Supplementary Information

Redox of naphthalenediimide radicals in a 3D polyimide for stable Li-ion batteries

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Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA) and N-methyl pyrrolidone were purchased from Energy Chemical Technology (Shanghai) Co., Ltd. Tetra(4-aminophenyl)methane (TAPM) was purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. Isoquinoline was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Mesitylene was purchased from TCI Shanghai Co., Ltd. All other reagents were purchased from commercial sources and used without further purification.

Methods

Fourier Transform Infrared (FTIR) spectra were recorded on a PerkinElmer Frontier spectrometer. The synthesized samples and monomers were tested by reflection mode and the electrode materials were tested via KBr pellet technology. Scanning electron microscopy (SEM) images were collected 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. Raman spectra were obtained on a Renishaw inVia Raman Spectrometer with a laser wavelength of 633nm and a power of 0.5mW. Solid-state $^{13}C/^{7}Li$ 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. Structure optimization followed by vibrational frequency calculations was carried out on the

G09 software package at the level of UB3LYP/6-31G(d). And the calculated chemical structures were displayed by ball & stick model in this work.

Synthesis of 3DPI

The synthesis of 3DPI-B: A mixed solution of mesitylene (1.0 mL), NMP (0.2 mL), and isoquinoline (0.02 mL) in a 10 mL stainless steel reactor was degassed by argon bubble for 10 min. NTCDA (53.6 mg, 0.2 mmol) and TAPM (38.1 mg, 0.1 mmol) was added into the above solution and stirred for 20 min at room temperature. Then the reactor was placed in an oven and heated at 160 °C for 7 days. After cooled to room temperature, a brown precipitate was obtained by filtration and washed with plenty of DMF. Then the precipitate was immersed into hot DMF at 90 °C for 30 min and recycled by filtration. The process was repeated for several times until the solution was clear. Then the precipitate was washed with plenty of water and Soxhlet extracted with THF, DOL, and DME, respectively. At last, the polymer powder 3DPI was dried at 120 °C in dynamic vacuum about 12 h.

The synthesis of 3DPI-N: The polymer 3DPI-B and steel balls with a weight of 1:20 were grinded by a ball grinder for 30 min. Then the obtained polymer powder (40 mg) were added in 200 mL methanesulfonic acid. After treated by ultrasonic for 4 h, the solution was stirred at room temperature for 12 h. Then the solution was dropped into 1000 mL methanol drop by drop under vigorous stirring conditions. The methanol solution was centrifuged to afford the nanostructured polymer 3DPI-N. After washed with plenty of methanol and water, the material was dried by freeze drying.

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 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 LiTFSI in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1in v/v) was used as the electrolyte.

Galvanostatic charge-discharge (GCD) tests were carried out on NEWARE battery cycler (CT-4008T-5V10mA-164, Shenzhen, China) testing systems. Cyclic voltammetry (CV) experiments were carried out on a Bio-Logic VMP3 workstation in the voltage range of 1.5-3.5 V.

For the ex-situ FTIR and NMR experiments, the cells discharged/charged to the specified voltage were disassembled in the argon-filled glovebox and the electrodes were washed with DOL and DME for three times, respectively. The resultant electrodes were dried in vacuum for 12 h and then the samples were collected by scraping the electrodes in glovebox. For the ex-situ EPR experiments, the electrodes were prepared by mixing the Al powder (30-50 nm), 3DPI, and PVDF with a weight rate of 7:2:1 in NMP. The samples were collected in the same method as that for ex-situ FTIR experiments. For the in-situ Raman experiments, the samples were obtained by the in-situ polymerization of the monomers on the Al meshes. The resultant Al meshes were used as the work electrodes for the in-situ cells, where mica sheets were used as the windows for the laser.

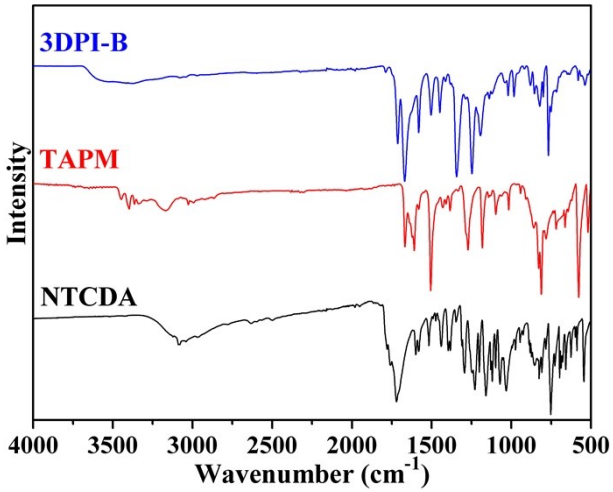

Figure S1. The FTIR spectra of 3DPI-B and the monomers. The disappearance of the characteristic peaks of -NH_2 around 3400 cm-1 and the emergence of the stretching vibration peaks of C=O at 1710 and 1670 cm^{-1} indicated the successful preparation of 3DPI.

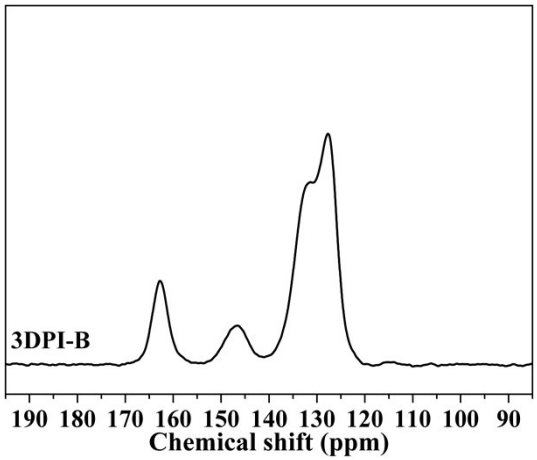

Figure S2. The solid state ^{13}C-NMR spectra of 3DPI-B. The chemical shifts of the carbonyl carbon atoms and N-substituted phenyl carbon atoms appeared at 163 and 146 ppm, respectively. And the overlapping signals from 127 to 133 ppm were attributed to the aromatic carbons in the polymers.

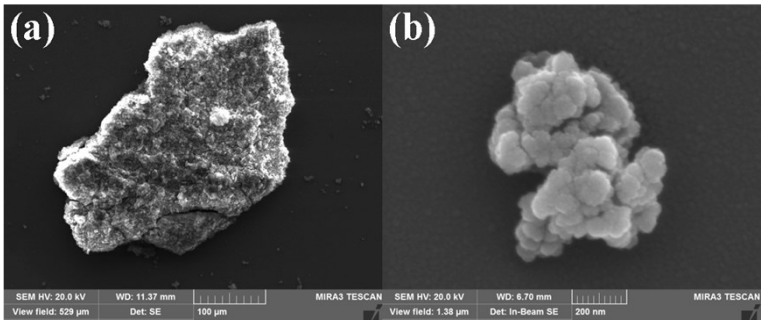

Figure S3. The SEM images of 3DPI-B (a) and 3DPI-N (b).

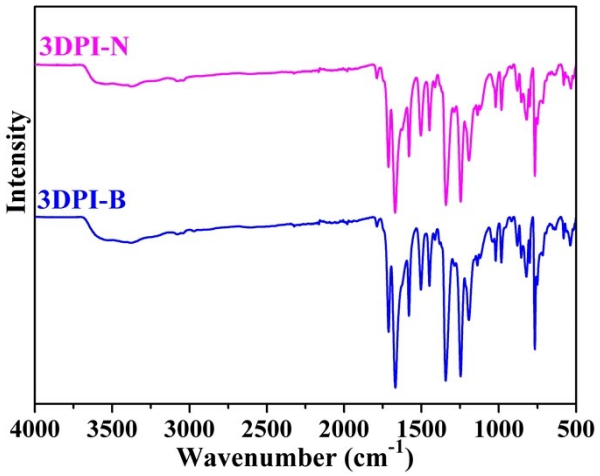

Figure S4. The FTIR spectra of 3DPI-B and 3DPI-N.

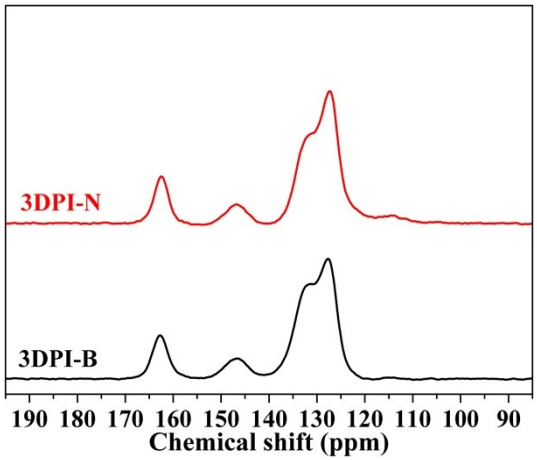

Figure S5. The solid state ^{13}C-NMR spectra of 3DPI-B and 3DPI-N.

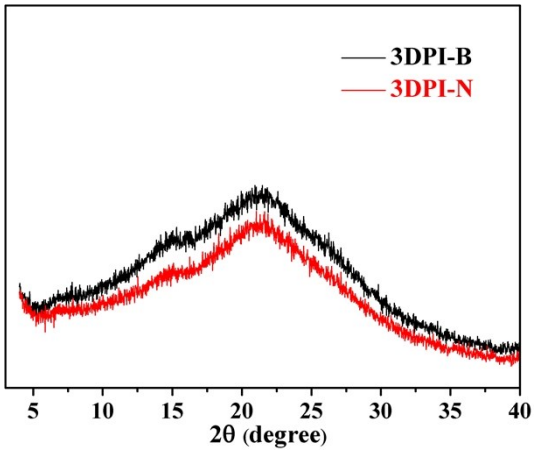

Figure S6. The XRD patterns of 3DPI-B and 3DPI-N.

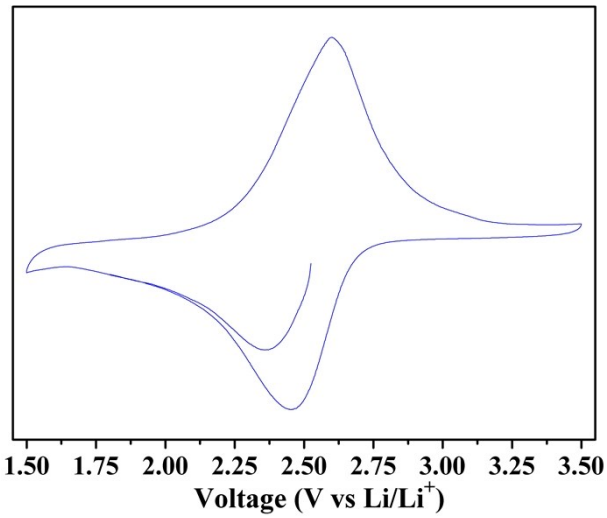

Figure S7. The CV curves of 3DPI-N at the scan rate of 0.1 mV/s.

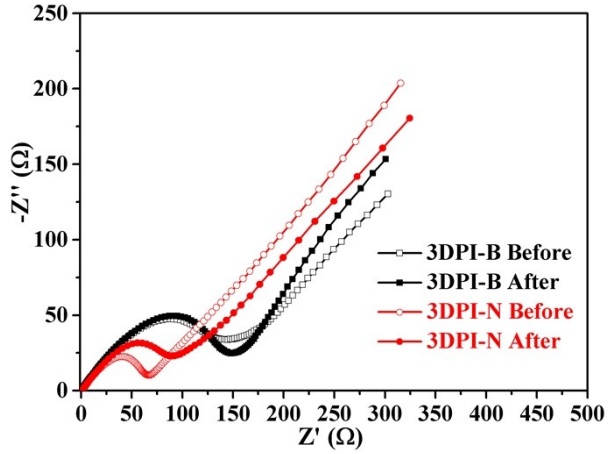

Figure S8. Electrochemical impedance spectra of 3DPI-N and 3DPI-B before and after 50 cycles at mA g^{-1}.

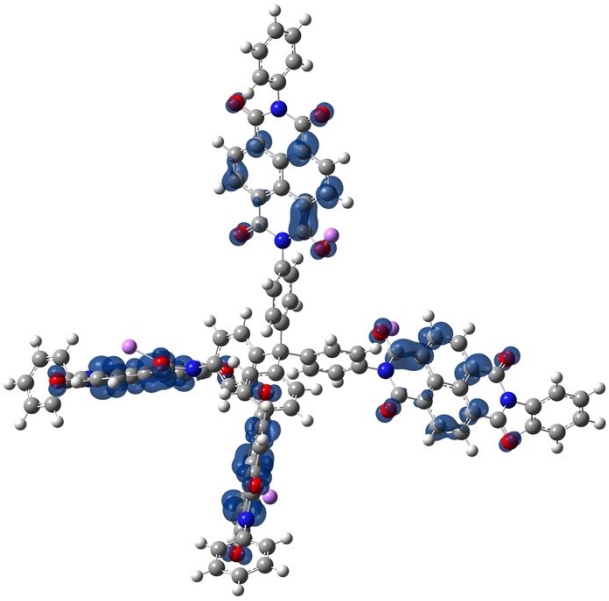

Figure S9. Spin density distribution of 3DPI.

Table S1. The cycling stabilities of organic electrodes.

Sample	Capacity Retention	References
3DPI-N	**96%, 100 cycles, 50 mA/g** **93%, 3000 cycles, 1000 mA/g**	**This work**
POI-1	64.5%, 200 cycles, 100 mA/g 67.8%, 2000 cycles, 1000 mA/g	S1
(−)-3PMDI-Δ	64%, 50 cycles, C/5	S2
PDI-EDA/CB	86%, 1000 cycles, 1000 mA/g	S3
PDI-HDA/CB	74%, 1000 cycles, 1000 mA/g	S3
PI-CMP	60.2%, 200 cycles, 50 mA/g 74%, 1000 cycles, 1000 mA/g	S4
PI-ECOF-1	65.5%, 300 cycles, 14.2 mA/g	S5
PIT	91.2%, 100 cycles, 25 mA/g 80.7%, 5000 cycles, 1500 mA/g	S6

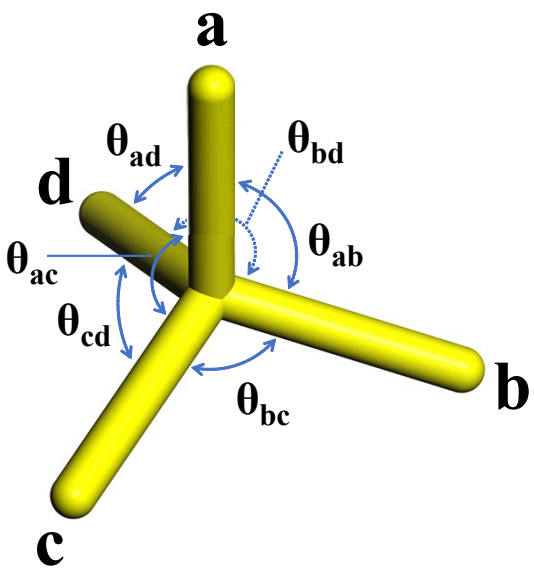

Figure S10. The bond angles of the core units of 3DPI. The letters a, b, c, and d represent the four direction of the core units and the symbol θ represents the bond angles of two directions.

References

S1. Bingbing Tian, Guo-Hong Ning, Wei Tang, Chengxin Peng, Dingyi Yu, Zhongxin Chen, Yinglin Xiao, Chenliang Su, Kian Ping Loh. Polyquinoneimines for lithium storage: more than the sum of its parts. *Mater. Horiz.*, **2016**, 3, 429-433.

S2. Dong Jun Kim, Keith R. Hermann, Aleksandrs Prokofjevs, Michael T. Otley, Cristian Pezzato, Magdalena Owczarek, and J. Fraser Stoddart. Redox-Active Macrocycles for Organic Rechargeable Batteries. *J. Am. Chem. Soc.*, **2017**, 139, 6635-6643.

S3. Dongqing Wu, Guangfeng Zhang, Deng Lu, Lie Ma, Zhixiao Xu, Xin Xi, Ruili Liu, Ping Liu, Yuezeng Su. Perylene diimide-diamine/carbon black composites as high performance lithium/sodium ion battery cathodes. J. Mater. Chem. A, 2018, 6, 13613-13618.

S4. Bingbing Tian, Ji Zheng, Chenxi Zhao, Cuibo Liu, Chenliang Su, Wei Tang, Xing Li, Guo-Hong Ning. Carbonyl-based polyimide and polyquinoneimide for potassium-ion batteries. J. Mater. Chem. A, 2019, 7, 9997-10003.

S5. Zhaolei Wang, Yongjun Li, Pengju Liu, Qiaoyan Qi, Fang Zhang, Guolin Lu, Xin Zhao, Xiaoyu Huang. Few layer covalent organic frameworks with graphene sheets as cathode materials for lithium-ion batteries. Nanoscale, 2019, 11, 5330-5335.

S6. Hydrothermally self-templated synthesis of rectangular polyimide submicrotubes and promising potentials in electrochemical energy storage. Sheng Lei, Xun Cui, Xufei Liu, Xiaofang Zhang, Xiaoyan Han, Yingkui Yang. *Chem. Commun.*, 2020, 56, 1429-1432.