

Supporting Information

***From benzodiazaborole-based compound to
donor-acceptor polymer via electropolymerization***

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Experimental

All reagents and solvents were purchased from commercial sources. Synthesis of **M1** and **M2** were carried out according to the previous work.^[2b] Electrodes (Pt and Ag) were polished with Al₂O₃ before use. ITO electrode was used as received. ¹H- and ¹³C-NMR spectra were recorded on a JEOL EX-270 (¹H: 300 MHz, ¹³C: 75.45 MHz) spectrometer. Elemental analyses were performed on a Thermo Finnigan Flash EA1112 CHN-O analyzer. UV-vis spectra were obtained on a Shimadzu UV-1650 spectrometer. Solid-state absorption spectra of **M1**, **M2** and **M3** were recorded by film casted on a glass plate from a toluene solution. PL spectra were obtained on a SPEX FL-3-21 Tau spectrometer. CV measurements and electropolymerization were carried out on a

HOKUTO DENKO HABF501. The XPS spectra were obtained using a PHI-1600 ESCA system.

M3: **M2** (54 mg, 0.20 mmol) and 3,5-dimethylbenzene-1-boronic acid (30 mg, 0.20 mmol) were dissolved in a toluene solution (2 ml). The mixture was stirred at 105 °C for 24 h. The solvent was then removed on a rotary evaporator to yield a red colored powder. The sample was then recrystallized from dichloromethane / hexane (1:9). Yield 71 mg (92 %). ¹H-NMR (300 MHz, CDCl₃, ppm): δ 7.44-7.34 (Ar-*H*, m), 7.231 (Ar-*H*, *J* = 3.6, 2H), 7.165 (NH, s, 2H), 7.092 (Ar- *H*, s, 2H), 2.374 (-CH₃,s, 6H). ¹³C-NMR (75.45 MHz, CDCl₃, ppm): δ 148.70, 141.54, 137.99, 134.52, 132.14, 131.34, 128.39, 125.37, 125.13, 120.31, 118.07, 21.748. Anal. Calcd. for (C₂₂H₁₉BN₂S₂): C, 68.39; H, 4.96; N, 7.25. Found: C, 68.29; H, 4.89; N, 7.14.

Electropolymerization of **M1** and **M3** (10 mM) was carried out in 0.1 M tetraethylammonium tetrafluoroborate / acetonitrile solution by a cyclic potential-sweep method in an undivided cell equipped with an ITO working electrode for UV-vis absorption measurements or a platinum wire working electrode for CV measurements, a platinum wire counter electrode, and a silver wire as a reference. The deposited polymer on the working electrode was rinsed with dry acetonitrile, then dry chloroform and dried under reduced pressure.

Electrochemical properties of **M1** show both the reversible oxidation and reduction potentials ($E_{pa} = 0.94$ V, $E_{pc} = -1.65$ V (vs. Ag/Ag⁺)), respectively, whereas cyclic voltammogram of **M3** shows a reversible oxidation potential at ($E_{pa} = 0.97$ V (vs Ag/Ag⁺)) and an irreversible reduction potential ($E_{pc} = -1.31$ V (vs. Ag/Ag⁺)) (Figure S1).

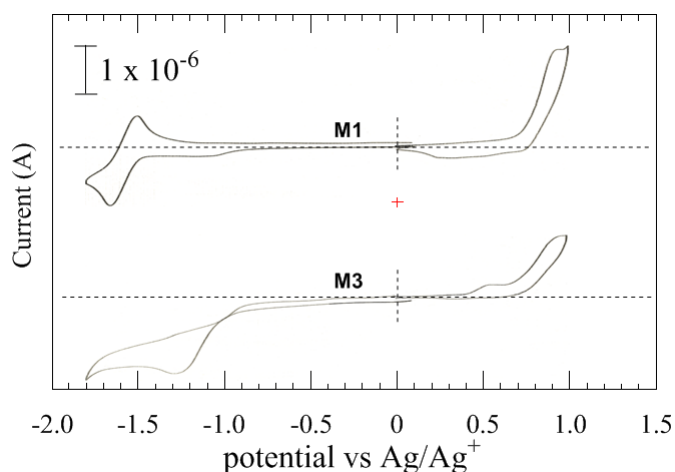


Figure S1. Cyclic voltammograms of **M1** (top) and **M3** (bottom) at 0.1 V/sec. $\text{Fe/Fe}^+ = 0.41$ V. A three electrode system equipped with a platinum electrode, a platinum counter electrode and a Ag wire as a reference electrode was used in an electrolytic solution of acetonitrile containing 0.1 M tetraethylammonium tetrafluoroborate.

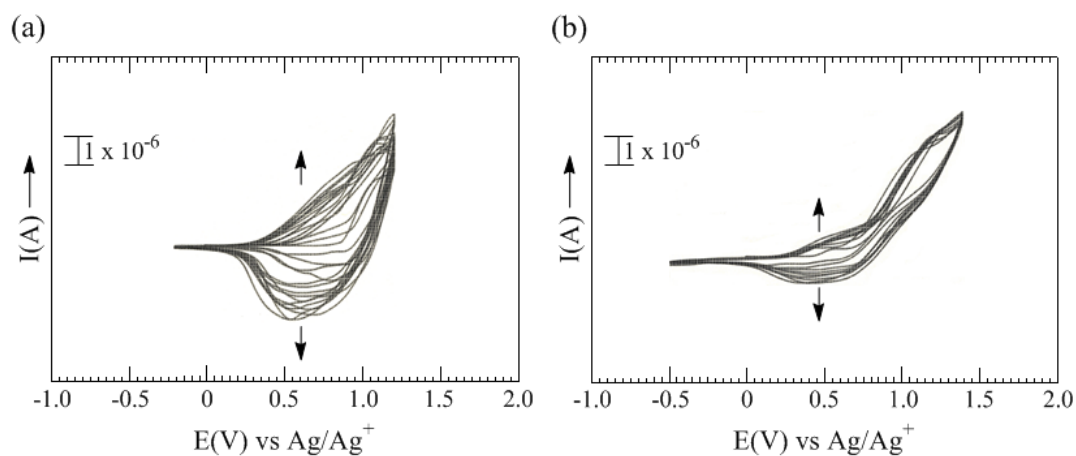


Figure S2. Electropolymerization of **M1** (a) and **M3** (b) in 10 mM Et_4NBF_4 /acetonitrile at 0.1 V/sec. $Fe/Fe^+ = 0.41$ V. A three electrode system equipped with a ITO electrode, a platinum counter electrode and a Ag wire as a reference electrode was used in an electrolytic solution of acetonitrile containing 0.1 M tetraethylammonium tetrafluoroborate.

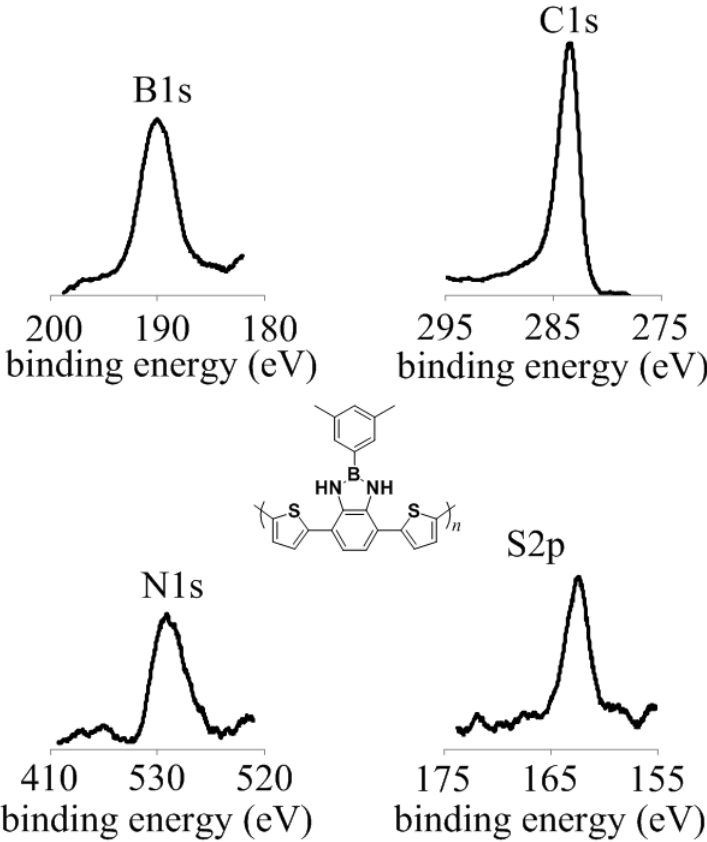


Figure S3. XPS results of **P3**.