Supporting Information

Heteroatom-Enhanced Dual-Ion Storage of Thiophene-based Bipyridine Polymer for High-Capacity and High-Rate Lithium-Ion batteries

Cong Cao[1], Chen-Xing Zhang[1], Han Xu[1], Hong Yang[2], Shi-Lin Mei,* Chang-Jiang Yao*

C. Cao, C.-X. Zhang, H. Xu, Prof. Dr. S.-L. Mei, Prof. Dr. C.-J. Yao
State Key Laboratory of Explosion Science and Safety Protection, School of Mechatronical Engineering, Beijing Institute of Technology, Beijing, 100081, China
E-mail: cjyao@bit.edu.cn

H. Yang, Prof. Dr. S.-L. Mei
Xi'an Safty Energy Technology Co., Ltd. Xi'an, 710299, China

1 Supplementary Experimental Section

1.1 Materials Characterizations

All starting chemicals and solvents were obtained from Energy Chemical or Bide Pharmatech, and used without further purification. Nuclear magnetic resonances (^{1}H NMR) were conducted on Bruker Avance III 400 MHz. Transform Infrared Spectroscopy (FTIR) was recorded with Bruker 46 TENSOR Π. Ultraviolet-Visible spectroscopy (UV-Vis) was obtained by FS5 spectrofluorimeter (Edinburgh Instruments Ltd.). The microstructure and morphology (SEM) were observed by high-resolution cold field-emission scanning electron microscopy (Hitachi s-4800). X-ray photoelectron spectroscopy (XPS) was recorded on Thermo Scientific K-Alpha (USA) using monochromatized Al Kα radiation (1486 eV). The binding energies of all spectrawere calibrated with respect to the C ls peak of ubiquitous carbon at a binding energy of 284.8 eV. The cycled electrodes used for the characterization were washed with diethyl carbonate (DEC) and dried for 6 h in vacuum at 60°C.

2 Sythesis routes

2.1 The preparation of 4-(2-Thienyl)-2,2′-bipyridine (TBPY):

TBPY was synthesized according to the literature.[1] Ingredients Pyridinium, 1-[2-oxo-2-(2-pyridinyl)ethyl]-, iodide (1:1) and 3-(2-Thienyl)-2-propenal are synthesized as follows.

2.1.1 Synthesis of Pyridinium, 1-[2-oxo-2-(2-pyridinyl)ethyl]-, iodide (1:1)

Pyridine (15 eq), 3-Acetylpyridine (1 eq) and Iodine (1.2 eq) were mixed and heated at 140°C for 3 h. The reaction was terminated and the product Pyridinium, 1-[2-oxo-2-(2-pyridinyl)ethyl]-, iodide (1:1) was collected by filtration and washed with cold pyridine (100 mL). The product was dried under vacuum at 80°C.

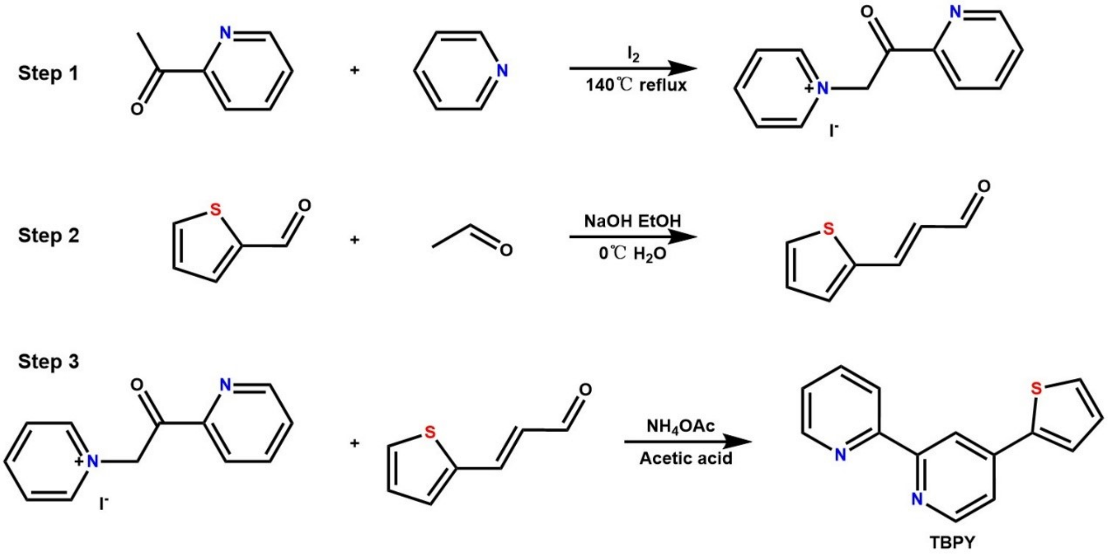
2.1.2 Synthesis of 3-(2-Thienyl)-2-propenal

3-(2-Thienyl)-2-propenal was synthesized by dissolving NaOH (4.48 g, 106 mmol) in a mixture of ethanol (24 mL) and water (46 mL), adding thiophene-2-carbaldehyde

(17.9 g, 160 mmol) slowly dropwise with a funnel over a period of one hour, and completing the ethanal (25.4 g, 728 mmol, dissolved in 250 mL of water) dropwise over a period of 4.5 h. The reaction was stirred at 0°C throughout, and the reaction was quenched with 10% acetic acid (10%, 100 mL) and the pH adjusted to 4.5. Purify the residue by column chromatography (silica; toluene/EtOAc, 95:5) to obtain 3-(2-thienyl)propenal, a bright yellow oily liquid.

2.1.3 Synthesis of 4-(2-Thienyl)-2,2′-bipyridine (TBPY)

3-(2-thienyl)propenal (5.86 g, 42 mmol), 2-[2-(1-pyridinio)-1-oxoethyl]pyridine iodide (16.6 g, 50.4 mmol) and NH_4OAc (16.2 g, 210 mmol) were added to acetic acid (250 mL). The mixture was heated to 80 °C and the reaction was stirred for 48 hours. The reaction mixture was made basic by addition of NaOH (aq. 10 m, ca. 450 mL) and the black precipitate was filtered. It will be Soxhlet extracted with petroleum ether (boiling range 40-60 °C) for 72 hours. The residue was recrystallized from methanol to give 4-(2-thienyl)-2,2'-bipyridine. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73, 8.69-8.64, 8.44, 7.85, 7.67, 7.53, 7.45, 7.36, 7.17 ppm



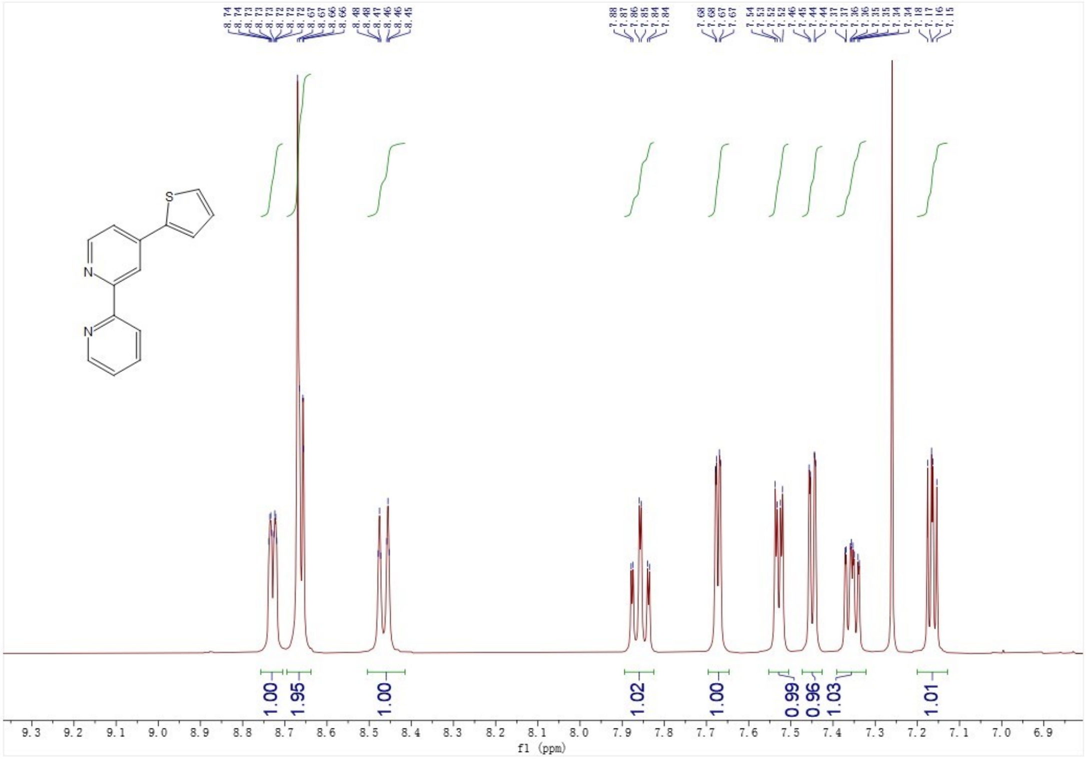
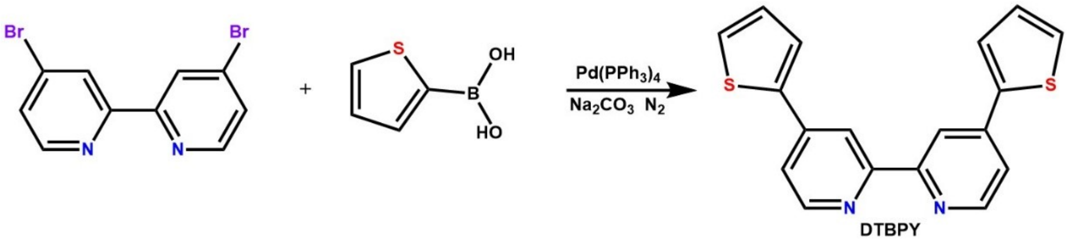


Fig. S1 ^{1}H NMR spectrum of TBPY.

2.2 The preparation of 4,4′-Di-2-thienyl-2,2′-bipyridine (DTBPY):

DTBPY was synthesized according to the literature.[2] Tetrahydrofuran (10 mL), 4,4'di-bromo-2,2' bipyridine (151 mg) and thiophene-2-boronic acid (123 mg), aqueous 2M Na_2CO_3 (1 mL) was added to a round bottom flask protected by N_2 and pumped to fill three times. $Pd(PPh_3)_4$ (3mol% , 17mg) was added to the mixture. The mixture was refluxed at 85°C for 27h, then mixture was cooled to room temperature. Tetrahydrofuran was removed under reduced pressure, the product was dissolved in dichloromethane and the salts were removed by extraction with water three times. Column chromatography was used to purify the product with a 98:2 $CHCl_3$/MeOH eluate in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (dd, J = 4.95, 3.58 Hz, 2 H), 7.44 (dd, J = 5.12, 1.02 Hz, 2 H), 7.53 (dd, J = 5.12, 1.71 Hz, 2 H), 7.67 (dd, J = 3.75, 1.02 Hz, 2 H), 8.66–8.71 (m, 4 H) ppm.



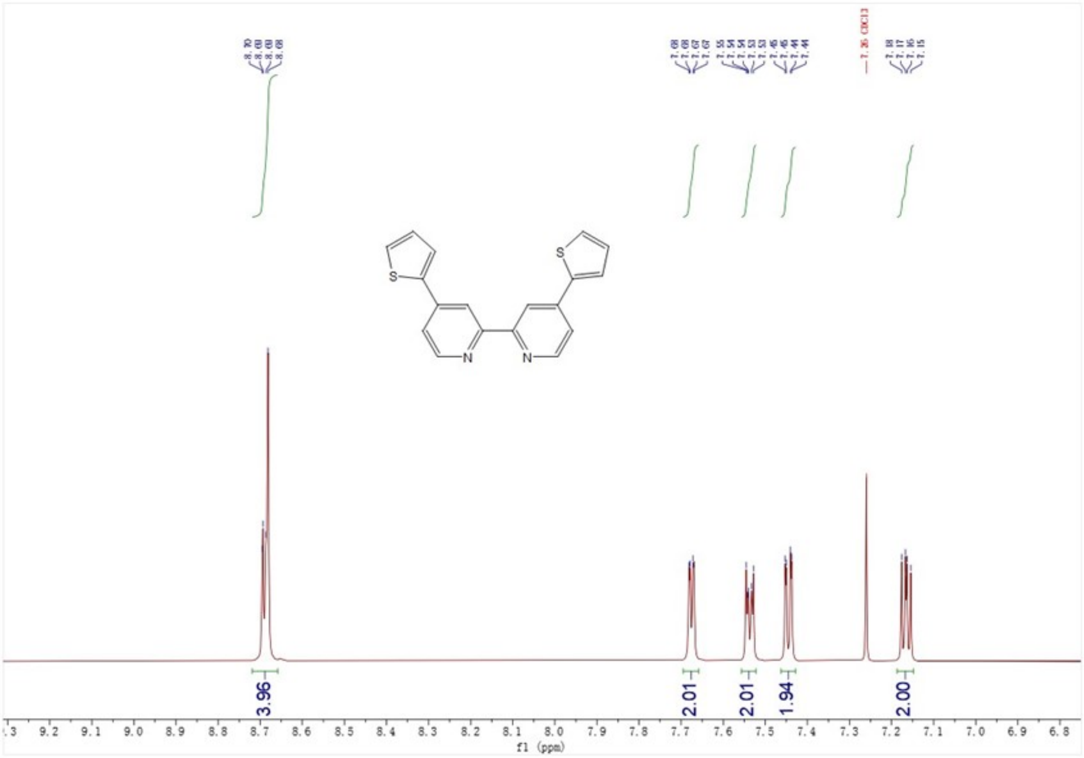


Fig. S2 ^{1}H NMR spectrum of DTBPY.

3. Electrochemical measurements

The electrodes were prepared by mixing 40 wt.% active material (TBPY or DTBPY) with 50 wt.% conductive addition (Ketjen Black) and 10 wt.% binder (water-based binders polyacrylic latex, LA133) in deionized water. After full grinding, homogeneous TBPY and DTBPY electrode slurries were separately obtained and uniformly coated on carbon-coating aluminum foils. The electrodes were dried in vacuum at 60°C for 12 hours and cut into disk with a diameter of 12 nm and the mass loading of active material in the electrode was 1-1.2 mg cm^{-2}. We assembled the 2032 coin-type cells in a glove box ($H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm), a polypropylene separators (Celgard 2400, LLC Corp., USA) with a diameter of 16 mm as a separator and 1 M $LiPF_6$ in mixed solution of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) at a volume ratio of 3:7 as the electrolyte. The half-cells were galvanostatically cycles in different voltage ranges on the XINWEI (NEWARE TECHNOLOGY LIMITED) test system at 30°C. All of the cyclic voltammetry tests, electropolymerization process and EIS test performed in the frequency range of 100 kHz to 10 mHz were recorded by the electrochemical workstation (CHI 660E) at room temperature. Galvanostatic charge/discharge tests and galvanostatic intermittent titration technique (GITT) measurements were performed in the potential range of 1.6-4.5 V (vs. Li/Li$^+$) using a LAND CT2001A battery test system (Wuhan, China) at room temperature. The Galvanostatic charge/discharge tests were performed at different current densities. For the GITT measurements, the cells were charged and discharged at a current density of 0.1 A g^{-1} for a 10 min pulse and followed with a 30 min rest with a potential range of 1.6-4.5 V (vs. Li/Li$^+$).

The electrodes for the ex-situ FT-IR test and SEM characterizations were prepared by grinding TBPY and DTBPY, Carbon nanotube and LA133 binders in a weight ratio of 7:2:1. Then, the slurry was uniformly coated on aluminum foils. After dried at 60°C for 12 h under vacuum, the coin-type cell was assembled in the Ar-filled glove box. The assembled cells for ex-situ FTIR measurements were cycled to a certain voltage state of charge or discharge and disassembled in an Ar-filled glove box. The electrodes were washed by EMC and dried in vacuum at 80°C.

The theoretical capacities of P-DTBPY and D-TBPY were calculated based on the application of Faraday's Law in electrochemistry, as expressed by the following formula:

$$C = \frac{nF}{3.6M}$$

where n is the number of transferred electrons, F is the Faraday constant, and M represents the molecular weight of the active material. The calculated theoretical capacities are 334 mAh g^{-1} for P-DTBPY and 337 mAh g^{-1} for D-TBPY.

4 Supplementary Figures and Tables

	P-DTBPY (This work)	CuTP (Ref. 50)	PPY-1 (Ref. 57)
Oxidation peak location (vs.Li/Li$^+$)	3.8-4.2 V thiophene	3.2-3.8 V porphyrins	0.7-1.3 V pyridine
Max Specific Discharge Capacity (mAh g^{-1}) Current density: 0.1 A g^{-1}	269.6	203	956.8
Long cycle performance (mAh g^{-1}) Current density: 5 A g^{-1}	140.1	82	not mentioned
Capacity retention (%) Up to 2,000 cycles	93.6	91	not mentioned

Table S1 Related studies on thiophene and pyridine as cathode active functional groups.

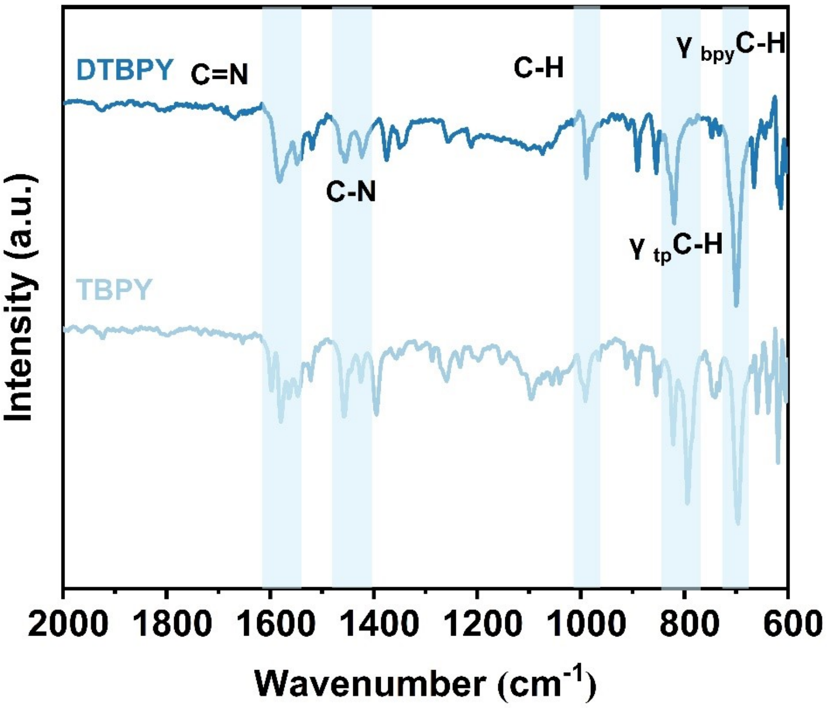


Fig. S3 FTIR spectra of TBPY and DTBPY.

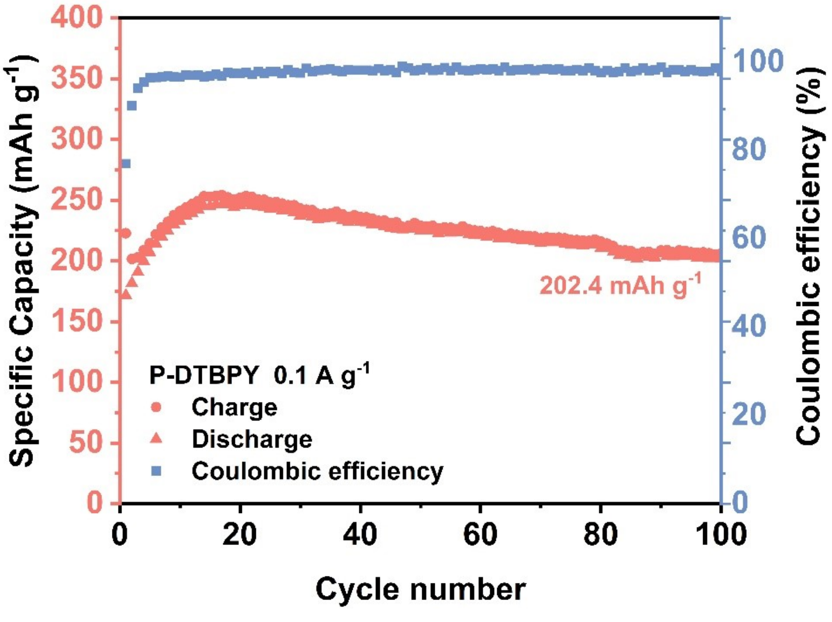


Fig. S4 Cycling stability of P-DTBPY at 0.1 A g^{-1} for 100 cycles (Active materials: Ketjen black: LA133=5: 4: 1).

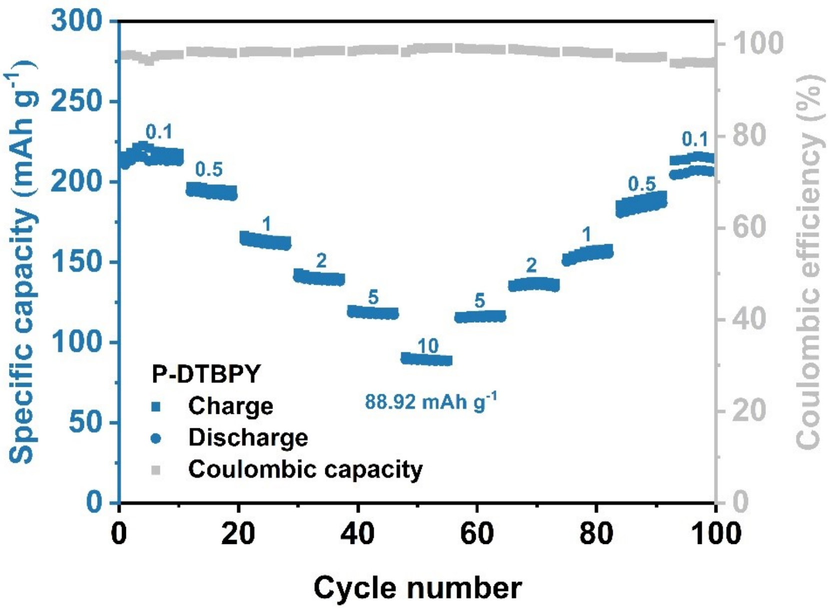


Fig. S5 Rate performance and of P-DTBPY at different current densities (0.1, 0.5, 1, 2, 5, 10 A g^{-1}, Active materials: Ketjen black: LA133=5: 4: 1).

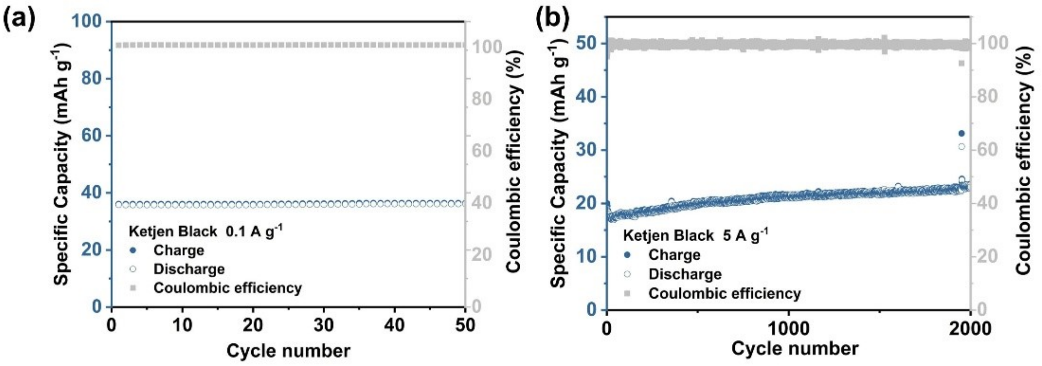


Fig. S6 Specific capacitance of discharge of Ketjen black at 0.1 A g^{-1} and 5 A g^{-1} current densities (Ketjen black: LA133=1: 1).

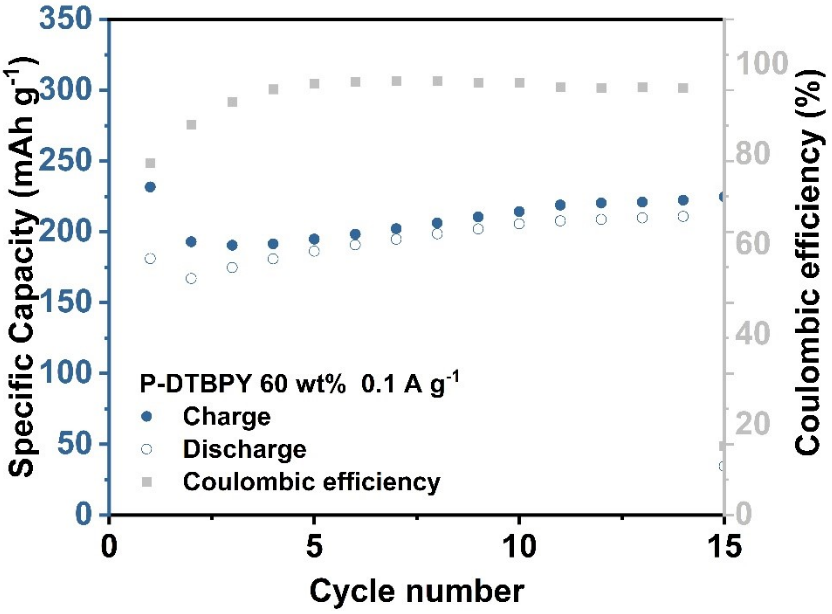


Fig. S7 Cycling stability of P-DTBPY at 0.1 A g^{-1} (Active materials: Ketjen black: LA133=6: 3: 1).

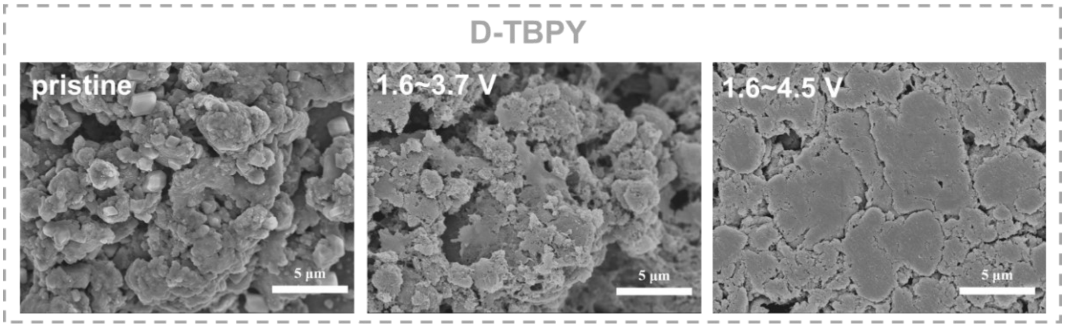


Fig. S8 SEM images of D-TBPY cycled in different voltage ranges (At pristine, 1.6-3.7 V, 1.6-4.5 V).

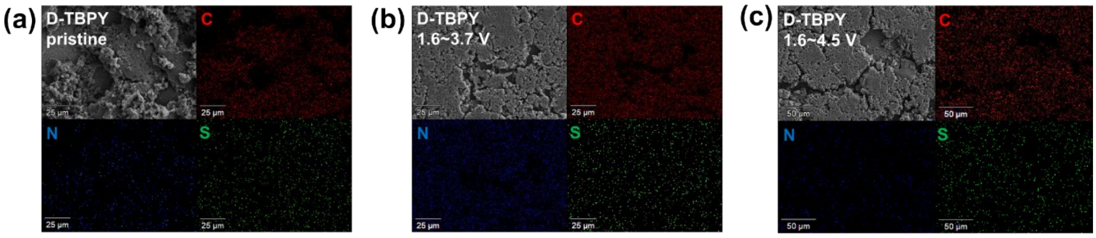


Fig. S9 Elemental mapping of D-TBPY at pristine and 1.6-4.5 V after 100 cycles.

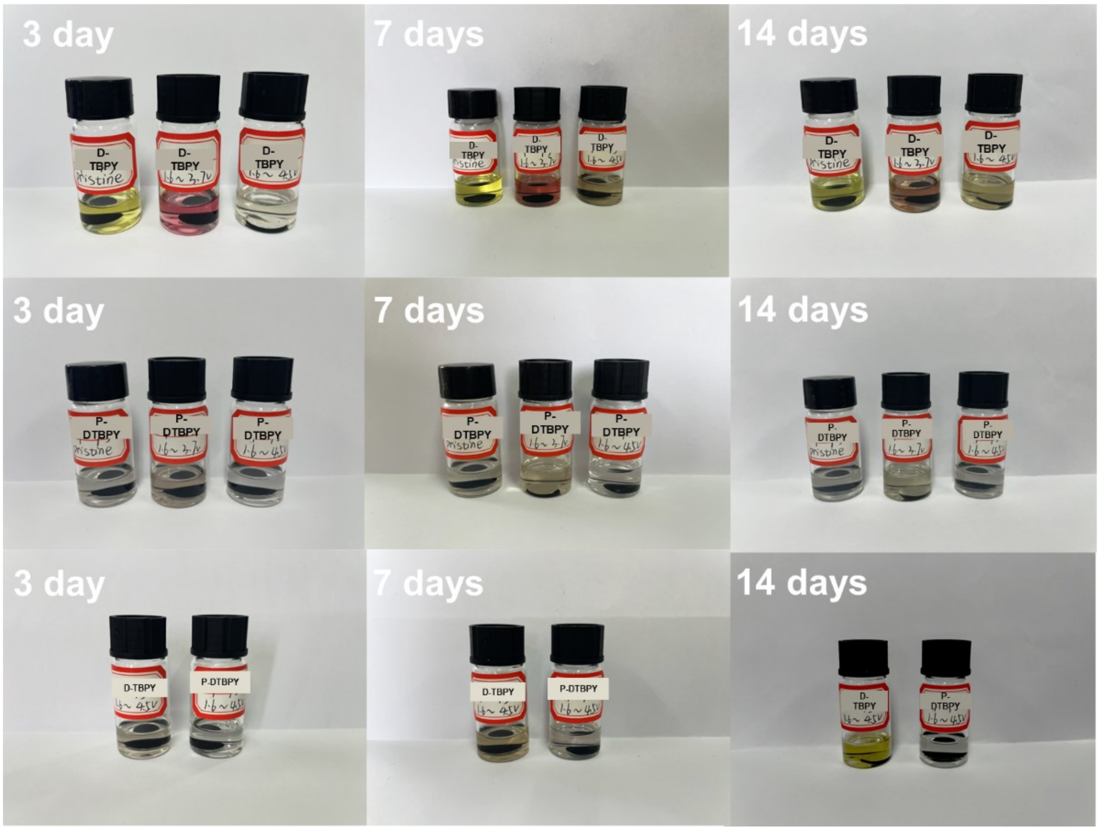


Fig. S10 Images of D-TBPY and P-DTBPY anodic immersed in electrolyte (1 M $LiPF_6$ in EC: EMC=3:7 Vol%) for 3 days,7 days, 14 days after cycling in 1.6-3.7 V and 1.6-4.5 V.

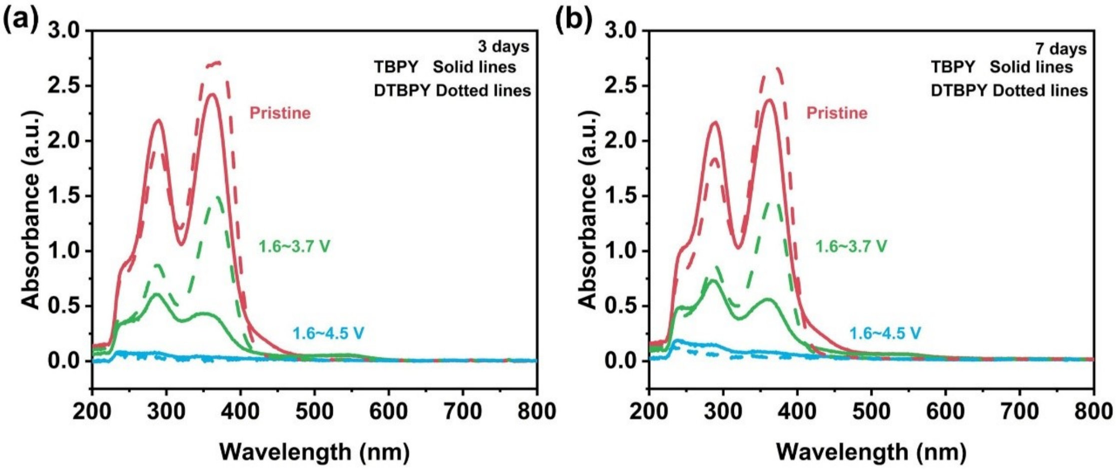


Fig. S11 UV-vis spectra of D-TBPY and P-DTBPY anodic immersed in electrolyte (1 M $LiPF_6$ in EC:EMC = 3:7 Vol%) for 3 days, 7 days at pristine and after cycling in 1.6-3.7 V and 1.6-4.5 V.

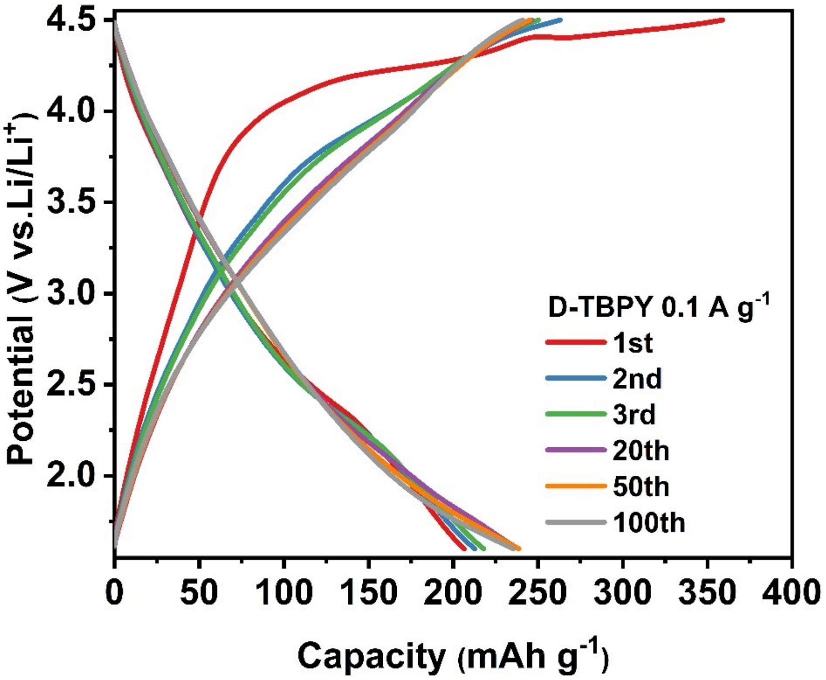


Fig. S12 The different cycles GCD curves of the D-TBPY cathodes at 0.1 A g^{-1} in 1.6-4.5 V.

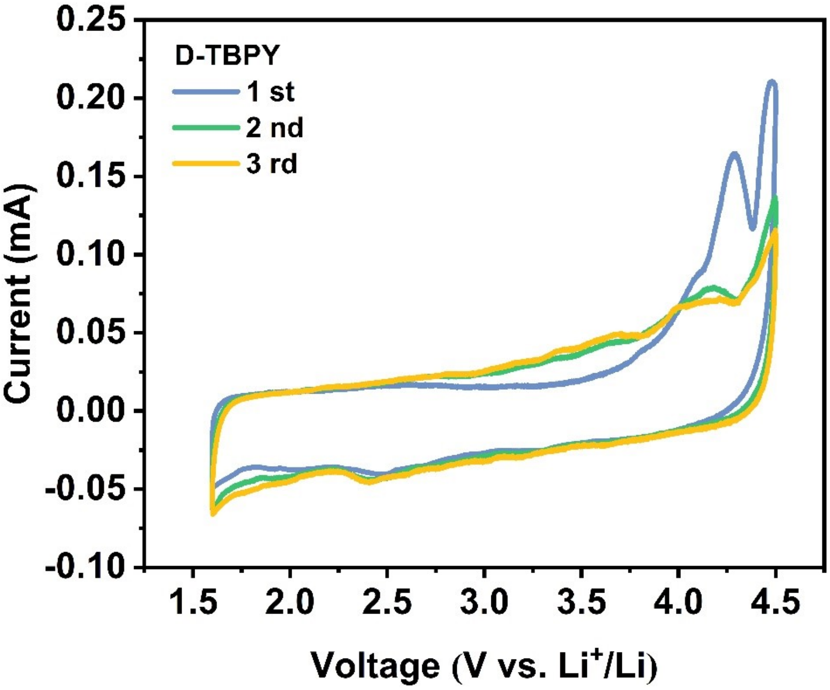


Fig. S13 CV curves for the first three cycles of D-TBPY at scan rate of 0.2 mV s^{-1}.

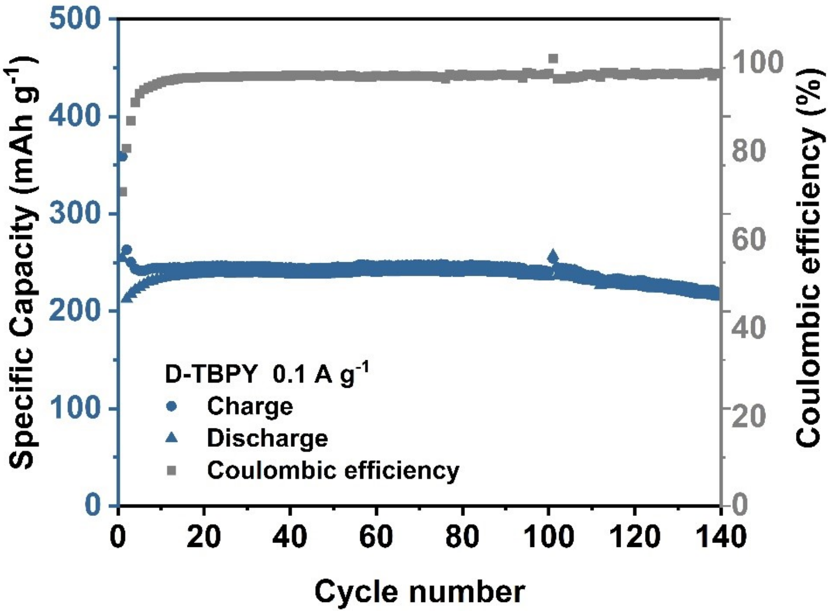


Fig. S14 Cycling stability of D-TBPY at 0.1 A g^{-1} for 140 cycles.

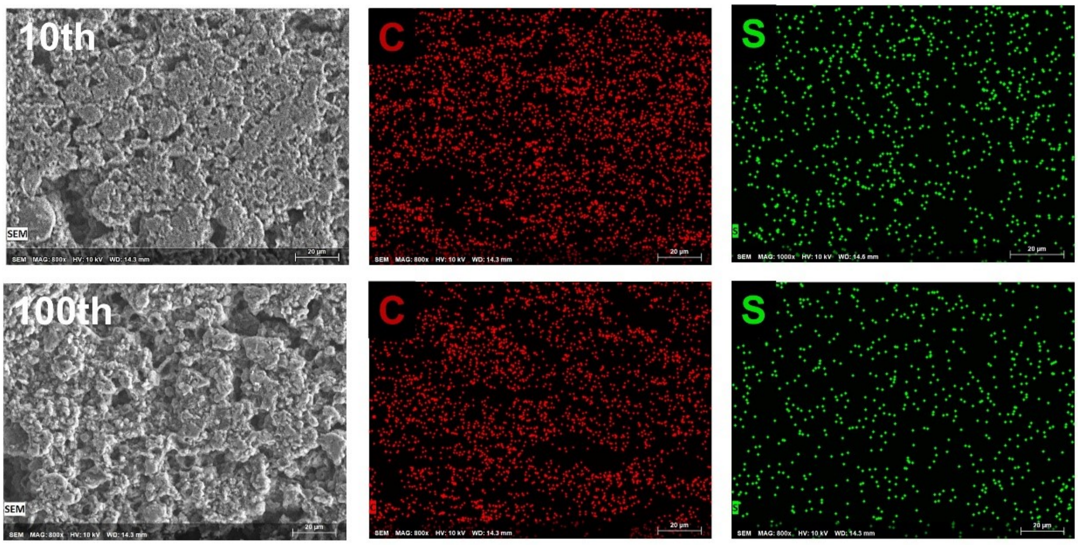


Fig. S15 Elemental mapping of P-DTBPY after 10th and 100th cycles at 5A g^{-1}.

	10th		100th	
	Mass Norm %	Atom %	Mass Norm %	Atom %
C	93.38	97.41	93.72	97.55
S	6.62	2.59	6.28	2.45

Table S2 Elemental C, S content (%) after 10th and 100th cycles.

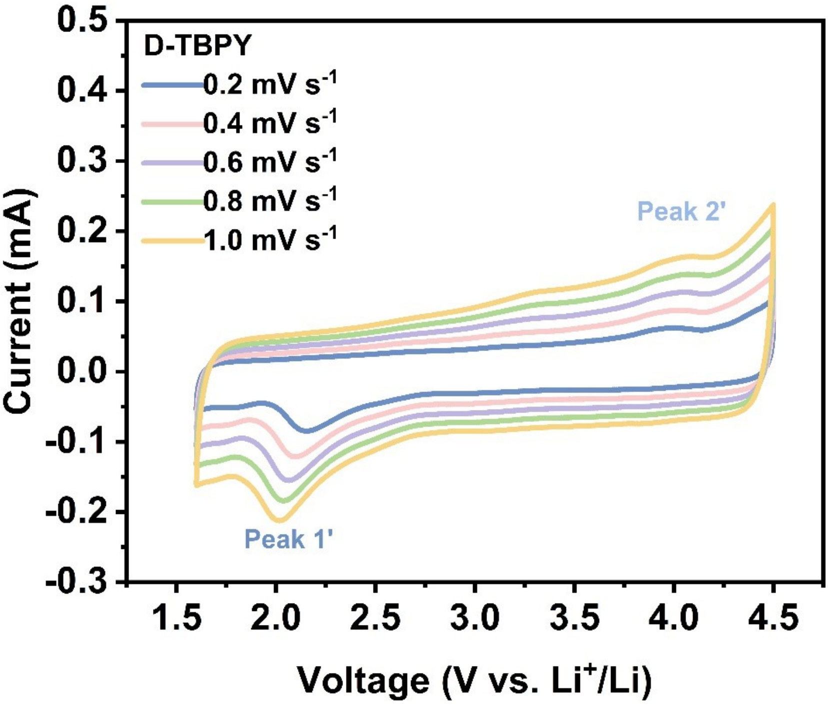


Fig. S16 CV curves of D-TBPY electrode after 10 cycles at various scan rates from 0.2 to 1.0 mV s^{-1}.

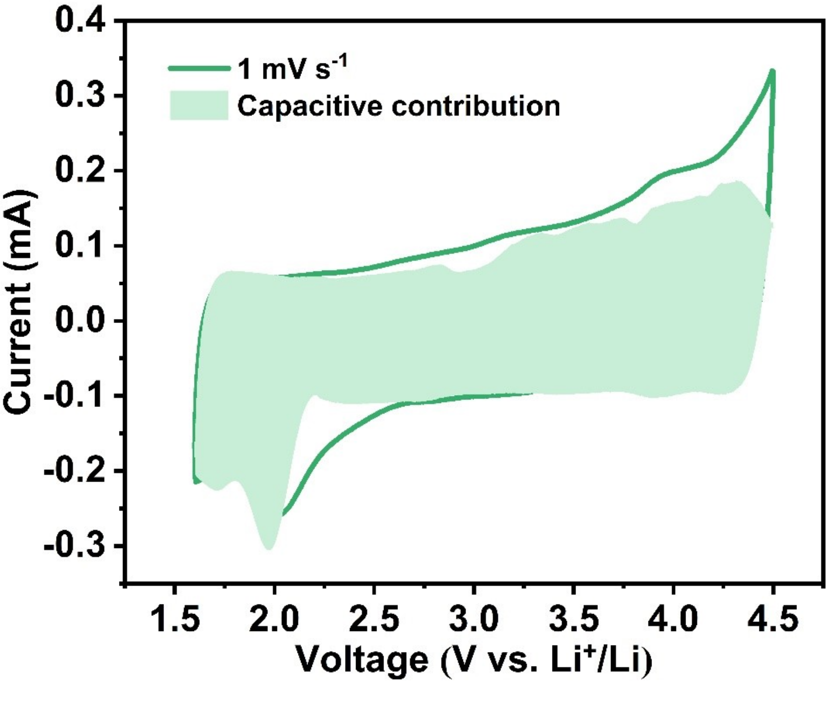


Fig. S17 Fitted pseudo-capacitive contribution (green area inside) of P-DTBPY at 1 mV s^{-1}.

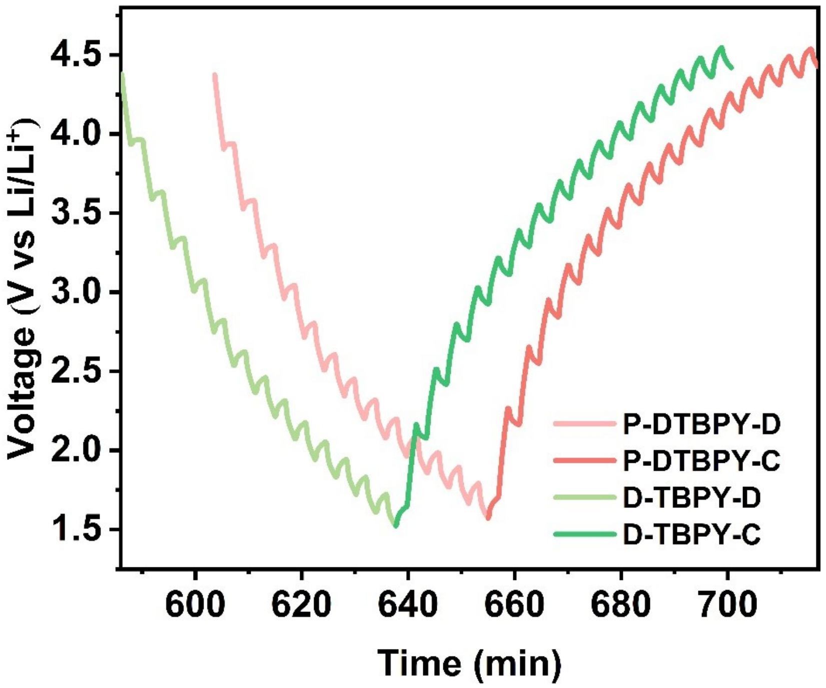


Fig. S18 GITT curves of D-TBPY and P-DTBPY.

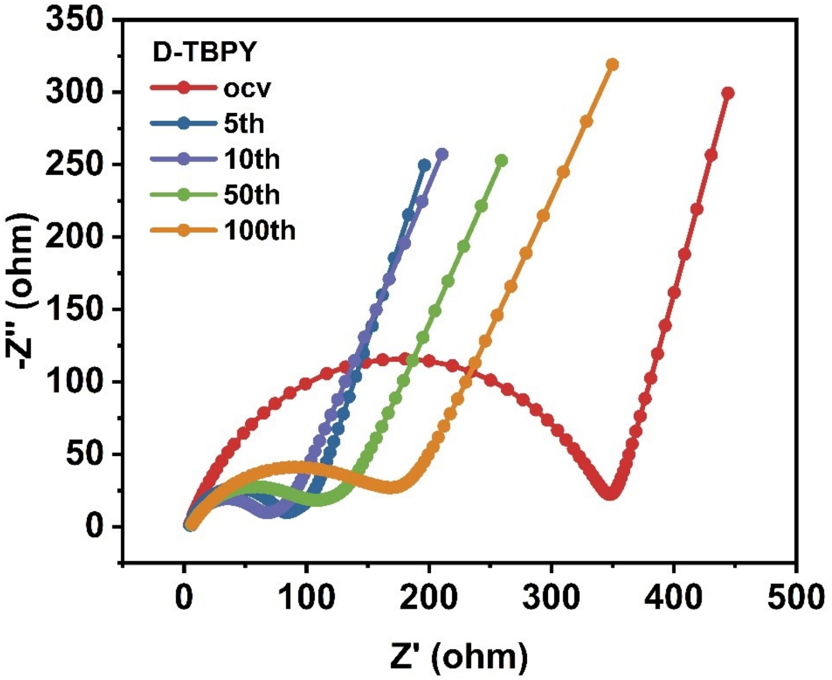


Fig. S19 Nyquist plots of D-TBPY cathodes after different cycles.

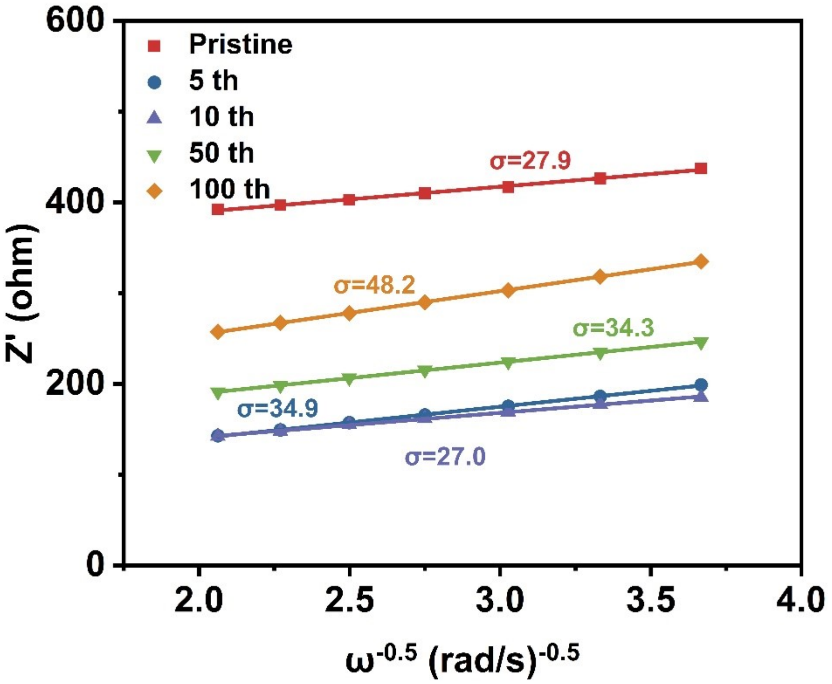


Fig. S20 Relationship between Z' of D-TBPY with reciprocal square root of the angular velocity.

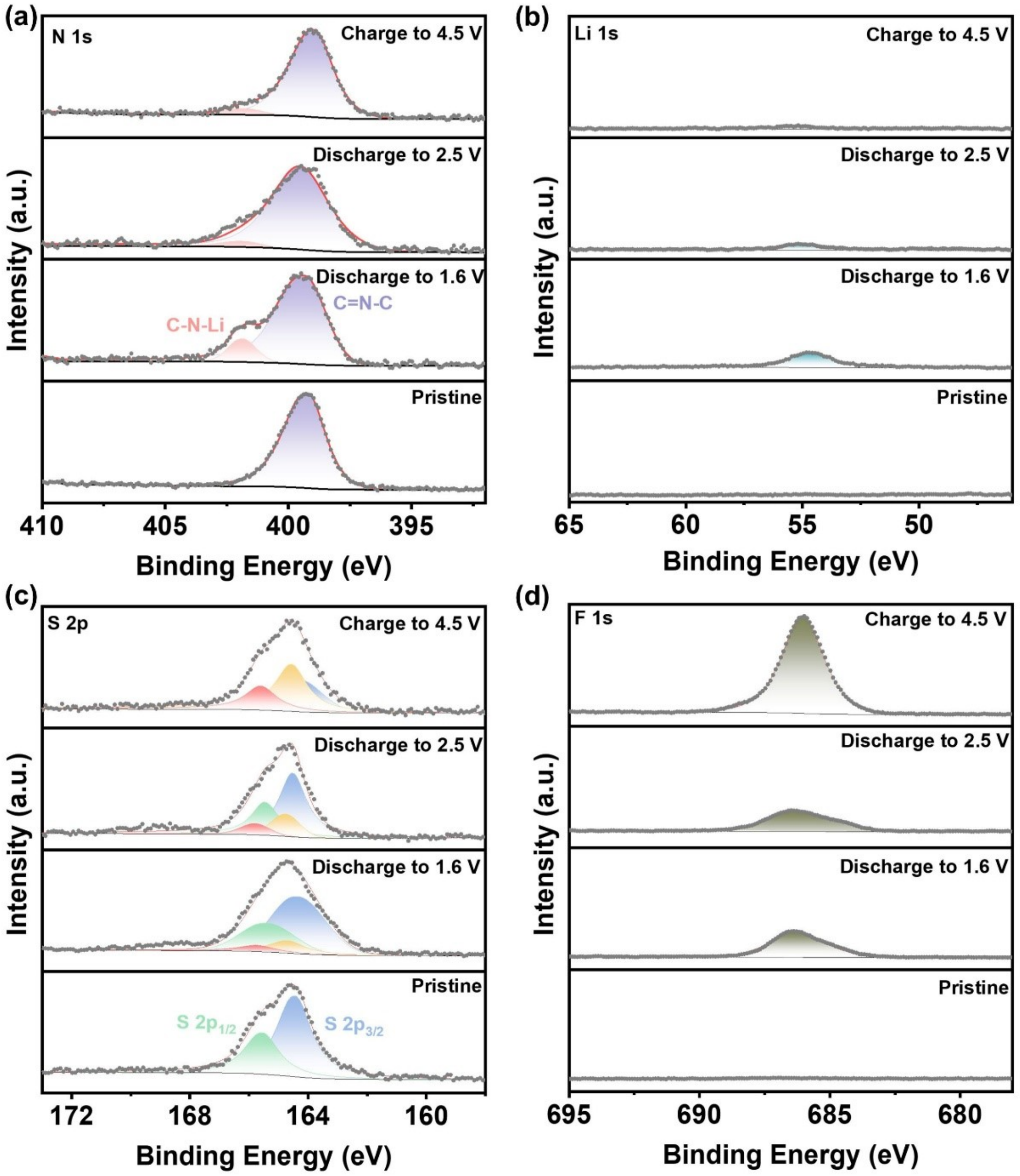


Fig. S21 (a)N 1s, (b) Li 1s, (c) S 2p and (d) F 1s ex-situ XPS spectrum of D-TBPY.

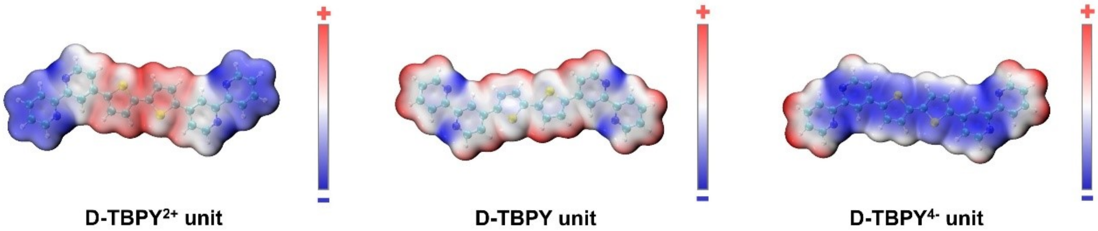


Fig. S22 Molecular electrostatic potential (MESP) of individual polymeric units of D-TBPY molecule during the redox process.

1. L. J. Nurkkala, R. O. Steen, H. K. J. Friberg, J. A. Häggström, P. V. Bernhardt, M. J. Riley and S. J. Dunne, *Eur. J. Inorg. Chem.*, 2008, **2008**, 4101-4110.

2. M. B. Majewski, J. G. Smith, M. O. Wolf and B. O. Patrick, *Eur. J. Inorg. Chem.*, 2016, **2016**, 1470-1479.