Supplementary Information

Star-shaped polyimide covalent organic framework for high-voltage lithium-ion batteries

Shuai Gu,[12] Rui Hao,[1] Jingjing Chen,[1] Xi Chen,[2] Kun Liu,[1] Iftikhar Hussain,[2] Guiyu Liu,[1] Zhiqiang Wang,[1] Qingmeng Gan,[1] Hao Guo,[1] Muqing Li,[1] Kaili Zhang,[2*] Zhouguang Lu[1*]

[1] Department of Materials Science and Engineering, Shenzhen Key Laboratory of Interfacial Science and Engineering of Materials, Guangdong-Hong Kong-Macao Joint Laboratory for Photonic-Thermal-Electrical Energy Materials and Devices, Southern University of Science and Technology, Shenzhen 518055, Guangdong, P. R. China

[2] Department of Mechanical Engineering, City University of Hong Kong, Kowloon, Hong Kong, P. R. China

Materials

The monomers N,N,N',N'-Tetrakis(4-aminophenyl)-1,4-phenylenediamine (TPPDA) and pyromellitic dianhydride (PMDA) were purchased from Energy Chemical Technology (Shanghai) Co., Ltd. Isoquinoline was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Mesitylene was purchased from TCI Shanghai Co., Ltd. N-methylpyrrolidone (NMP) was purchased from Guangdong Canrd New Energy Technology Co., Ltd. All other reagents were purchased from commercial sources and used without further purification.

Methods

Fourier Transform Infrared (FTIR) data were obtained on a PerkinElmer Frontier spectrometer. The FTIR spectra of the small molecules and polymer were recorded by reflection mode and the prepared electrodes were tested by KBr pellet technology. Scanning electron microscopy (SEM) pictures were obtained on a TESCAN MIRA3 microscope. A Bruker EMXplus-10/12 spectrometer (9.8 GHz and 1 mW) was used to collect the electron paramagnetic resonance (EPR) spectra by one scan at room temperature. The thermogravimetric analysis (TGA) was conducted on a METTLER instrument under N_2 atmosphere with a heating rate of 10 °C/min. Solid-state ^{13}C

CP (cross polarization) MAS (magic angle spinning) NMR spectra were gathered on a 600 MHz Bruker Avance III wide-bore Instrument with a 4 mm MAS probe and a sample spin rate of 12 kHz. X-ray photoelectron spectroscopy (XPS) tests were conducted on an Thermo ESCALAB Xi+ system with Al Kα X-ray as the irradiation source. Gas adsorption/desorption data were collected at 77 K with a BELSORP-max analyzer. The sample was degassed in vacuum at 120 °C for 10 h before the measurement. Pore size distribution data were derived from the adsorption branches of the isotherms. Structure optimization followed by vibrational frequency calculations was carried out on the Gaussian 16 software package at the level of UB3LYP/6-31G(d,p).

Synthesis of TPPDA-PICOF

PMDA (100.3 mg, 0.46 mmol), TPPDA (108.7 mg, 0.23 mmol), mesitylene (1.5 mL), NMP (1.5 mL), and isoquinoline (0.15 mL) were added into a 15 mL stainless steel reactor. Then the above solution was stirred and degassed by argon bubble for 15 min at room temperature. The reactor was transferred in an oven and heated at 200 °C for 7 days. After cooled, a brown solid was got by vacuo filtration and washed with DMF. Then the solid was stirred in hot DMF at 90 °C for 30 min and recycled by filtration. This procedure was repeated until the solution was clear. Then the precipitate was washed with enough water and dried at 150 °C in dynamic vacuum for 12 h to get the final product.

Electrochemical measurements

The electrodes were prepared by mixing the active material 3DPI, conductive agent super P, and binder PVDF (weight rate of 5:4:1) in NMP. The obtained slurry was spread on Al foil and heated at 120 °C in vacuum to remove the NMP. The loading of the active material is about 1 mg/cm^2. The resultant Al foil was punched into 12 mm circle disks and used as work electrodes in the half-cells, where the lithium foils were used as counter electrode and Celgard membranes were used as separator. And 1 M $LiPF_6$ in ethylene carbonate (EC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) (1:1:1 in v/v) was used as the electrolyte. Galvanostatic charge-discharge (GCD) tests were conducted on NEWARE battery cycler (CT-4008T-5V10mA-164, Shenzhen, China) testing systems. Cyclic voltammetry (CV) tests were carried out on a Bio-Logic VMP3 workstation.

For the ex-situ XPS and FTIR experiments, the button cells discharged/charged to different voltage were disassembled in the argon-filled glovebox and the electrodes were washed with dimethyl carbonate (DMC). The resultant electrodes were transferred in transition warehouse of the glovebox and dried in vacuum for 12 h. Then the materials for tests were obtained by scraping the electrodes in glovebox. For the ex-situ EPR experiments, the electrodes were prepared by mixing the active materials, Cabot carbon (no EPR signal), and PVDF with a weight rate of 5:4:1 in NMP. The samples were collected in the same method as that for ex-situ FTIR experiments.

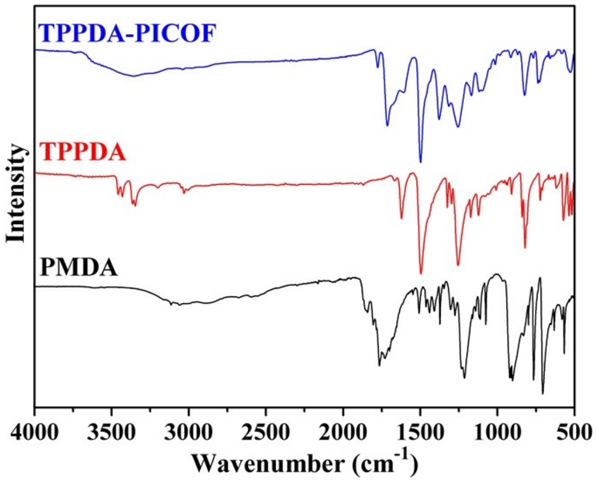

Figure S1. The FTIR spectra of TPPDA-PICOF.

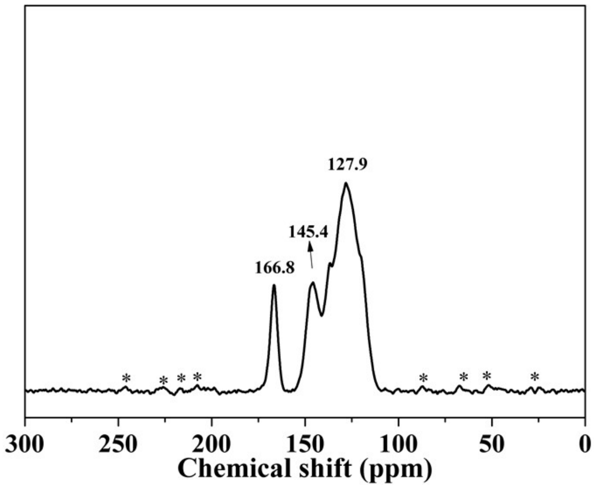

Figure S2. The solid state NMR spectrum of TPPDA-PICOF.

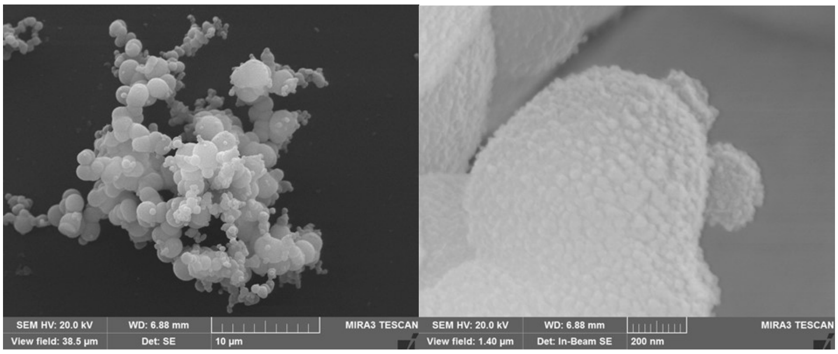

Figure S3. The SEM images of TPPDA-PICOF.

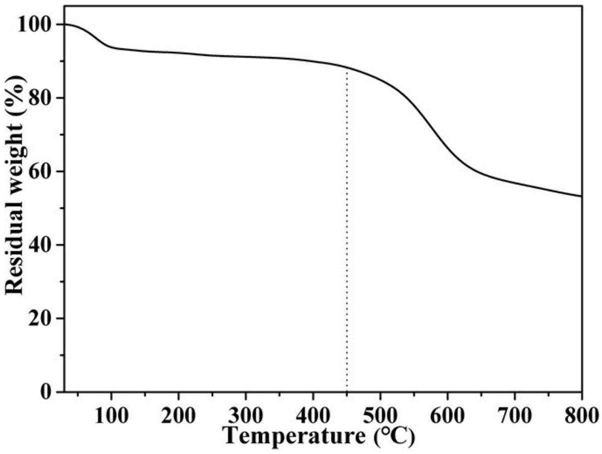

Figure S4. The TGA curve of TPPDA-PICOF. The weight loss below 100 °C in the TGA curve was attributed to the adsorbed air and water in the porous COF material.

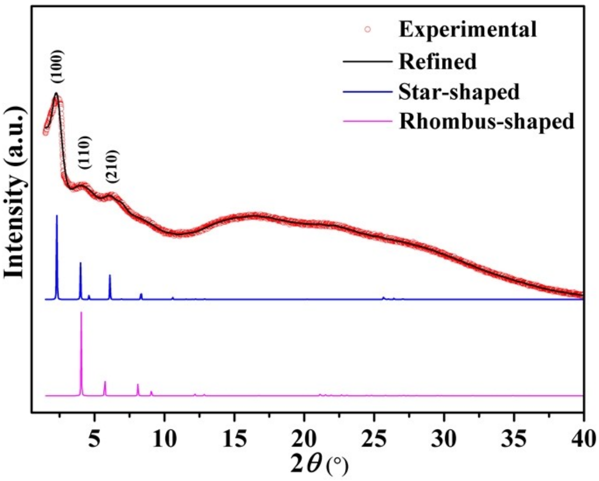

Figure S5. The simulated XRD patterns of the hypothetic rhombus-shaped and star-shaped structure of TPPDA-PICOF.

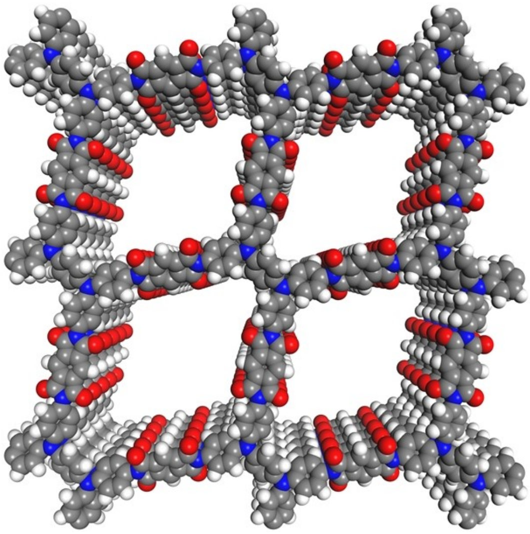

Figure S6. The simulated packing structures of the hypothetic rhombus-shaped TPPDA-PICOF.

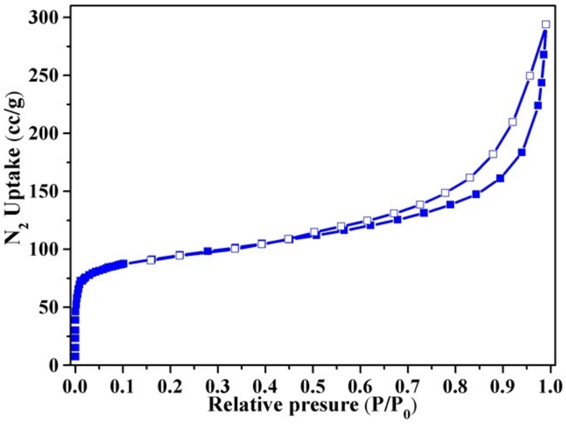

Figure S7. N_2 adsorption/desorption curves of TPPDA-PICOF at 77 K.

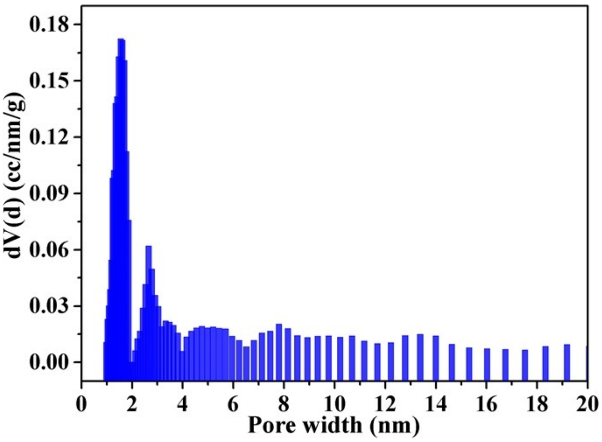

Figure S8. Pore size distribution of TPPDA-PICOF.

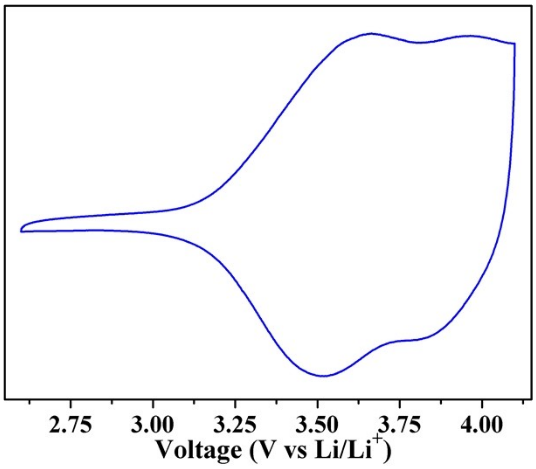

Figure S9. The CV curves of TPPDA-PICOF in the range 2.6-4.1 V at the scan rate of 0.1 mV/s.

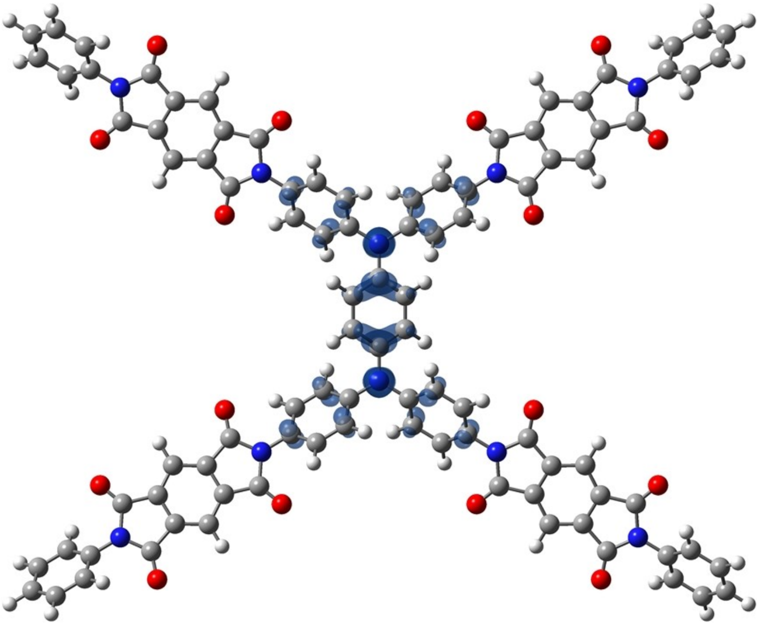

Figure S10. The calculated spin density distribution (azury part) of the radical cation intermediates in TPPDA-PICOF.

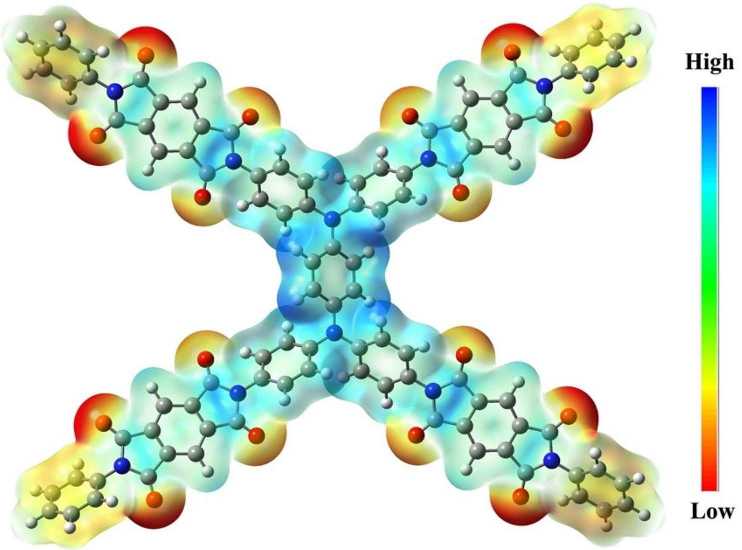

Figure S11. The calculated molecule electrostatic potential (MESP) mapping image of the radical cation intermediates in TPPDA-PICOF.

Table S1. Electrochemical performance comparison of organic cathode materials in lithium batteries

Samples	Reversible capacity (mAh g^{-1})	Discharge voltage (V)	Capacity retention, cycle Number, current density	References
TPPDA-PICOF	**47 at 0.2 A/g**	**3.6**	**98%, 200 cycles, 0.2 A/g**	**This work**
DAPH-TFP COF	< 40 at 1 C	2.76	< 50%, 500 cycles, 1 C	S1
D_{TP}-A_{NDI}-COF	67 at 0.2 A/g	2.4	100%, 700 cycles, 0.2 A/g	S2
PI-ECOF-1	90 at 10 C	2.1	72%, 300 cycles, 1 C	S3
Tb–DANT-COF	94 at 0.2 A/g	2.3	71%, 100 cycles, 0.2 A/g	S4
DAPO–TpOMe-COF	68 at 0.1 A/g	3.6	79%, 200 cycles, 0.1 A/g	S5
PVMPT	56 at 1 C	3.56	94%, 10000 cycles, 10 C	S6
PQI-1	136 at 0.1 A/g	2.3	65%, 200 cycles, 0.1 A/g	S7

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