Supporting Information

Organoboron Flank-substituted Donor-Acceptor Polymer Anode with Ultra-long Cycling Stability for Lithium-Ion Batteries

Hao Zhao[a,*], Ting Liu[a], Wenjing Zhang[a], Jiadong Wang[a], Kexuan Li[a], Yitong Zhou[a], Luzun Liu[a], Yunfei Bai[c], Xiaobo Pan[b,c,*]

[a] School of Physics and Electronic Information, Yantai University, Yantai 264005, People's Republic of China.

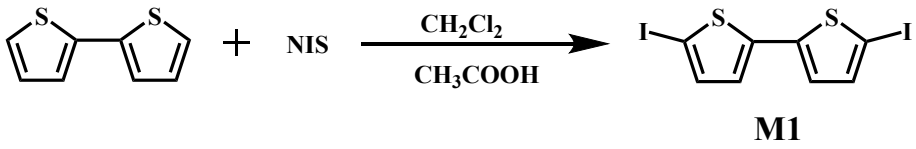
[b] New Energy (Photovoltaic) Industry Research Center, Qinghai University, Xining 810006, People's Republic of China.

[c] State Key Laboratory of Applied Organic Chemistry (Lanzhou University), Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000 (P.R. China).

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.

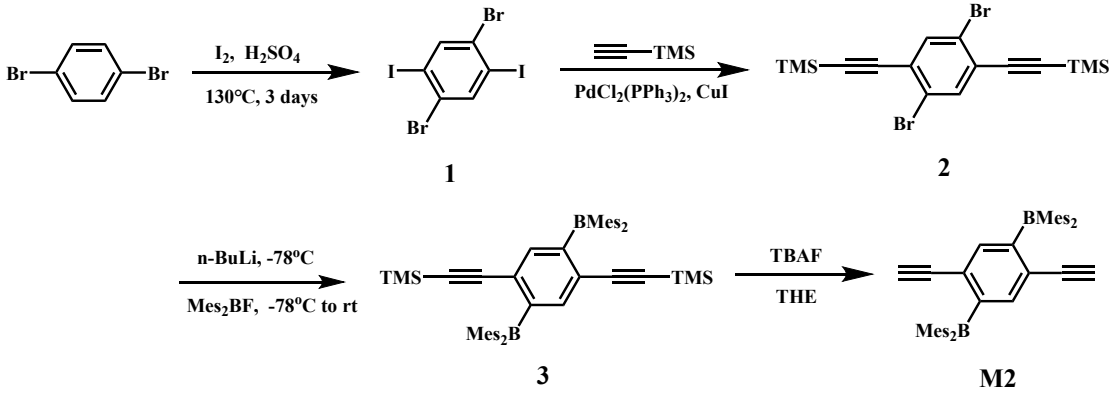
NEWARE battery cycler (CT-4008T-5V10mA-164, Shenzhen, China) testing systems were used for galvanostatic charge/discharge experiments. Cyclic voltammetry (CV) analyses were performed with a Wuhan Corrtest CS310M workstation. Structure optimization at the level of b3lyp/6-31G and single point energy calculation 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.



M1

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

Synthesis of 5,5'-diiodo-2,2'-bithiophene (M1): 2,2'-Bithiophene (1.663 g, 10 mmol) and N-iodosuccinimide (4.95 g, 22 mmol) were dissolved in a mixture of 20 mL dichloromethane and 20 mL glacial acetic acid and stirred at room temperature for 4 h. After the reaction, the solid was filtered and washed with methanol to give a pure light pink solid (yield: 4.01 g, 96 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, 2H), 6.79 (d, 2H).



Scheme S2. Synthetic route of monomer **M2**. [S1]

1, 4-dibromo-2, 5-diiodobenzene (compound 1): 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).

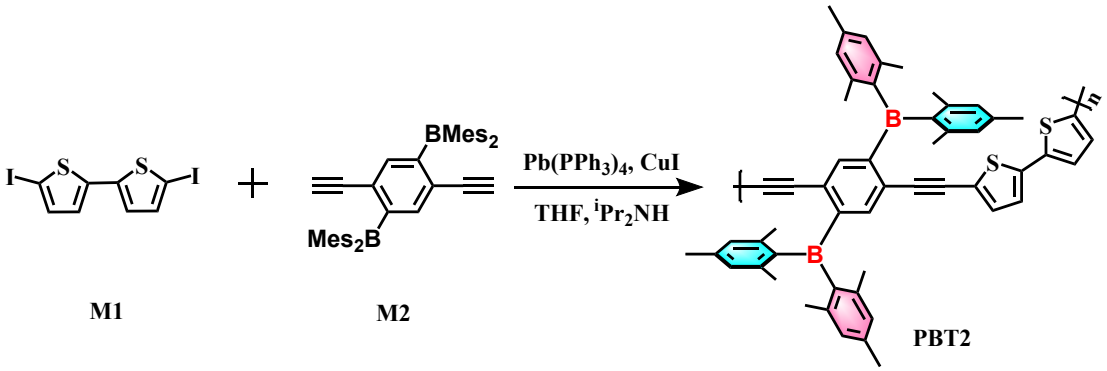
Synthesis of 1, 4-dibromo-2, 5-ditrimethylsilylacetylene benzene (compound 2): Under an N_2 atmosphere, compound 1 (19.508 g, 40 mmol), catalyst bis(triphenylphosphine)palladium dichloride (1.404 g, 2 mmol), and cuprous iodide (0.762 g, 4 mmol) in 200 mL of degassed toluene and 100 mL of degassed diisopropylamine, 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: 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): 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-2



Scheme S3. Synthesis route of **PBT-2.** [S1]

Synthesis of PBT-2: 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 anode was composed of 50 wt% active material, 40 wt% active carbon, and 10 wt% sodium alginate. The electrode plate is a copper circle with a radius of 6 mm, and after loading 300 um thick slurry on one face, the single electrode active material loading was around 1.1 mg. Average loading mass of the active material was 1 ± 0.2 mg cm^{-2}. Every electrode weighing was calculated as the difference in mass from the blank circle. The cathode and anode were separated by a glass fiber filter (Whatman GF/C).

[S1] Q. Wei, X. Yao, Q. Zhang, P. Yan, C. Ru, C. Li, C. Tao, W. Wang, D. Han, D. Han, L. Niu, D. Qin and X. Pan, *Small,* 2021, **17**, 2100132.

Characterization of polymer

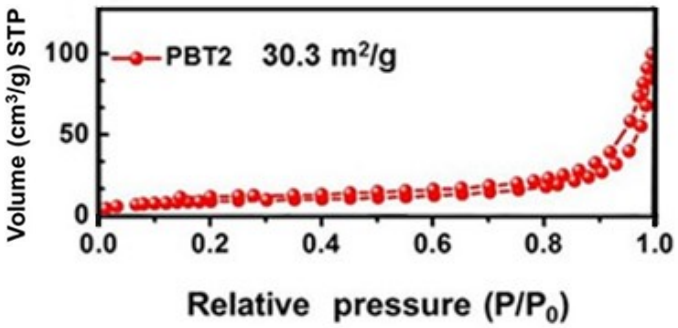


Figure S1. Nitrogen adsorption isotherms depicting the porosity of **PBT-2**.

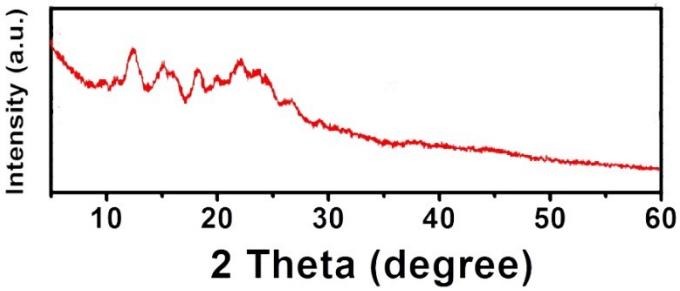


Figure S2. XRD pattern of **PBT-2**.

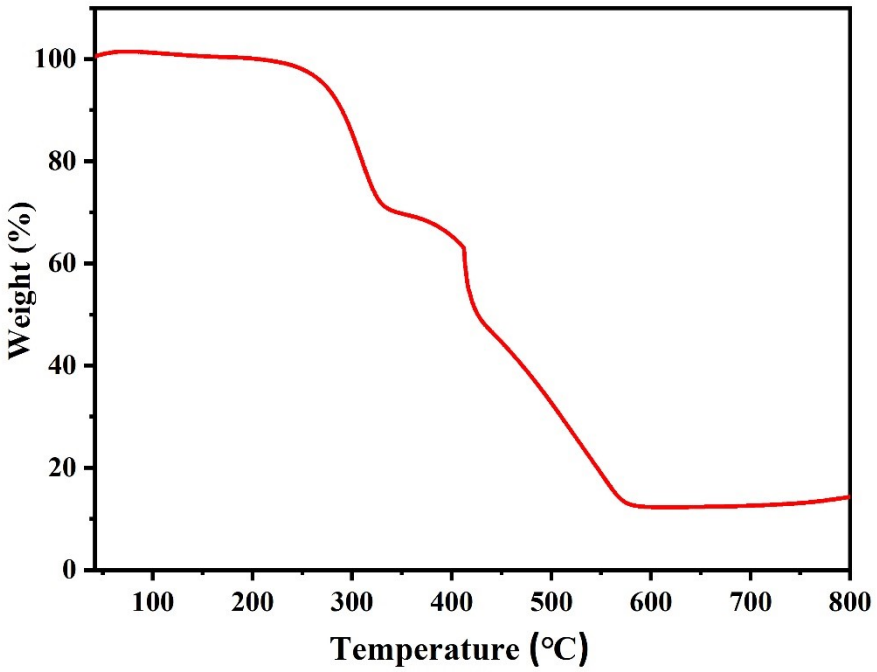


Figure S3. Thermogravimetric analysis curve of **PBT-2**.

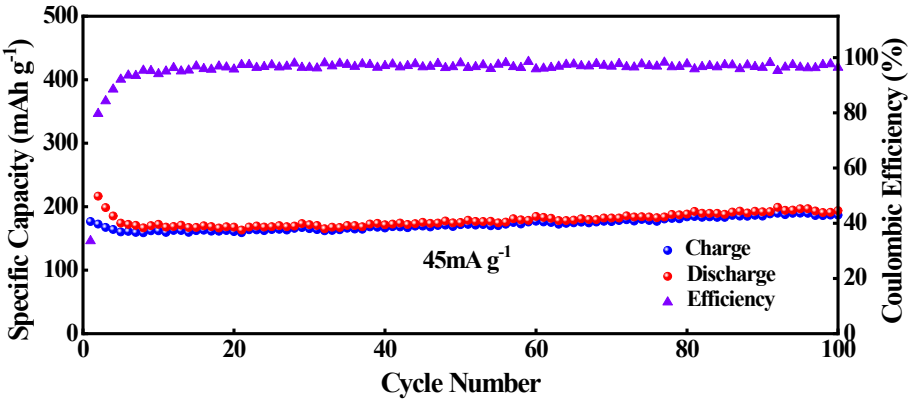


Figure S4. Detailed cyclic test data of the first 100 cycles at 45 mA g^{-1}.

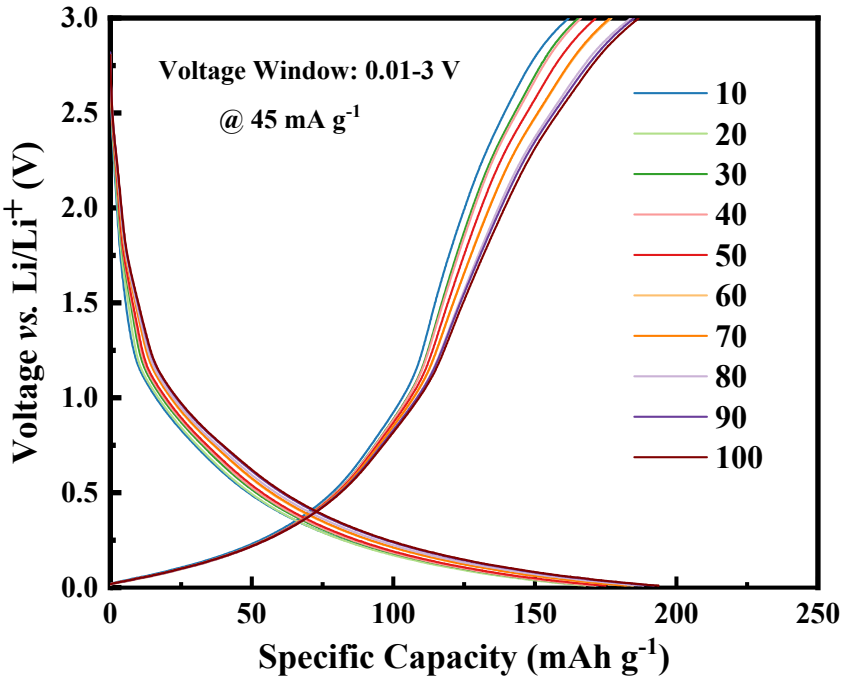


Figure S5. Charge and discharge curves of the first 100 cycles at 45 mA g^{-1}.

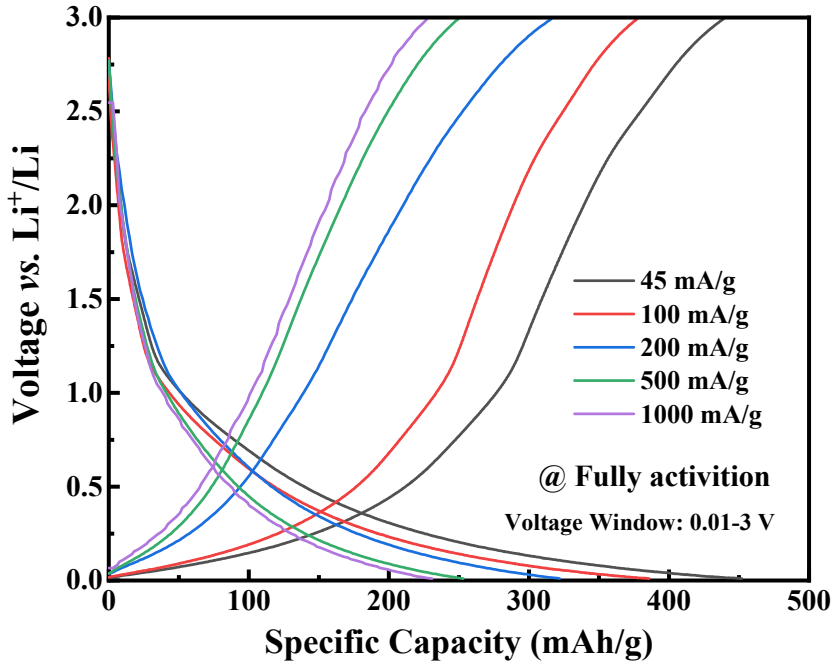


Figure S6. Charge and discharge curves of fully activated cell.

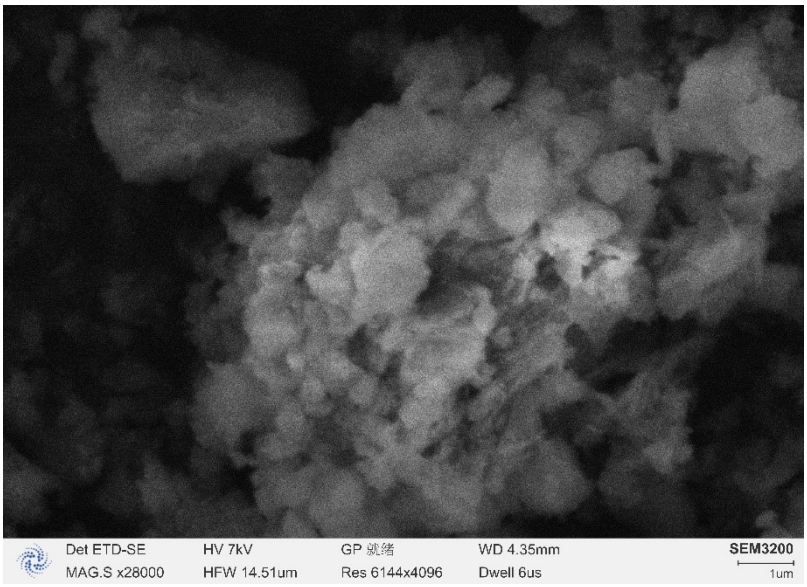


Figure S7. SEM of electrode after 10000 cycles at 1 A g^{-1}.

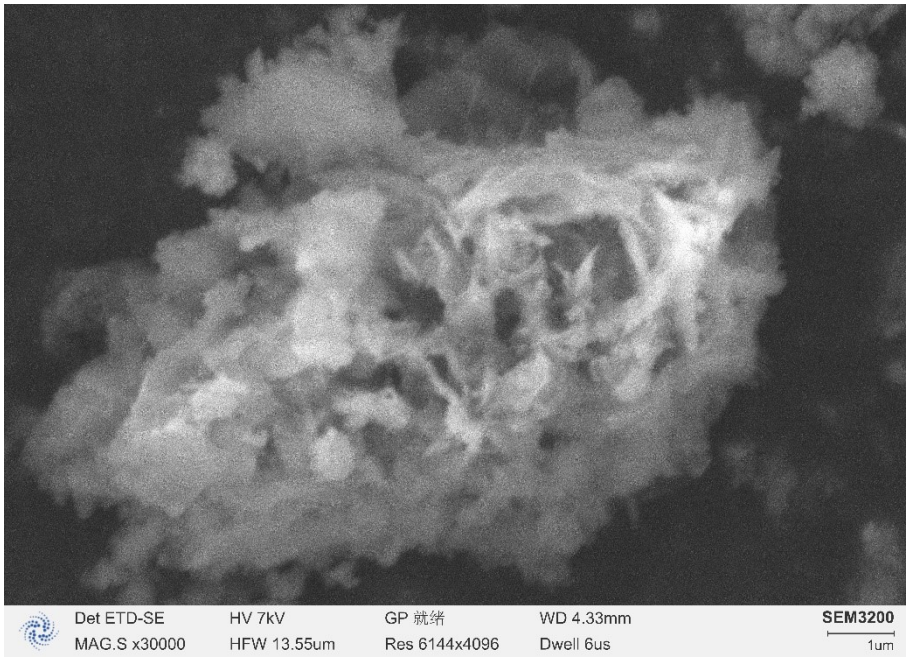


Figure S8. SEM of electrode after 10000 cycles at 1 A g^{-1}.

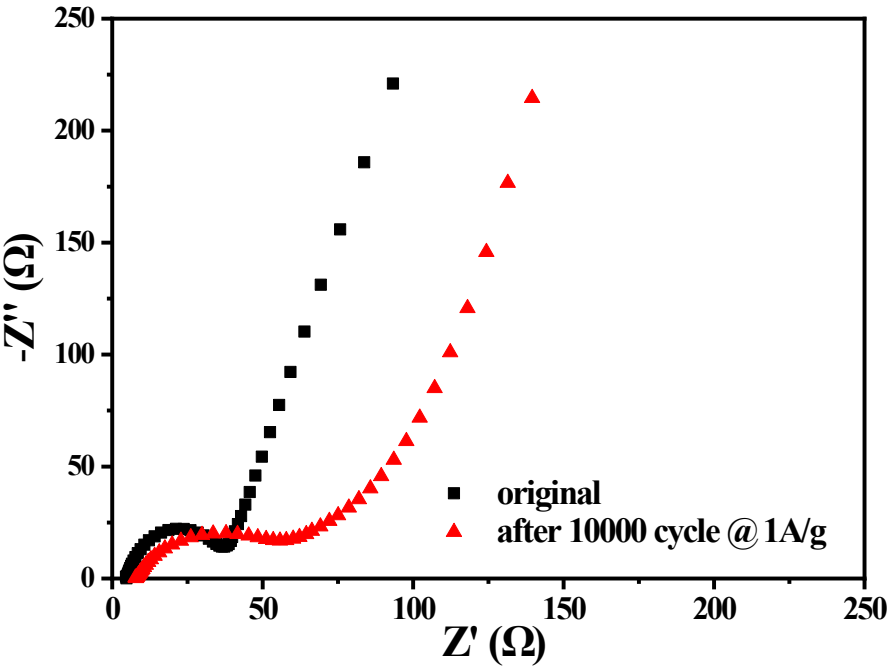
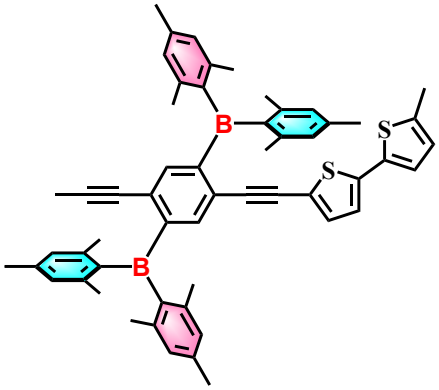


Figure S9. Nyquist plots of electrodes before and after cycling.

Cartesian coordinates for the optimized geometries



Coordinates from ORCA-b3lyp/6-31G

Row	Symbol	X	Y	Z
1	C	-0.51755	-1.39676	-0.51833
2	C	-1.30345	-0.20371	-0.47775
3	C	-0.61594	1.021327	-0.53035
4	C	0.79462	1.120777	-0.53139
5	C	1.58188	-0.07301	-0.52549
6	C	0.888904	-1.29716	-0.56455
7	C	1.36408	2.423338	-0.61
8	C	-1.1138	-2.69571	-0.57603
9	B	3.158401	-0.11586	-0.43463
10	C	1.747469	3.581476	-0.72291
11	C	-1.58652	-3.81612	-0.64839
12	C	-2.19463	-5.14183	-0.70196
13	C	2.171677	4.904871	-0.86201
14	C	1.413018	6.055739	-0.96119
15	C	2.158943	7.253365	-1.11817
16	C	3.528816	7.086768	-1.14963
17	S	3.95344	5.323952	-0.96116
18	C	5.930018	7.906772	-1.37554
19	C	6.669535	9.122663	-1.52507
20	C	5.910634	10.26035	-1.56762
21	S	4.144807	9.846487	-1.41198
22	C	4.566022	8.068156	-1.29675
23	C	6.340983	11.68458	-1.71591
24	B	-2.87785	-0.16992	-0.34401
25	C	5.938817	-4.22653	-3.72863
26	C	6.102005	3.505043	3.263318
27	C	5.576178	1.520808	-1.32588
28	C	2.363224	0.231555	2.511348
29	C	-2.57139	0.062165	-3.36678
30	C	-5.77842	3.9357	-3.54051
31	C	-4.78204	1.860619	0.934524
32	C	-5.23959	-1.8874	-1.21669

33	C	-2.05118	-0.48602	2.59189
34	C	-5.69777	-3.85317	3.393042
35	C	-3.65494	0.92048	-1.18684
36	C	-3.48023	1.009143	-2.59966
37	C	-4.17464	1.979372	-3.33731
38	C	-5.0286	2.905203	-2.72537
39	C	-5.18631	2.830298	-1.33516
40	C	-4.53598	1.855287	-0.56444
41	C	2.793073	-0.30671	-3.45185
42	C	5.051208	-2.18571	0.786133
43	C	3.90343	-1.20692	-1.30514
44	C	3.702372	-1.27647	-2.71487
45	C	4.36904	-2.24821	-3.47581
46	C	5.21926	-3.19373	-2.88932
47	C	5.402003	-3.13765	-1.50113
48	C	4.780034	-2.16187	-0.70837
49	C	-3.62173	-1.14667	0.649756
50	C	-4.73434	-1.92866	0.214683
51	C	-5.38093	-2.79481	1.108424
52	C	-4.98946	-2.90604	2.449564
53	C	-3.91167	-2.12409	2.880719
54	C	-3.21616	-1.27011	2.01123
55	C	3.932983	0.844405	0.547904
56	C	5.071825	1.586268	0.105308
57	C	5.74849	2.4347	0.991963
58	C	5.362988	2.569499	2.332848
59	C	4.264322	1.823784	2.773067
60	C	3.539235	0.985577	1.91218
61	H	-1.19158	1.941181	-0.56569
62	H	1.462114	-2.21716	-0.62387
63	H	-1.6419	-5.86264	-0.08626
64	H	-3.22772	-5.11193	-0.33369
65	H	-2.21704	-5.53559	-1.7265
66	H	0.330902	6.027539	-0.92583
67	H	1.693127	8.22734	-1.21235
68	H	6.401457	6.9318	-1.33173
69	H	7.750846	9.148812	-1.60166
70	H	5.920057	12.14945	-2.61667
71	H	6.035738	12.29761	-0.85825
72	H	7.4326	11.73479	-1.79189
73	H	6.95866	-3.89937	-3.97579
74	H	6.025814	-5.18263	-3.19979
75	H	5.416528	-4.40814	-4.67428
76	H	5.839914	4.552424	3.059629
77	H	5.858192	3.302341	4.311516
78	H	7.18858	3.415485	3.143791
79	H	4.79303	1.772474	-2.05087

80	H	6.395773	2.231469	-1.47441
81	H	5.944199	0.522361	-1.58307
82	H	2.413034	0.257784	3.605126
83	H	1.405913	0.675476	2.21441
84	H	2.335024	-0.81982	2.206897
85	H	-2.84602	0.044035	-4.42708
86	H	-1.52194	0.375005	-3.30247
87	H	-2.61909	-0.96639	-2.99492
88	H	-6.78782	3.583806	-3.79647
89	H	-5.8942	4.875734	-2.98912
90	H	-5.26163	4.155256	-4.48117
91	H	-5.42922	2.698651	1.213405
92	H	-5.26289	0.93606	1.269904
93	H	-3.8518	1.962329	1.507119
94	H	-4.45025	-2.13658	-1.93637
95	H	-6.05119	-2.60907	-1.35811
96	H	-5.61947	-0.89678	-1.48639
97	H	-2.0868	-0.50378	3.686402
98	H	-1.08894	-0.91325	2.28561
99	H	-2.04773	0.563065	2.278362
100	H	-5.2878	-4.87052	3.319653
101	H	-5.59047	-3.53433	4.435534
102	H	-6.76814	-3.91923	3.166409
103	H	-4.04078	2.01446	-4.41634
104	H	-5.8371	3.544919	-0.83615
105	H	3.035136	-0.2909	-4.52002
106	H	1.738981	-0.59484	-3.3555
107	H	2.87721	0.719617	-3.07958
108	H	5.688466	-3.03724	1.046499
109	H	5.553131	-1.27238	1.121584
110	H	4.128775	-2.27648	1.373285
111	H	4.216323	-2.26859	-4.55272
112	H	6.049969	-3.86806	-1.0216
113	H	-6.22085	-3.38645	0.750272
114	H	-3.59904	-2.18049	3.921095
115	H	6.601063	3.002256	0.62617
116	H	3.957251	1.897927	3.813828