Supporting Information

Organoboron-Thiophene Based Polymer Electrodes Achieving High Performance Lithium-ion Batteries

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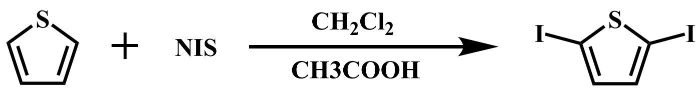
Instrumentation / General Methods

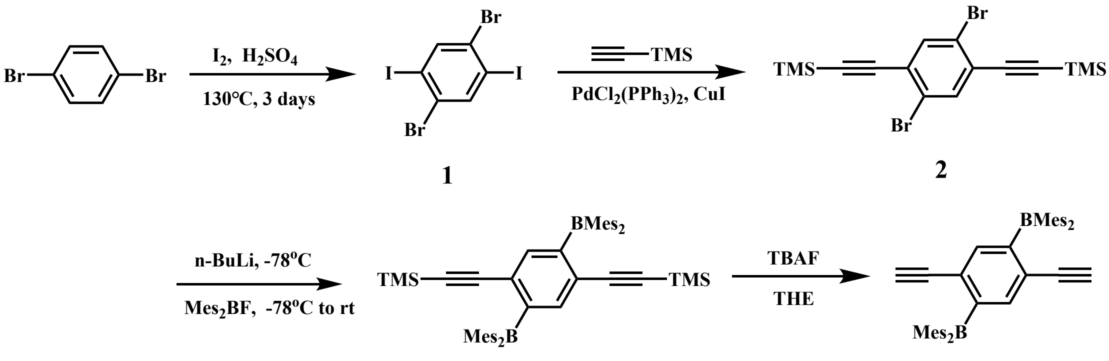
Part of the reactions and manipulations were carried out under an argon atmosphere by using standard Schlenk techniques or an inter-atmosphere glovebox. Prior to use, all the solvents were dried by refluxing with sodium and benzophenone and degassed by applying three freeze-pump-thaw cycles. Dichloromethane was dried by refluxing with phosphorus pentoxide for more than 5 hours. Chloroform-d was dried by using a 4 Å molecular sieve (2-3 days). All chemicals (reagents and solvents) were obtained from commercial suppliers (Energy Chemical, Heowns) and directly used without further purification. 2,5-diiodothiophene and (2,5-diethynyl-1,4-phenylene)bis(dimesitylborane) were synthesized according to literature previously reported procedures.

LANHE-CT2001A (Wuhan, China) testing systems were used for galvanostatic charge/discharge experiments. Ex situ charge/discharge cycling was tested on Neware battery test system (CT-4008T-5V10mA-164, Shenzhen, China). Cyclic voltammetry (CV) analyses were performed with a Wuhan Corrtest CS310M workstation. Structure optimization at the level of b3lyp/6-31G and single point energy calculation at the level of b3lyp/def2-SVP were carried out on the ORCA 5.0.1 software package provided by Lanzhou University Supercomputing Centre. Molecular electro-static potential and molecular dipole moment were calculated by Multiwfn3.8(dev) on a personal computer. Electron paramagnetic resonance (EPR) spectra were obtained using Bruker ER200DSRC10/12 instrument.



Scheme S1. Synthetic route of monomer **M1**.

Synthesis of 2,5-diiodothiophene (M1)[S1]: Thiophene (0.841 g, 10 mmol) and N-iodosuccinimide (4.95 g, 22 mmol) were dissolved in 20 mL of dichloromethane and 20 mL of glacial acetic acid and stirred at room temperature for 4 h. After the reaction, 50 mL of aqueous sodium thiosulfate was added to burst the reaction and extracted with dichloromethane (3 × 20 mL), the organic phase was dried with anhydrous magnesium sulfate, filtered, and the solvent was spun dry to obtain a pure pale yellow solid (yield: 3.19 g, 95 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (s, 2H).



Scheme S2. Synthetic route of monomer **M2**.

1, 4-dibromo-2, 5-diiodobenzene (compound 1)[S2]: Weigh 1,4-dibromobenzene (23.59 g, 100 mmol) in a 500 mL flask, add 300 mL of concentrated sulphuric acid and slowly add iodine monomers (55.836 g, 220 mmol) to the above reaction solution, heat the mixture to 130°C and stir at reflux for 3 d. During the reaction, the reaction solution was shaken manually every 2-3 h to dissolve the sublimated iodine monomers. At the end of the reaction, the reaction solution is cooled to room temperature. The mixture was slowly poured into a 350 mL ice-water mixture with concentrated sulfuric acid in small amounts, and then extracted with dichloromethane (3 × 150 mL). The organic phase was separated by removing excess iodine monomers with 300 mL of aqueous sodium hydroxide, and the organic phase was extracted again with dichloromethane (3 × 50 mL), the organic layers were combined, dried with anhydrous magnesium sulfate, filtered, and the organic phase was removed by rotary evaporator and recrystallized with hot dichloromethane/methanol solvent mixture to obtain a white compound **1** (yield: 85 %, 41.45 g) ◦ ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 2H).

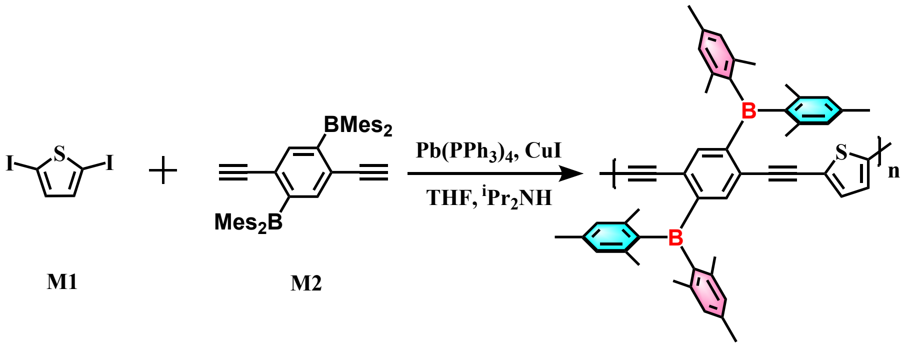
Synthesis of 1, 4-dibromo-2, 5-ditrimethylsilylacetylene benzene (compound 2)[S3]: Under an N_2 atmosphere, compound 1 (19.508 g, 40 mmol), catalyst bis(triphenylphosphine)palladium dichloride (1.404 g, 2 mmol), and cuprous iodide (0.762 g, 4 mmol) in 200 mL of degassed toluene and 100 mL of degassed diisopropylamine, and add trimethylsilyl acetylene (8.25 g, 84 mmol) to the above reaction mixture, stirred at room temperature for 24 h. After the reaction, 150 mL of water was added and extracted with dichloromethane (3 × 50 mL), combined with the organic phase, dried with anhydrous magnesium sulfate, filtered, spun off the solvent by rotary evaporator, and purified by column chromatography using hexane as eluent to obtain a light yellow solid (yield: 11.26 g, 66 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 2H), 0.27 (s, 18H).

Synthesis of compound 3[S3]: Under an N_2 atmosphere, Compound 2 (12.849 g, 30 mmol) was dissolved in 240 mL of dry tetrahydrofuran at -78 °C, and n-butyl (1.6 M, 63 mmol, 39.4 mL) was added dropwise and reacted at this temperature for about 2 h. Then Mes2BF (16.895 g, 63 mmol) was dissolved in 30 mL of tetrahydrofuran and transferred dropwise to the the above reaction solution. After that, the reaction system was slowly brought to room temperature and reacted overnight. After the reaction, 100 mL of water was added to quench the reaction, extracted with dichloromethane (3 × 50 mL), combined with the organic phase, dried with anhydrous magnesium sulfate, spun off the solvent, added hexane, and filtered under reduced pressure to obtain a white solid (yield: 14.95 g, 65 %).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 2H), 6.75 (s, 8H), 2.27 (s, 12H), 1.99 (s, 24H), -0.06 (s, 18H).

Synthesis of (2,5-diethynyl-1,4-phenylene)bis(dimesitylborane) (M2)[S4]: Compound 3 (11.503 g, 15 mmol) was dissolved in 150 mL of tetrahydrofuran and tetrabutylammonium fluoride (1 M, 150 mmol) was added to the above solution and stirred at room temperature for 6 d. After the reaction, most of the solvent was spun off, followed by dilution with 100 mL of water, extraction with dichloromethane (3 × 50 mL), combining the organic phase, drying with anhydrous magnesium sulfate, and spinning off the solvent. Purified by column chromatography (dichloromethane:

petroleum ether = 1: 20) to afford a white solid (yield: 6.349 g, 68 %) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (s, 2H), 6.75 (s, 8H), 2.74 (s, 2H), 2.27 (s, 12H), 2.00 (s, 24H).

Synthesis of polymers PBT-1



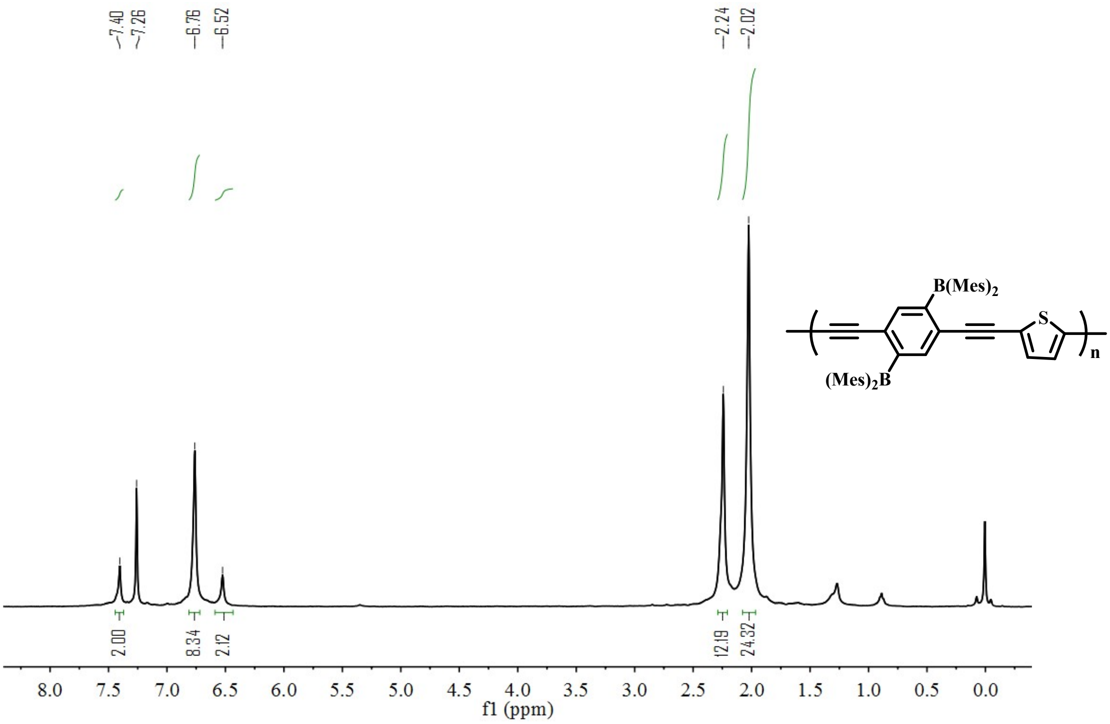
Scheme S3. Synthesis route of **PBT-1.**

Synthesis of PBT-1: Under an N_2 atmosphere, Monomer **M1** (0.336 g, 1 mmol), **M2** (0.622 g, 1 mmol), catalyst tetrakis(triphenylphosphine)palladium (0.577 g, 0.05 mmol), and cuprous iodide (0.019 g, 0.1 mmol) were dissolved in a degassed mixture of 30 mL tetrahydrofuran and 10 mL diisopropylamine, heated to 70 °C, and stirred After 48 h, the reaction was completed and cooled to room temperature. The reaction mixture was filtered under reduced pressure to remove a small amount of insoluble material and catalyst, and the filtrate was concentrated and precipitated by repeatedly dissolving in precipitant methanol and hexane in sequence until the supernatant was essentially colorless, centrifuged and dried in a vacuum oven at 60 °C for 24 h to obtain a yellow polymer solid (yield: 520 mg, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 2H), 6.76 (s, 8H), 6.52 (s, 2H), 2.24 (s, 12H), 2.02 (s, 24H). ^{11}B NMR (128.3 MHz, $CDCl_3$): δ (ppm): 70.27. GPC: Mn = 13091, Mw = 19559, PDI = 1.49.

Electrochemical measurements

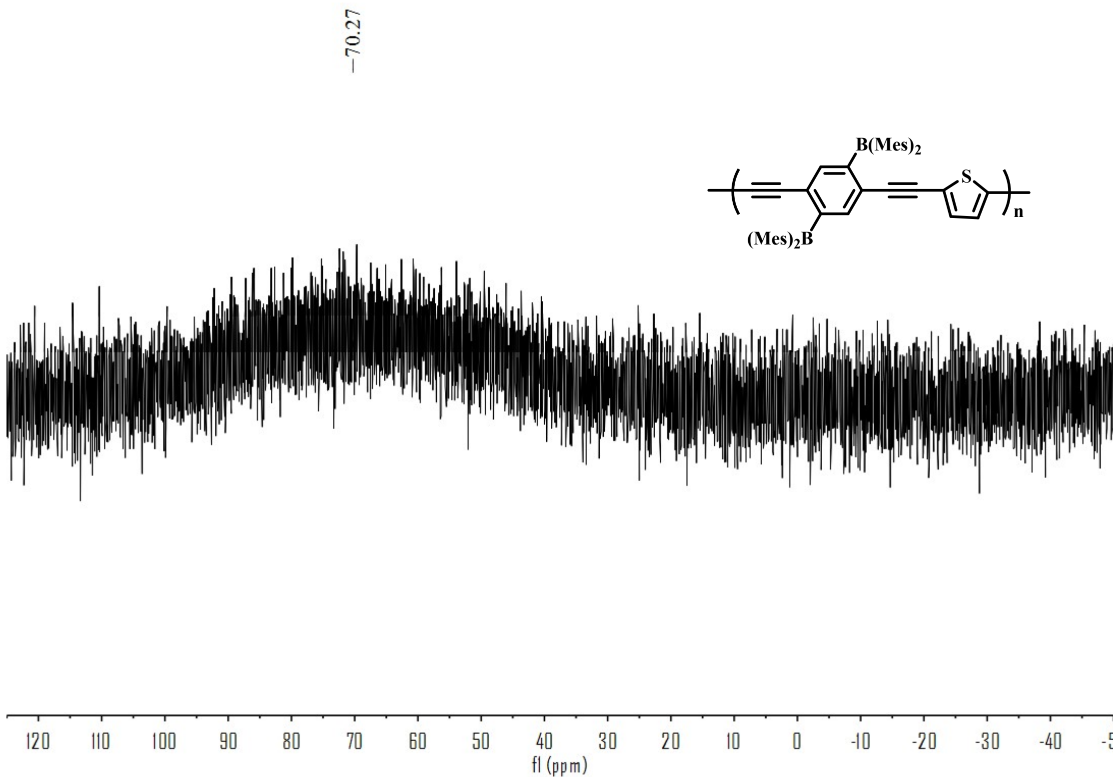
Electrochemical characterization was conducted on CR2032-type coin cells using a piece of metallic Li foil as the reference electrode. The electrode was composed of 50 wt% active material, 40 wt% active carbon, and 10 wt% sodium alginate, which was pasted on a Cu current collector and then cut into discwith an area of 0.64 cm^2 and dried in vacuum oven at 120 °C for 12 h. The loading mass of the active material was 1 ± 0.2 mg cm^{-2}. The cathode and anode were separated by a Celgard separator and 1 M KPF_6 in ethylene carbonate/ethyl methyl carbonate/dimethyl carbonate (EC/EMC/DMC, 1:1:1 volume ratio) as electrolyte. For ex-situ test, the coin cells were full discharged/charged (0.01 and 3.0 V) at a current density of 45 mA g^{-1}, then disassembled and washed in glove box for EPR measurement. For consistency, the open circuit voltage (OCV), full discharge and full charge electrode was all assembled in coin cells, then disassembled in glovebox and put in to a EPR tube.

Characterization of polymer



^{1}H NMR (400 MHz, CDCl$_3$)

Figure S1. ^{1}H NMR spectrum of **PBT-1** in CDCl3 (400 MHz, 25 ºC).



^{11}B NMR (128.3 MHz, $CDCl_3$)

Figure S2. ^{11}B NMR spectrum of **PBT-1** in CDCl3 (128.3 MHz, 25 ºC).

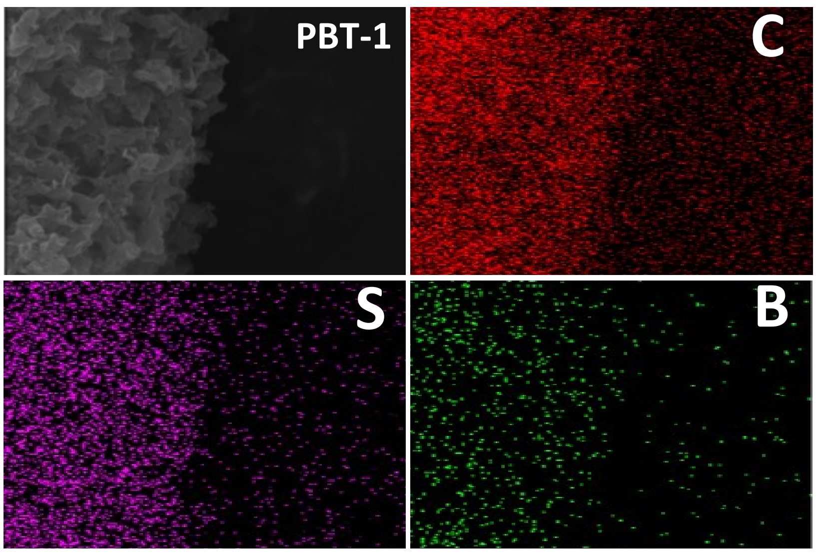


Figure S3. EDS elemental mapping of **PBT-1**.

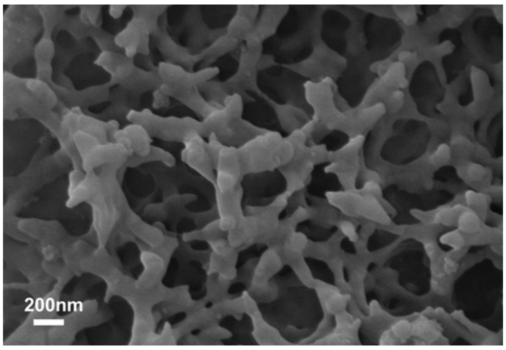


Figure S4. Scanning electron microscope image of polymer **PBT-1**.

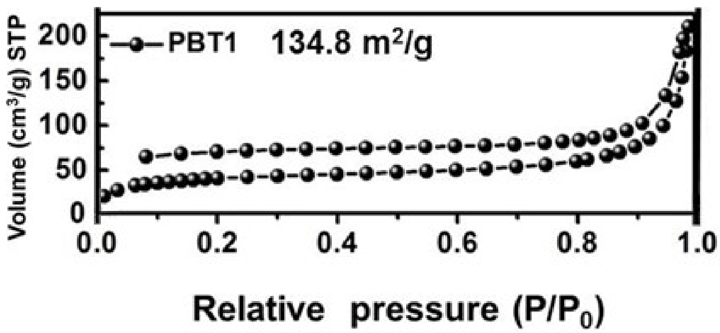


Figure S5. BET surface area of **PBT-1**.

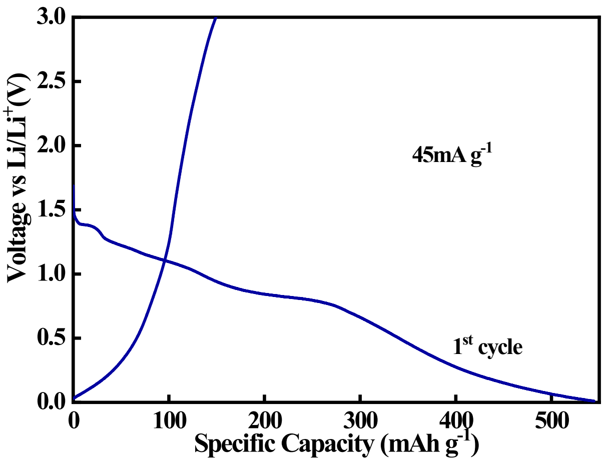


Figure S6. The1st charge/discharge profile.

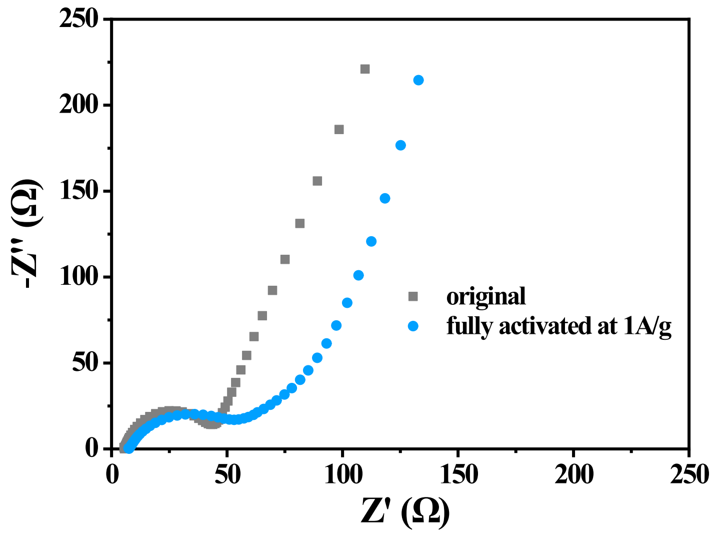


Figure S7. Nyquist plots of electrodes before and after activation.

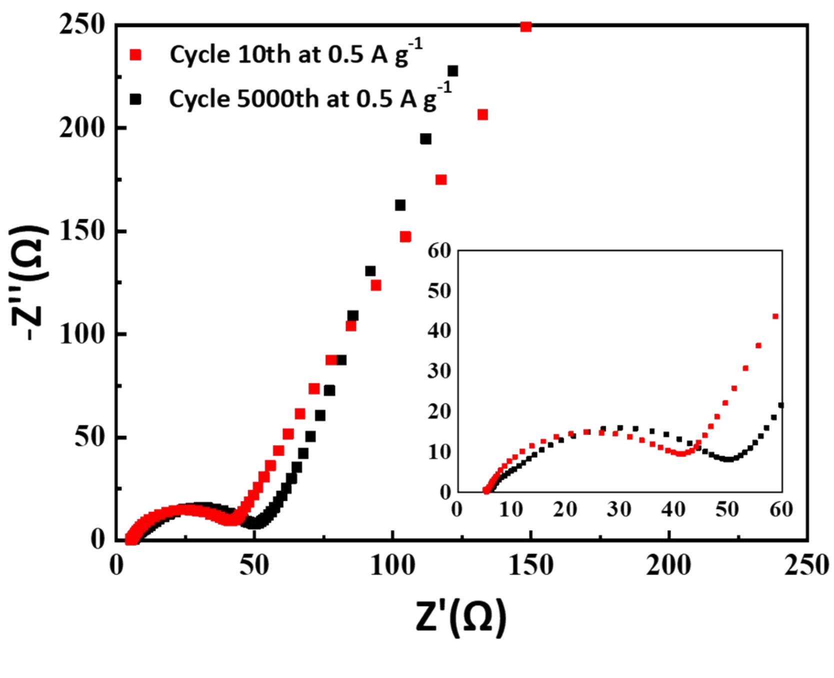
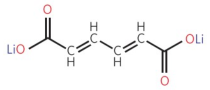
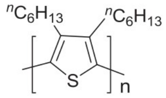
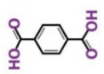
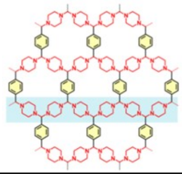
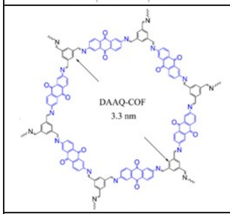
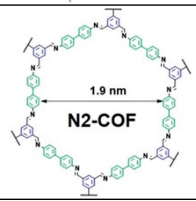
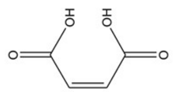
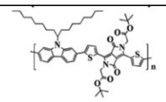
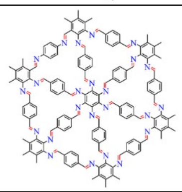
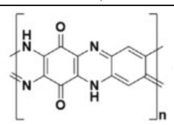
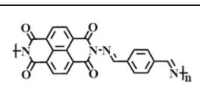
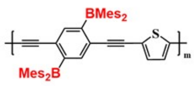


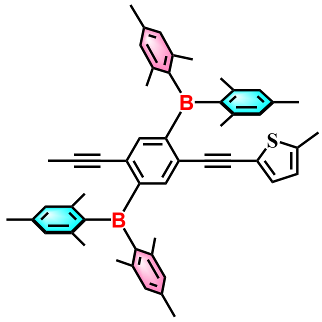
Figure S8. Nyquist plots of electrodes before and after cycling.

Table S1. Cycling properties of other anodes comprised of polymeric organic materials in previous reports.

Anode Material	Current density of cycling test (mA/g)	Maximum reversible capacity (mAh/g)	Cycly number↑	Capacity retention ratio	Reference
	1 C	170	80	73.5%	*Nat Mater,* 2009, **8**, 120-5.
	40	290	100	82.8%	*J. Electroanal. Chem.*, 2013, **688**, 118-122.
	50	282	150	90.6%	*Org. Electron.*, 2018, **62**, 536-541.
	1000	543	400	108.6%	*Nano Research,* 2021, **15**, 9779-9784.
	1000	787	500	95%	*ACS Appl. Energy Mater.*, 2021, **4**, 11377-11385.
	1000	680	500	82%	*J. Mater. Chem. A,* 2016, **4**, 14106-14110.
	2310	1027.7	500	98.1%	*ACS Energy Lett.*, 2017, **2**, 2140-2148.
	1000	203	1000	80%	*Nanoscale,* 2021, **13**, 2673-2684.
	1000	1255	1100	784%	*J. Mater. Sci., 2022,* ***57****, 9980-9991.*
	500	310	1500	58%	*Nano Energy, 2021,* ***86***, 106055.
	2000	215.5	1600	85.7%	*J. Power Sources,* 2021, **482**, 228931.

	1000	252	10000	47.6% *vs.* Peak	This work

Cartesian coordinates for the optimized geometries



Coordinates from ORCA-b3lyp/6-31G

Row	Symbol	X	Y	Z
1	C	-0.51675	-1.40293	-0.51268
2	C	-1.30113	-0.2089	-0.47427
3	C	-0.6119	1.015402	-0.52729
4	C	0.798428	1.113525	-0.52685
5	C	1.583748	-0.08097	-0.51934
6	C	0.88968	-1.30478	-0.55775
7	C	1.368768	2.416675	-0.60761
8	C	-1.11468	-2.70135	-0.56982
9	B	3.160174	-0.1241	-0.43003
10	C	1.747435	3.57522	-0.72456
11	C	-1.58909	-3.82106	-0.64157
12	C	-2.19939	-5.14583	-0.69461
13	C	2.160753	4.904173	-0.87069
14	C	1.391458	6.035969	-1.03674
15	C	2.134311	7.247996	-1.17769
16	C	3.495397	7.101303	-1.12773
17	S	3.938605	5.358697	-0.88284

18	B	-2.87521	-0.17227	-0.34162
19	C	5.937322	-4.22342	-3.74129
20	C	6.113494	3.473886	3.282372
21	C	5.567555	1.527246	-1.32087
22	C	2.371693	0.206417	2.518815
23	C	-2.56758	0.058795	-3.36412
24	C	-5.76672	3.938932	-3.53987
25	C	-4.77513	1.863235	0.93596
26	C	-5.23933	-1.88608	-1.21589
27	C	-2.05246	-0.48839	2.595172
28	C	-5.71004	-3.84372	3.396036
29	C	-3.65007	0.919828	-1.18489
30	C	-3.47498	1.007661	-2.59769
31	C	-4.16718	1.979173	-3.33578
32	C	-5.01919	2.907076	-2.72428
33	C	-5.17719	2.833014	-1.33409
34	C	-4.52903	1.856814	-0.56297
35	C	2.791426	-0.305	-3.44714
36	C	5.055955	-2.19769	0.781394
37	C	3.904848	-1.21211	-1.30491
38	C	3.701923	-1.277	-2.71461
39	C	4.367768	-2.24605	-3.4797
40	C	5.218887	-3.19341	-2.89756
41	C	5.403561	-3.14189	-1.50947

42	C	4.782549	-2.16882	-0.71261
43	C	-3.62245	-1.14699	0.651853
44	C	-4.7365	-1.9266	0.216336
45	C	-5.38682	-2.78967	1.110337
46	C	-4.9976	-2.90005	2.452192
47	C	-3.91816	-2.12062	2.883712
48	C	-3.21901	-1.26977	2.014026
49	C	3.935619	0.832816	0.555305
50	C	5.070971	1.580112	0.113389
51	C	5.750376	2.422751	1.003493
52	C	5.370571	2.546122	2.347095
53	C	4.273964	1.796661	2.786013
54	C	3.546097	0.964436	1.921638
55	H	-1.1863	1.935982	-0.56354
56	H	1.462089	-2.22537	-0.61633
57	H	-1.64887	-5.86699	-0.0773
58	H	-3.23297	-5.11379	-0.32782
59	H	-2.22109	-5.54075	-1.71873
60	H	0.309396	5.990997	-1.06086
61	H	1.663263	8.214925	-1.31673
62	H	6.957435	-3.89624	-3.98735
63	H	6.023523	-5.18179	-3.21643
64	H	5.41461	-4.40063	-4.68755
65	H	5.848947	4.52286	3.090176

66	H	5.875685	3.260924	4.329951
67	H	7.199502	3.386908	3.156049
68	H	4.78006	1.786362	-2.03852
69	H	6.386566	2.238854	-1.46768
70	H	5.933202	0.53082	-1.58913
71	H	2.421126	0.230114	3.612682
72	H	1.413628	0.648992	2.222379
73	H	2.345716	-0.84434	2.211876
74	H	-2.84106	0.041568	-4.42474
75	H	-1.51749	0.369161	-3.29833
76	H	-2.61801	-0.96971	-2.99249
77	H	-6.77648	3.588751	-3.79684
78	H	-5.8815	4.879041	-2.98836
79	H	-5.2488	4.157866	-4.48007
80	H	-5.42109	2.702356	1.214453
81	H	-5.25727	0.939508	1.271767
82	H	-3.84468	1.963884	1.508407
83	H	-4.44965	-2.13961	-1.9337
84	H	-6.05338	-2.60497	-1.35737
85	H	-5.61497	-0.89452	-1.48808
86	H	-2.08885	-0.50567	3.689676
87	H	-1.09119	-0.91816	2.289538
88	H	-2.04604	0.560531	2.281159
89	H	-5.30377	-4.86264	3.323909

90	H	-5.60234	-3.52429	4.43831
91	H	-6.78049	-3.90608	3.168689
92	H	-4.03303	2.013619	-4.41482
93	H	-5.82646	3.549218	-0.83534
94	H	3.032035	-0.28581	-4.51561
95	H	1.737574	-0.59376	-3.35016
96	H	2.875776	0.720075	-3.07158
97	H	5.693717	-3.05003	1.037894
98	H	5.558227	-1.28541	1.119156
99	H	4.134419	-2.29055	1.369604
100	H	4.213562	-2.26285	-4.55648
101	H	6.052327	-3.87378	-1.03326
102	H	-6.22786	-3.3795	0.751791
103	H	-3.60703	-2.17654	3.924572
104	H	6.6002	2.994648	0.638114
105	H	3.970736	1.862883	3.82846
106	C	4.559254	8.147377	-1.23909
107	H	4.098951	9.128997	-1.39571
108	H	5.236685	7.955433	-2.08083
109	H	5.17405	8.206026	-0.33174