capacitance. If the value of b is close to 1, the capacity storage is predominantly attributed to the pseudo-capacitance.

Furthermore, the capacity contribution distribution was also calculated by equation S5:8

$$i = k_1 v + k_2 v^{1/2}$$
 S5

where k_1 and k_2 are constants, and k_1v and $k_2v^{1/2}$ represent the contribution of pseudocapacitance and diffusion capacitance, respectively.

Ions Diffusion Coefficient (Dions)

The D_{ions} were measured by the galvanostatic intermittent titration technique (GITT)

on Neware instrument at a current density of 0.3 A g^{-1} for 5 min, followed by 60 min relaxation period. The D_{ions} was calculated by the following equation S6:⁷

$$D_{ions} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B A} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2$$
 S6

where m_B , V_M , and M_B represent the mass, molar volume, and molecular weight of active material, respectively. A is the contacting area between active material and electrolyte.

Activation Energy (E_a) of electrode

The E_a was calculated from the slope of the Arrhenius plot based on charge transfer resistance (R_{ct}) at selected temperatures from 30 to 55 °C by using the equation S7:⁹

$$ln(T/R_{ct}) = (lnA - E_a)/RT$$
 S7

where A is the pre-exponential factor, R is the gas constant and T (K) is the testing absolute temperature.

Energy density (E) and power density (P)

The energy density and power density were calculated by using the equations S8 and S9:^{10, 11}

$$E = C \times V_{avg}$$
 S8

$$P = E/t$$
 S9

where E, C, and V_{avg} represent the energy density (Wh kg⁻¹), specific capacity, and average charge voltage. P and t are the power density (W kg⁻¹) and charge time, respectively.

Computational Details

Generation of structural models for PPCMP and PPCMP-Cu

Like the modelling strategy developed by Maji et al., hypothetical PPCMP and PPCMP-Cu dimers are modelled by fusing two PP units (PPCMP-monomer) and two Cu-PP units (PPCMP-Cu-monomer), and were optimized first by DFT (B3LYP/6-311G) in Gaussian 09 software.¹² The subsequent MD simulations for the energy minimization of the initial configuration was performed in LAMMPS package.¹³ The details of MD stimulations were followed the reference 13.

Calculation of pore size distribution of PPCMP and PPCMP-Cu models

The established PPCMP and PPCMP-Cu models were used to analyse the pore size distribution using PoreBlazer v4.0 (PB v4.0) developed by Lev Sarkisov and co-worker.¹⁴ The PB v4.0 was taken as input four files. All the simulations presented in this article have been carried out using the default values.

DFT calculation

The Gaussian 09 software package performed the DFT calculation of all molecules.¹⁵ The geometry optimizations were carried out with the B3LYP hybrid functional¹⁶ and 6-311G (d, p) basis set¹⁷ with Grimme–D3 dispersion corrections.¹⁸ The Single point energies in the liquid state were computed at the B3LYP-D3 (BJ)/6-311G (d, p) theory level. The Lanl2TZ potential basis set was also applied for the Cu atom. The electrostatic potential analysis and HOMO–LUMO were processed using Multiwfn 3.8¹⁹ and visualized by the VMD 1.9.3 package.²⁰ Based on the above data, the binding

energy was calculated from the following equation:

$$\Delta G = G_{*Li/PF_6} - G_* - nG_{Li/PF_6}$$

Where $*Li/PF_6$ presents the pristine model of PPCMP-Cu absorbed Li/PF₆ groups, the n was determined by the number of adsorbed Li/PF₆ groups.

Molecule dynamics simulation

The amorphous model is built through the Amorphous Cell module, and optimized by the geometric optimization method to obtain a more stable structure in 1 M LiPF₆ without solvent components of electrolyte.²¹ The force field is COMPASSII. In the dynamic study of lithium-ion migration and diffusion properties, the canonical ensemble (NVT)was applied for each system using the velocity Verlet algorithm. The temperature, simulation time, and time step are 300 K, 10 ps, and 1 fs, respectively. The diffusion of ions in modified CMP system were also studied. In the amorphous model, due to the small voids, the dynamics of 500 ps were carried out with NVT ensemble to obtain the effective diffusion coefficient. The pressure and temperature are set as atmospheric pressure and 300 K, respectively. Vander Waals interactions were calculated by an atom-based method with a cutoff distance of 12.5 Å. Electrostatic interactions were calculated by the Ewald method, which takes a long time but is accurate for long-range interactions. Finally, the diffusion coefficient and migration energy barrier of ions in systems are obtained.

Supplementary Figures



Figure S1. (a) FT-IR spectra of 4-(1H-pyrrol-1-yl) benzaldehyde (TT) and PP monomer. (b)The liquid ¹H NMR spectra of PP. ¹H NMR (400 MHz, CDCl₃-d6) δ/ppm: 8.93 (s, 8H), 8.26 (s, 8H), 7.82 (s, 8H), 7.43 (s, 8H), 6.53 (s, 8H), -2.76 (s, 2H).



Figure S2. The solid-state ¹³C CP/MAS NMR spectrum of PPCMP.

¹³C NMR (400 MHz, CDCl₃): δ 166.58, 151.67, 138.75, 135.43, 132.41, 128.60, 124.69, 118.18, 110.67.



Figure S3. FI-TR spectra of PPCMP-Cu-10, PPCMP-Cu, PPCMP-Cu-1 and PPCMP.



Figure S4. XRD patterns of PPCMP, PPCMP-Cu, $CuCl_{2}$, and Cu.



Figure S5. (a) N₂ adsorption and desorption curves and (b) the pore size distribution of PPCMP,

PPCMP-Cu-1, PPCMP-Cu-10, and PPCMP-Cu at 77.3 K.



Figure S6. The optimized geometric structures of (a) PPCMP-oligomer and (b) PPCMP-Cuoligomer with the spatial angle and total energy. The calculated pore size distribution of (c) PPCMP and (d) PPCMP-Cu.



Figure S7. SEM images of (a) PPCMP and (b) PPCMP-Cu.



Figure S8. (a)TEM images of PPCMP and (b) PPCMP-Cu.



Figure S9. TEM and element mapping images of PPCMP-Cu.



Figure S10. TGA scans of PPCMP and PPCMP-Cu under 0.6 sunlight irradiation.



Figure S11. EXFAS fitting curves for PPCMP-Cu in K-space.



Figure S12. Simulated structures of (a) PP and (b) Cu-PP.



Figure S13. The electron conductivities of PPCMP and PPCMP-Cu fitted from I-V curves.



Figure S14. The CV curves of PPCMP and PPCMP-Cu at 0.2 mV s⁻¹.



Figure S15. Charging and discharging curves of (a) PPCMP and (b) PPCMP-Cu.



Figure S16. (a) Rate performance and (b) long-term cycling stability at a current density of 2000 mA g^{-1} of PPCMP-Cu with high areal loading as 1.0 mg cm⁻².



Figure S17. (a) CV curves at various scan rates and (b) the b values of different peaks of PPCMP.



Figure S18. CV profiles at different scan rates for (a-e) PPCMP and (f-j) PPCMP-Cu with

capacitive-controlled process.



Figure S19. GITT curve and corresponding ions diffusion coefficient for PPCMP.



Figure S20. (a) Molecular dynamics (MD) modeling in 1 M LiPF_6 excluding solvent components of electrolyte and (b) the time evolution of the mean square displacement (MSD) of PPCMP and PPCMP-Cu with Li ions.



Figure S21. The rate performance of full-battery with PPCMP-Cu as cathode and pre-lithiated graphite as the anode.



Figure S22. (a) Charging and discharging curve of PPCMP-Cu with selected voltages. (b) Ex-situ

FT-IR spectra corresponding to the selected voltages of PPCMP-Cu.



Figure S23. The Cu2p XPS spectra of PPCMP-Cu at pristine, discharge, and charge state.

Supplementary Tables

Sample	PPCMP-Cu-1	PPCMP-Cu	PPCMP-Cu-10	Calculated
(PPCMP : CuCl ₂)	(1:1)	(1:5)	(1:10)	/
Cu content (mg g ⁻¹)	42.7	54.0	48.5	68.4

Table S1. The metal content of samples in different ratios from ICP tests.

Table S2. The different peaks content ratios of N1s XPS test for PPCMP and PPCMP-Cu.

Content ratio	amine N	Cu-N	imine N
PPCMP	78.1%	/	21.9%
PPCMP-Cu	58.9%	18.2%	22.9%

Table S3. EXAFS fitting parameters at the Cu K-edge for various samples.

Samula	Shall	CNa	$\mathbf{D}(\hat{\mathbf{x}})\mathbf{b} = -2(\hat{\mathbf{x}}^2)\mathbf{c} + \mathbf{E}(\mathbf{x}^2)\mathbf{c}$		AE (aV)d	K-range R-range		D faatan
Sample	Sheh	CIN-	$\mathbf{K}(\mathbf{A})^{2}$	0-(A-)-	$\Delta L_0(ev)^2$	$/\mathrm{\AA}^{-1}$	$/{ m \AA}^{-1}$	K lactor
Cu foil	Cu-Cu	12.0*	2.55 ± 0.01	0.0091	5.6	2-12	1.0-3.0	0.0084
CuPc	Cu-N	4.0^{*}	1.94 ± 0.01	0.0027	4.9	2-12	1.0-2.0	0.0193
PPCMP-Cu	Cu-N	4.1±0.3	1.97 ± 0.01	0.0028	5.6	2-12	1.0-2.0	0.0132

CN: coordination number; R: distance between absorber and backscatter atoms; σ^2 : Debye-Waller factor to account for both thermal and structural disorders; ΔE_0 : inner potential correction; R factor indicates the goodness of the fit. S_0^2 was fixed to 0.736, according to the experimental EXAFS fit of Cu foil by fixing CN as the known crystallographic value. A reasonable range of EXAFS fitting parameters: $0.700 < S_0^2 < 1.000$; CN > 0; $\sigma^2 Å^2 > 0$; $|\Delta E_0| < 15 \text{ eV}$; R factor < 0.02.

Log scan rate	Log peak current (O1)	Log peak current (R1)	Log peak current (O2)	Log peak current (R2)
-0.69897	-1.45593	-2.07889	-1.23882	-2.02687
-0.39794	-1.21760	-1.7929	-1.04798	-1.74473
-0.22185	-1.04993	-1.63246	-0.94348	-1.52288
-0.09691	-0.98906	-1.4862	-0.86774	-1.4318
0	-0.90672	-1.38195	-0.80493	-1.33724

Table S4. The currents of redox peaks at different CV test rates.

	Power density	Energy density	Charging time	
Electrode	$(W k \sigma^{-1})$	$(Wh k \sigma^{-1})$	(min)	Ref.
	702	702	60.0	
	1154	702 556	28.9	
PPCMP_C11	2363	550 445	11.3	This work
	2303 1849	354	11.5	THIS WORK
	12464	263	13	
	680	205	24.0	
	1177	272	13.0	
PPCMP	2300	235	5 5	This work
	4721	181	2.3	THIS WORK
	12000	130	0.7	
	240	150	117.0	
	240 450	408	58.3	
p-DPPZ	706	3/7	29.5	22
	1059	205	11.6	
	26	308	710.8	
	20	208	710.8	
ΡΤ-RTΔ	284	298	58 5	23
11-01/1	1206	277	11.8	25
	3705	237	3.5	
	78	217	104.6	
	78 176	233	75.0	
	363	220	34.2	
TAPT-NTCDA@CNT	930	106	12.6	24
	1014	190	5.8	
	3901	176	5.8 2 7	
	170	368	120.0	
	353	378	64.2	
	712	380	32.0	
YPTPA	1786	372	12.5	25
	3529	357	6.1	
	6866	334	2.9	
	76		373 /	
	184	473	150.3	
TPA-co-DDP-	373	401	71.7	26
PROXYL	1128	417	71.7 22.2	20
	2413	417	11 7	
	2413	472	11.7	
	2413 1067	+/2 380	11./ 17	
<u>COP500-CuT2TP</u>	7500	307	+./ 27	27
CO1500-Cu1211	0067	205	2.7 1 Q	<i>4</i> /
	7702 12400	202	1.0	
	12400	282	1.4	

Table S5 Energy density and power density of POPs as cathodes for lithium-ion battery, the PPCMP-Cu show one of the best organic CMP cathode material in LIBs.

Battery systems	Highest energy density (Wh kg ⁻¹)	Fast-changing time (min)	Reference
NMC811//Gr	265	12	28
NCM811//Gr	276	6	29
EI-LMO//Li	484	6	30
LVPFO//TNO@C	319	4	31
NCM811//Li	758	6	32
LFP@BG/LCO//Li	397	6	33
NCMT//Li	763	12	34
PPCMP-Cu//Li	702	1.3	This work
PPCMP-Cu//Gr	216	0.6	This work

Table S6. The electrochemical performance comparison between PPCMP-Cu withconventional inorganic cathodes in energy density and fast-charging capability

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