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Electronic Supplementary Information

Post-Polymerization Modification and Release of Functional Groups Based on a NIR Light-Emitting Organoboron π-Conjugated Polymer

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General

^{1}H, $^{13}C\{^{1}H\}$, and ^{11}B spectra were recorded on JEOL ECZ400 instruments at 400, 100, and 128 MHz, respectively. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **P-py-BT** and **py-BT-py** were recorded on a JEOL ECZ600 instrument at 151 MHz. In particular, quantitative analysis of $^{13}C\{^{1}H\}$ NMR spectra of **py-BT-py** was conducted by inverse gated decoupling. Samples were analyzed in $CDCl_3$ and CD_2Cl_2. The chemical shift values were expressed relative to Me_4Si for ^{1}H and $^{13}C\{^{1}H\}$ NMR as an internal standard in $CDCl_3$ and $BF_3{\cdot}Et_2O$ for ^{11}B NMR as a capillary standard. Analytical thin layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel® C-300 silica gel and Millipore® aluminium oxide 90 active basic (0.063-0.200 mm). High-resolution mass (HRMS) spectrometry was performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the HRMS spectra were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer for electrospray ionization (ESI) a Thermo Fisher Scientific EXACTIVE spectrometer for atmospheric pressure chemical ionization (APCI). Elemental analyses were performed at the Microanalytical Center of Kyoto University. Gel permeation chromatography (GPC) was carried out on a SHIMADZU Prominence system equipped with three consecutive polystyrene gel columns (TSKgels: α-4000, α-3000, α-2500) using $CHCl_3$ as an eluent after calibration with standard polystyrene samples. Recyclable preparative high-performance liquid chromatography (HPLC) was carried out on Japan Analytical Industry Model LaboACE LC-5060 (JAIGEL-2.5H and 3HH columns) using $CHCl_3$ as an eluent. UV–vis–NIR absorption spectra were recorded on a SHIMADZU UV-3600i Plus spectrophotometer. Fluorescence (FL) and excitation spectra were recorded on a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer with PMT P928 (250–810 nm) and DSS-IGA (810–1100 nm) as detectors. Absolute FL quantum yield (Φ_{FL}) was recorded on a Hamamatsu Photonics Quantaurus-QY Plus C13534-01 with an integral sphere. A FL lifetime measurement was performed on a Horiba DeltaFlex spectrofluorometer system; excitation was carried out by using UV diode lasers (DeltaDiode 375 and 504 nm, DD-375L and DD-510L, respectively). Photoradial generation was conducted by UVP Benchtop UV Transilluminator (365 nm), LMS-20(3UV), 254/302/365 nm, 100V, 8W or by Compact UV Lamp, 4W, UVGL-15, 254/365nm, 115V as a handy lamp.

Materials

Commercially available compounds used without purification:

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (FUJIFILM Wako Pure Chemical Industries, Ltd.)

Diphenylphosphoryl azide (DPPA) (Tokyo Chemical Industry Co, Ltd.)

Trimethylsilyl trifluoromethanesulfonate (TMSOTf) (Tokyo Chemical Industry Co, Ltd.)

N-Ethyldiisopropylamine (DIEA) (FUJIFILM Wako Pure Chemical Industries, Ltd.)

$Pd_2(dba)_3$ (dba = dibenzylideneacetone) (Strem Chemicals, Inc.)

2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos) (Strem Chemicals, Inc.)

N,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDTA) (Tokyo Chemical Industry Co, Ltd.)

Copper(I) bromide (CuBr) (FUJIFILM Wako Pure Chemical Industries, Ltd.)

1-Ethynylpyrene (Tokyo Chemical Industry Co, Ltd.)

Commercially available solvents:

Acetonitrile (deoxidized grade, FUJIFILM Wako Pure Chemical Industries, Ltd.) and toluene (deoxidized grade, FUJIFILM Wako Pure Chemical Industries, Ltd.) were used without purification.

THF (Kanto Chemical Co., Inc.) was purified by passage through solvent purification columns under N_2 pressure.[1]

Compounds prepared as described in the literatures:

Potassium 4-(hydroxy-methyl)phenyltrifluoroborate (**1**)[2]

4,4′-(Diazene-1,2-diyl)bis(1-bromo-3-hydroxybenzene) (**OH-Br**)[3]

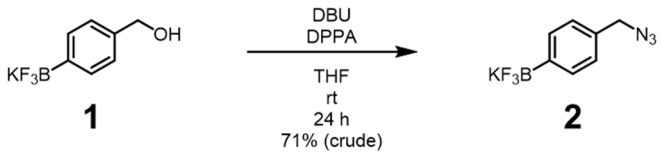
5,5′-Bis(trimethylstannyl)-3,3′-didodecyl-2,2′-bithiophene (**BT**)[4,5]

4,4′-(Diazene-1,2-diyl)bis(1-bromo-3-methoxybenzene) (**OMe-Br**)[3]

5-Trimethylstannyl-3,3′-didodecyl-2,2′-bithiophene (**3**)[3]

Synthetic Procedures and Characterization

Synthesis of potassium 4-(azidomethyl)phenyltrifluoroborate (2)



To a solution of the potassium 4-(hydroxymethyl)phenyltrifluoroborate (**1**) (0.642 g, 3.00 mmol) in dry THF (15 mL) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.58 mL, 3.90 mmol) and diphenylphosphoryl azide (DPPA) (0.77 mL, 3.60 mmol) at room temperature under nitrogen. After stirring for 24 h, 1 N HCl was added to quench the reaction. The mixture was extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ solution, brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was semi-purified with column chromatography on SiO_2 ($CHCl_3$ to $CHCl_3$/MeOH = 19/1 v/v as eluents). The resulting crude **2** as a pale-yellow liquid (0.509 g, 2.13 mmol, crude yield of 71%) was used in the subsequent step without further purification. The spectral data of ^1H NMR were identical with the literature reference.[6]

^1H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H), 4.38 (s, 2H) ppm.

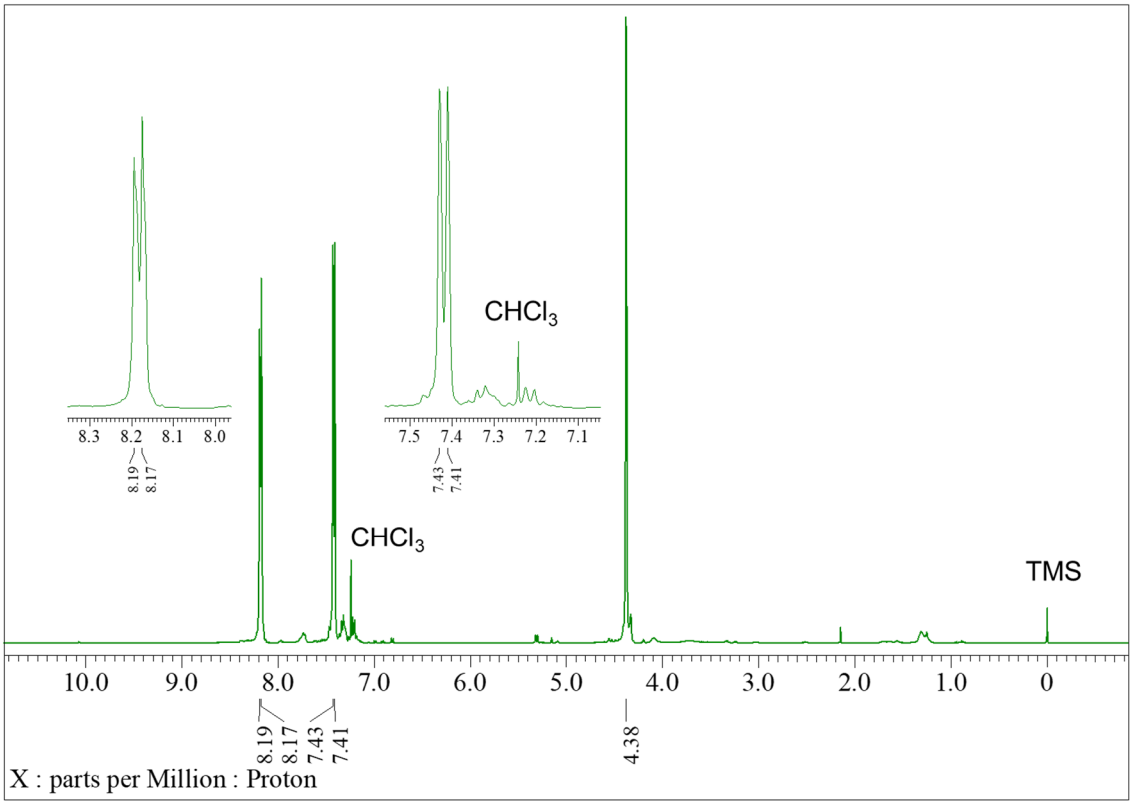
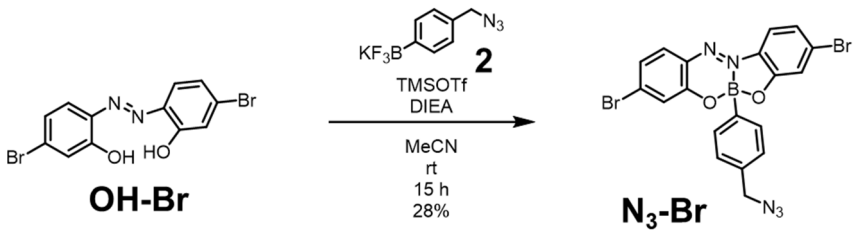


Chart S1. ^{1}H NMR spectrum of **2** in $CDCl_3$, 400 MHz.

Synthesis of N_3-Br



Potassium 4-(azidomethyl)phenyltrifluoroborate (0.359 g, 1.50 mmol), trimethylsilyl trifluoromethanesulfonate (TMSOTf) (0.90 mL, 5.00 mmol), and *N*-ethyldiisopropylamine (DIEA) (0.43 mL, 2.50 mmol) were added to a stirred solution of 4,4′-(diazene-1,2-diyl)bis(1-bromo-3-hydroxybenzene) (**OH-Br**) (0.372 g, 1.00 mmol) in MeCN (10 mL), and the mixture was stirred at room temperature for 2 h. The mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified with column chromatography on SiO_2 (hexane/CH_2Cl_2 = 1/1 v/v as an eluent) to afford **N_3-Br** as a red solid (0.293 g, 0.57 mmol, 57%).

R_f = 0.40 (hexane/CH_2Cl_2 = 1/1 v/v). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 7.69 (d, J = 8.7 Hz, 1H), 7.64 (d, J = 8.7 Hz, 1H), 7.45 (d, J = 2.3 Hz, 1H), 7.41 (d, J = 1.8 Hz, 1H), 7.27–7.23 (m, 2H), 7.24 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 4.23 (s, 2H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 162.9, 146.1, 139.4, 135.8, 132.7, 132.7, 132.2, 132.1, 132.0, 127.6, 125.7, 125.2, 123.4, 112.0, 117.8, 54.7 ppm; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 6.12 ppm. HRMS (ESI) calcd. for $C_{19}H_{12}BBr_2N_5O_2$ $[M]^-$: 510.9456, found: 510.9461. Elemental analysis calcd. for $C_{19}H_{12}BBr_2N_5O_2$: C 44.49 H 2.36 N 13.65, found: C 44.37 H 2.44 N 13.57.

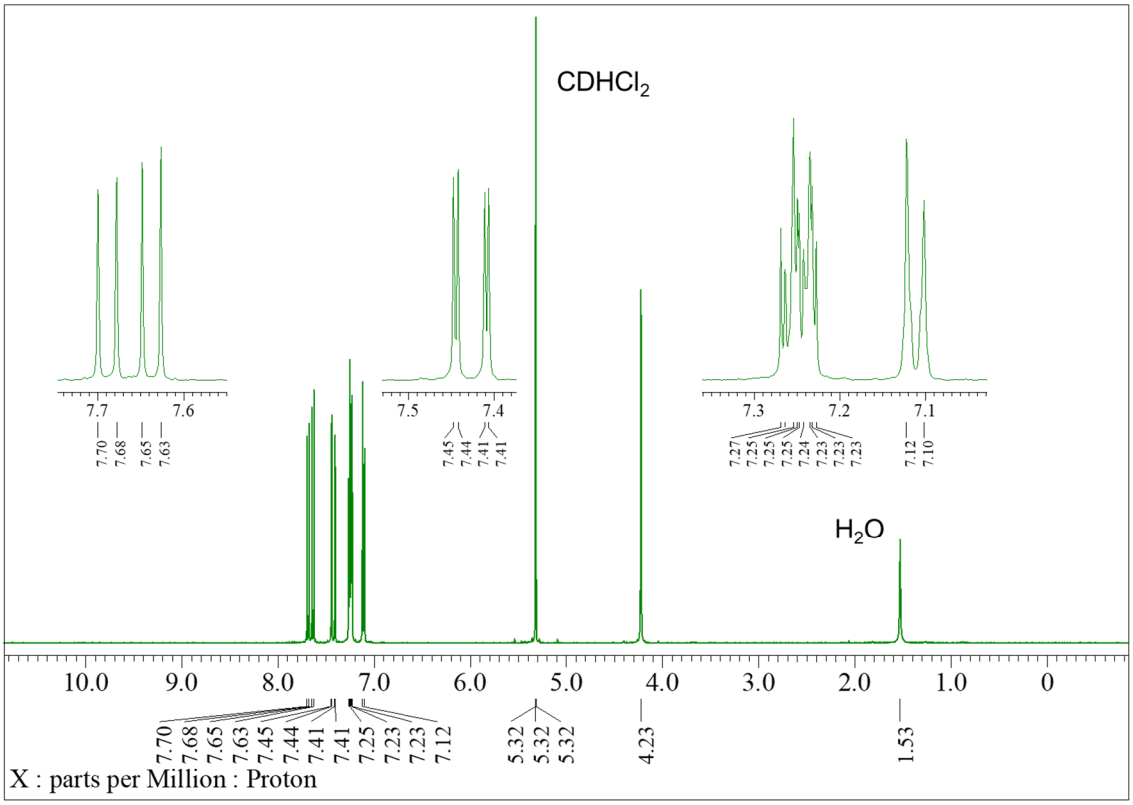


Chart S2. ^{1}H NMR spectrum of **N_3-Br** in CD_2Cl_2, 400 MHz.

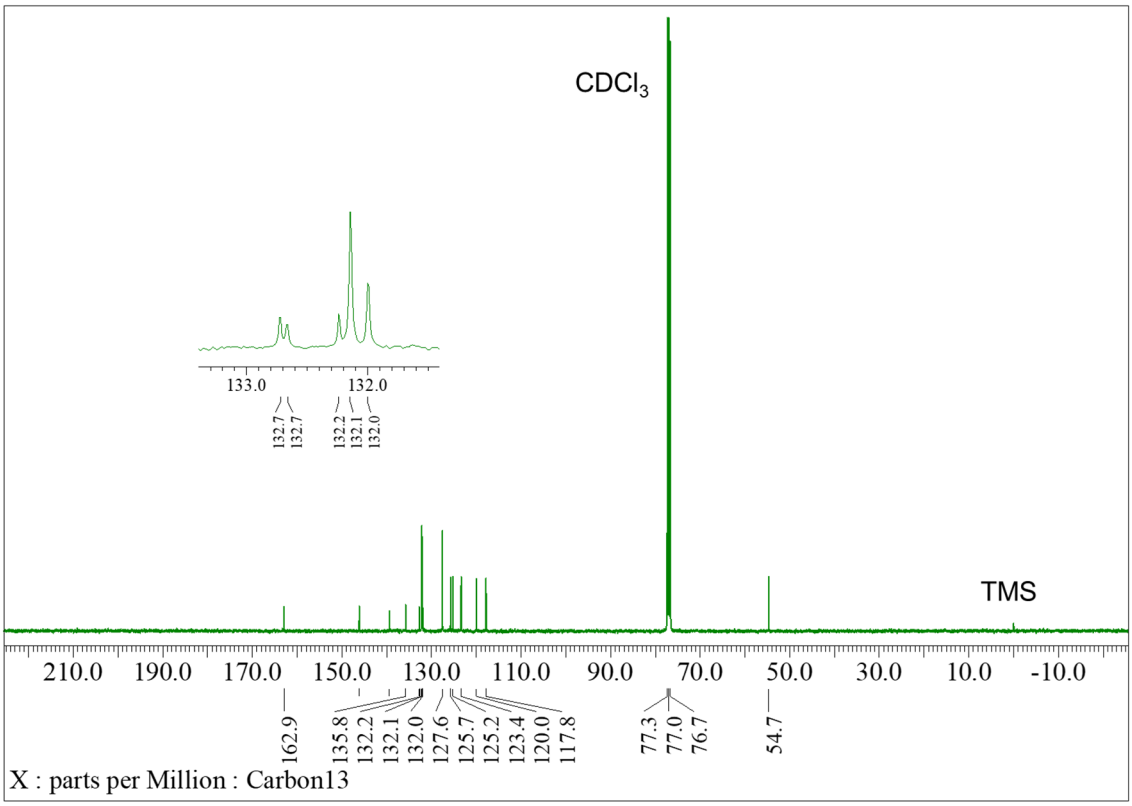


Chart S3. $^{13}C\{^{1}H\}$ NMR spectrum of **N_3-Br** in $CDCl_3$, 100 MHz.

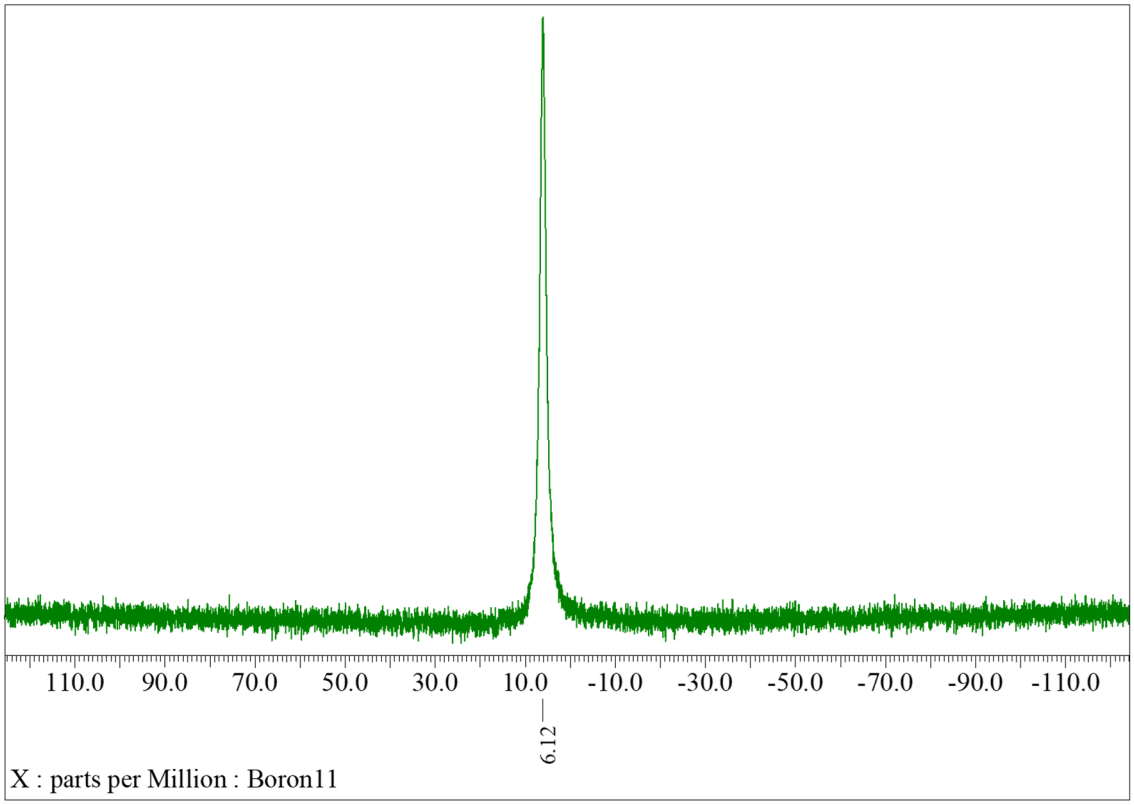


Chart S4. ^{11}B NMR spectrum of **N_3-Br** in $CDCl_3$, 128 MHz.

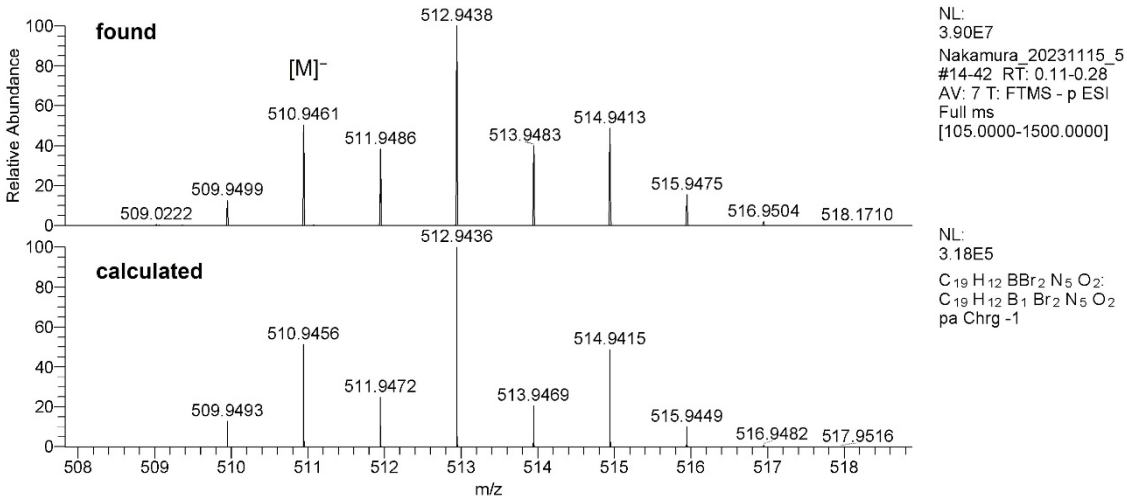
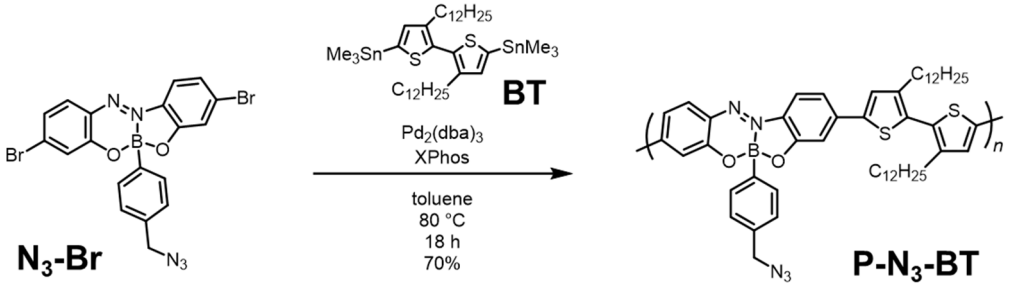


Chart S5. HRMS spectra of **N_3-Br**.

Synthesis of P-N_3-BT



A mixture of **N_3-Br** (38.5 mg, 0.075 mmol), 5,5′-bis(trimethylstannyl)-3,3′-didodecyl-2,2′-bithiophene (**BT**) (62.1 mg, 0.075 mmol), $Pd_2(dba)_3$ (2.1 mg, 0.0020 mmol), and XPhos (2.1 mg, 0.0050 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing and filling N_2 three times, toluene (1.5 mL) was added to the mixture. The reaction was carried out at 80 °C for 18 h. After the reaction, the small amount of $CHCl_3$ was added to the solution. The solution was passed through the aluminium oxide (Al_2O_3) column, and the eluent was directly added to MeOH to reprecipitate the polymer product. The polymer collected by filtration was dried *in vacuo* to afford **P-N_3-BT** (45 mg, 70%) as a black solid.

M_n = 15,100, M_w = 38,300, M_w/M_n = 2.54. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 7.80 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.51–7.34 (m, 8H), 7.12 (d, J = 8.3 Hz, 2H), 4.23 (s, 2H), 2.64 (br, 4H), 1.64 (br, 4H), 1.29–1.24 (br, 36H), 0.86 (t, J = 6.9 Hz, 6H) ppm; ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz) δ 163.2, 147.1, 145.2, 145.1, 142.9, 142.3, 142.5, 142.5, 140.6, 135.9, 133.4, 132.6, 131.9, 131.9, 131.8, 131.3, 131.3, 128.6, 128.1, 127.9, 119.8, 119.6, 117.7, 115.7, 111.7, 55.1, 32.3, 31.0, 30.1, 30.0, 29.8, 29.5, 23.1, 14.3 ppm; ^{11}B NMR (CD_2Cl_2, 128 MHz) δ 4.19 ppm.

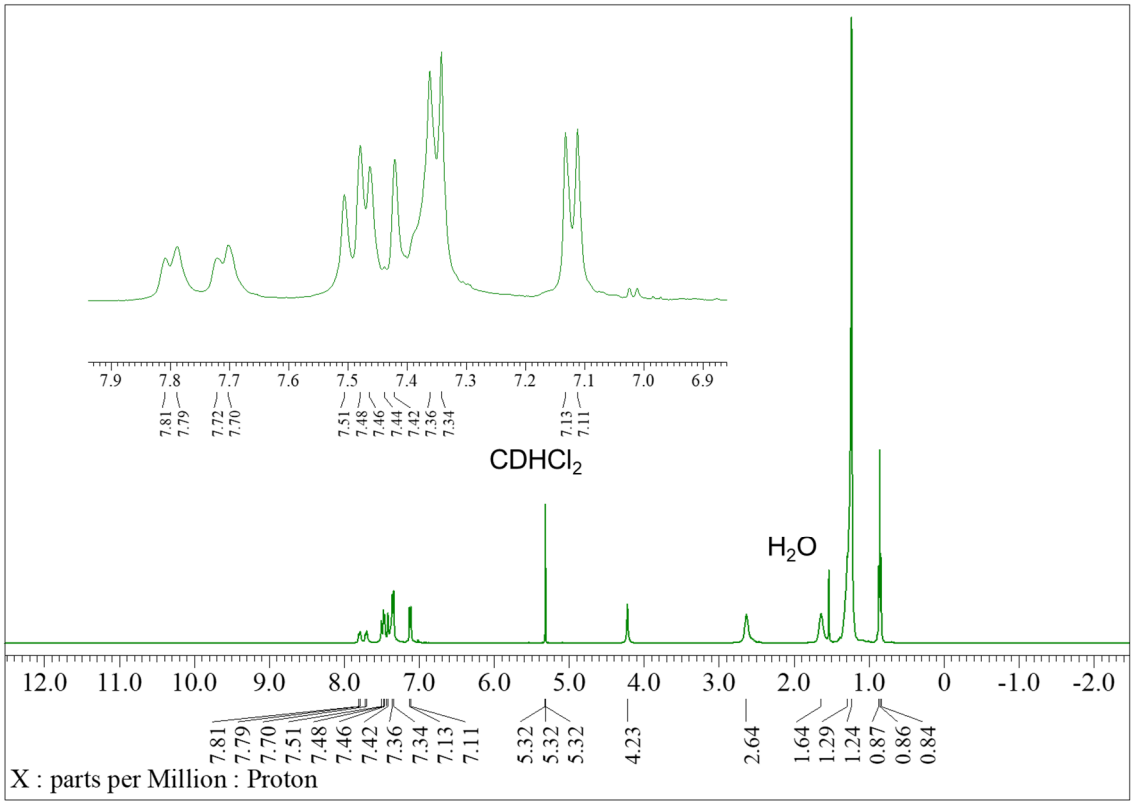


Chart S6. ^{1}H NMR spectrum of **P-N$_3$-BT** in CD_2Cl_2, 400 MHz.

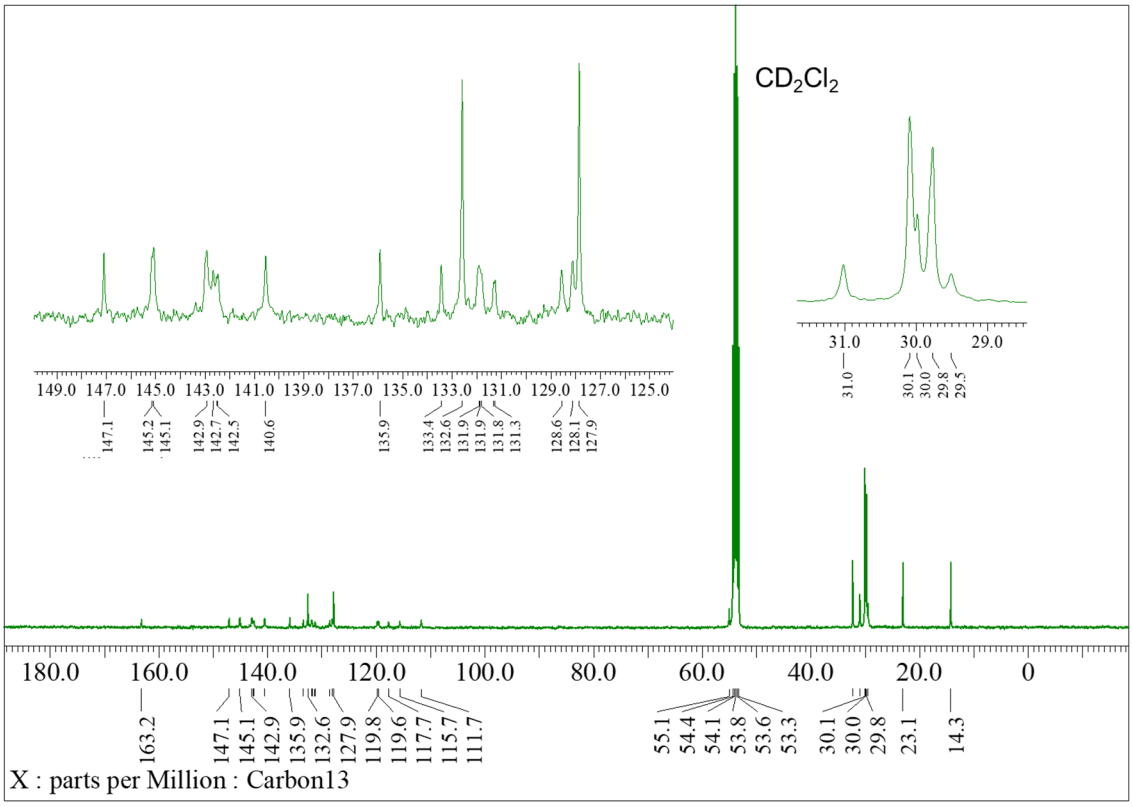


Chart S7. $^{13}C\{^{1}H\}$ NMR spectrum of **P-N$_3$-BT** in CD_2Cl_2, 100 MHz.

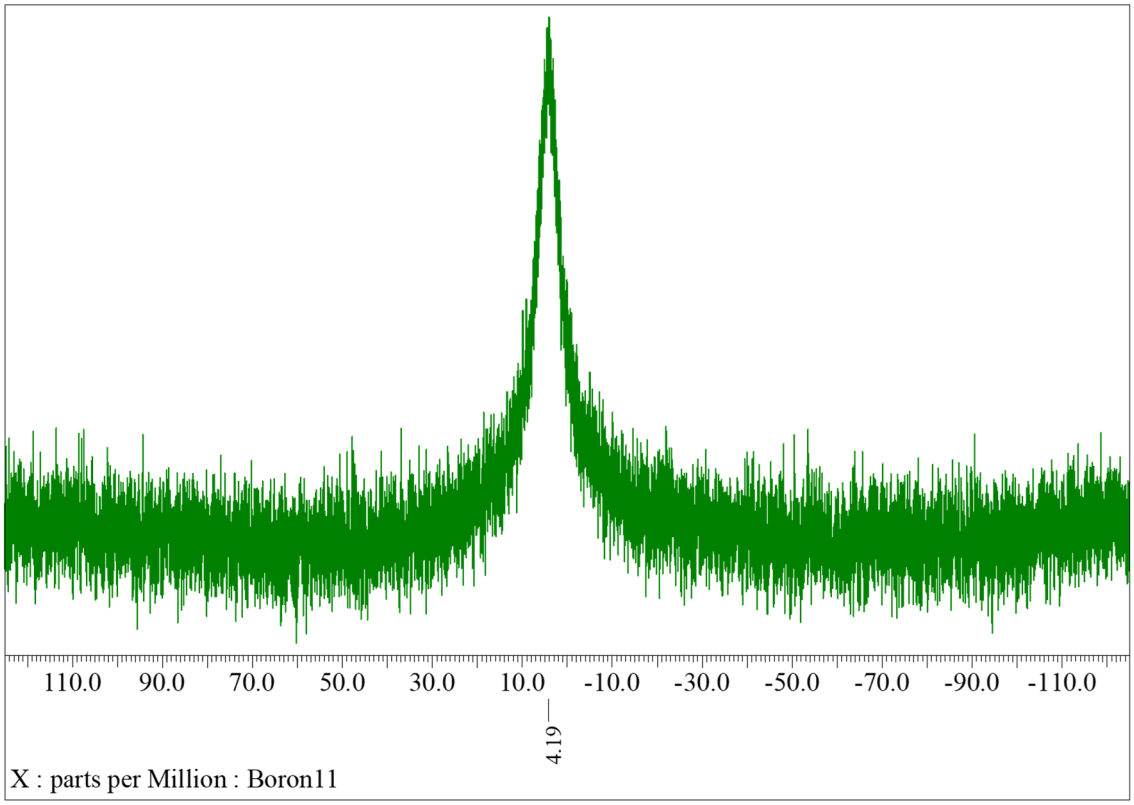
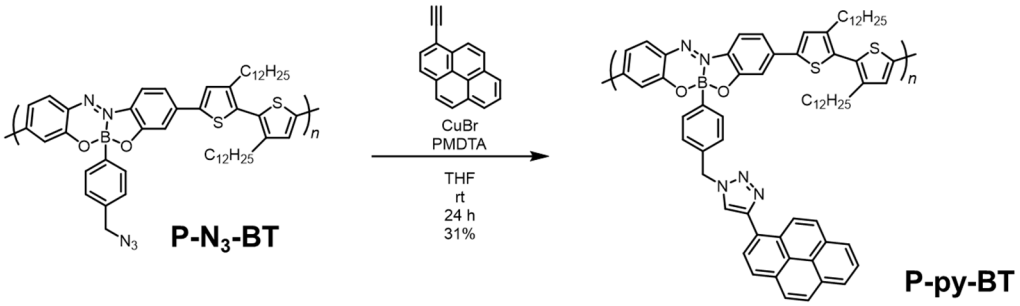


Chart S8. ^{11}B NMR spectrum of **P-N$_3$-BT** in CD_2Cl_2, 128 MHz.

Synthesis of P-py-BT



A mixture of **P-N$_3$-BT** (34.2 mg, 0.040 mmol), 1-ethynylpyrene (10.9 mg, 0.048 mmol), and copper(I) bromide (CuBr) (1.8 mg, 0.0096 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing and filling N_2 three times, THF (2.0 mL) and *N*,*N*′,*N*″,*N*‴-pentamethyldiethylenetriamine (PMDTA) (0.010 mL, 0.048 mmol) were added to the mixture. After stirring for 24 h at room temperature, the mixture was quenched by 28% aqueous NH_3 solution and extracted with $CHCl_3$. The organic layer was washed with brine dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was semi-purified with column chromatography on SiO_2 ($CHCl_3$ as an eluent) and reprecipitation with $CHCl_3$ (as a good solvent) and MeOH (as a poor solvent). The precipitate was purified by HPLC ($CHCl_3$ as an eluent) to afford **P-py-BT** (16 mg, 31%) as a black solid.

M_n = 14,400, M_w = 30,900, M_w/M_n = 2.15. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.64 (d, J = 6.2 Hz, 1H), 8.16–8.15 (br, 4H), 8.07–7.97 (m, 4H), 7.77 (br, 2H), 7.69 (d, J = 4.9 Hz, 1H), 7.45–7.31 (m, 8H), 7.22 (d, J = 5.2 Hz, 2H), 5.60 (s, 2H) ppm, 2.58 (br, 4H), 1.59 (br, 4H), 1.25–1.21 (br, 36H), 0.84 (t, J = 4.7 Hz, 6H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ 162.8, 147.8, 146.6, 144.6, 144.5, 142.6, 142.5, 142.3, 142.4, 140.2, 134.4, 133.0, 132.6, 131.6, 131.4, 131.3, 131.2, 130.9, 128.5, 128.1, 128.0, 127.8, 127.6, 127.3, 127.1. 126.0, 125.3, 125.1, 124.8, 124.8, 124.7, 122.7, 119.6, 119.3, 117.3, 115.4, 111.6, 54.4, 31.9, 30.7, 29.7, 29.7, 29.6, 29.4, 29.4, 29.1, 22.7, 14.1 ppm; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 4.65 ppm.

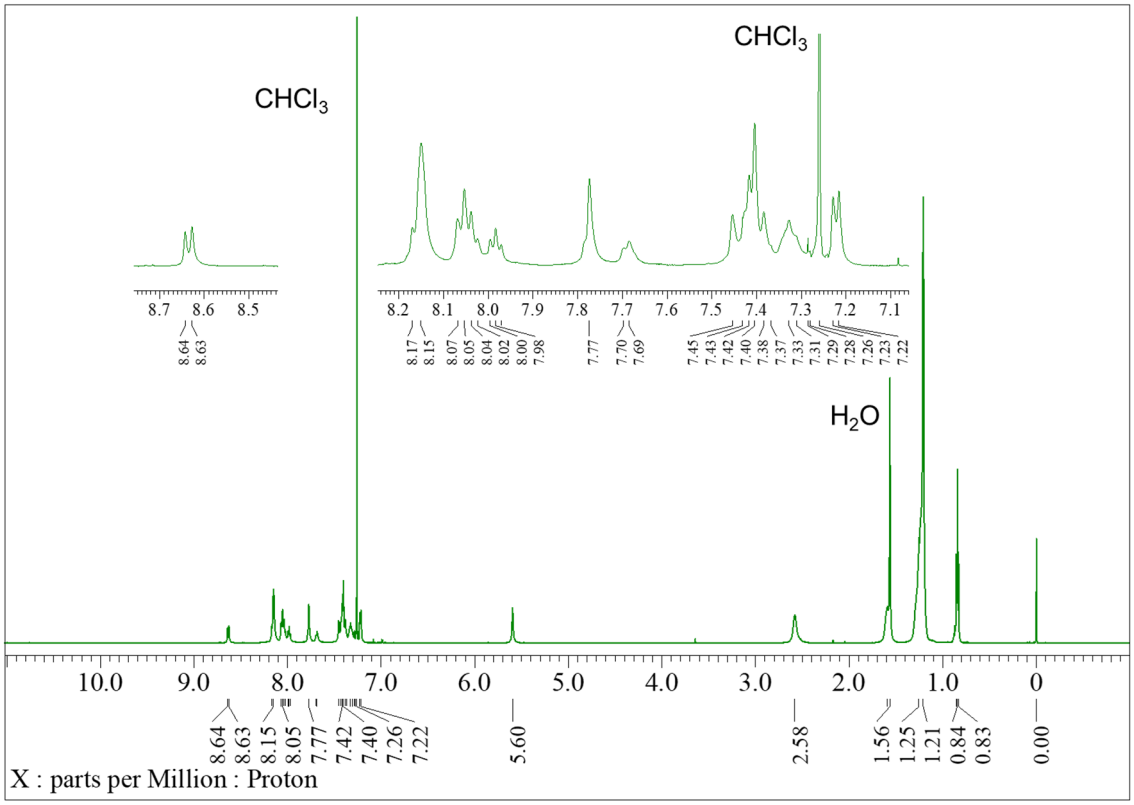


Chart S9. ^{1}H NMR spectrum of **P-py-BT** in $CDCl_3$, 600 MHz.

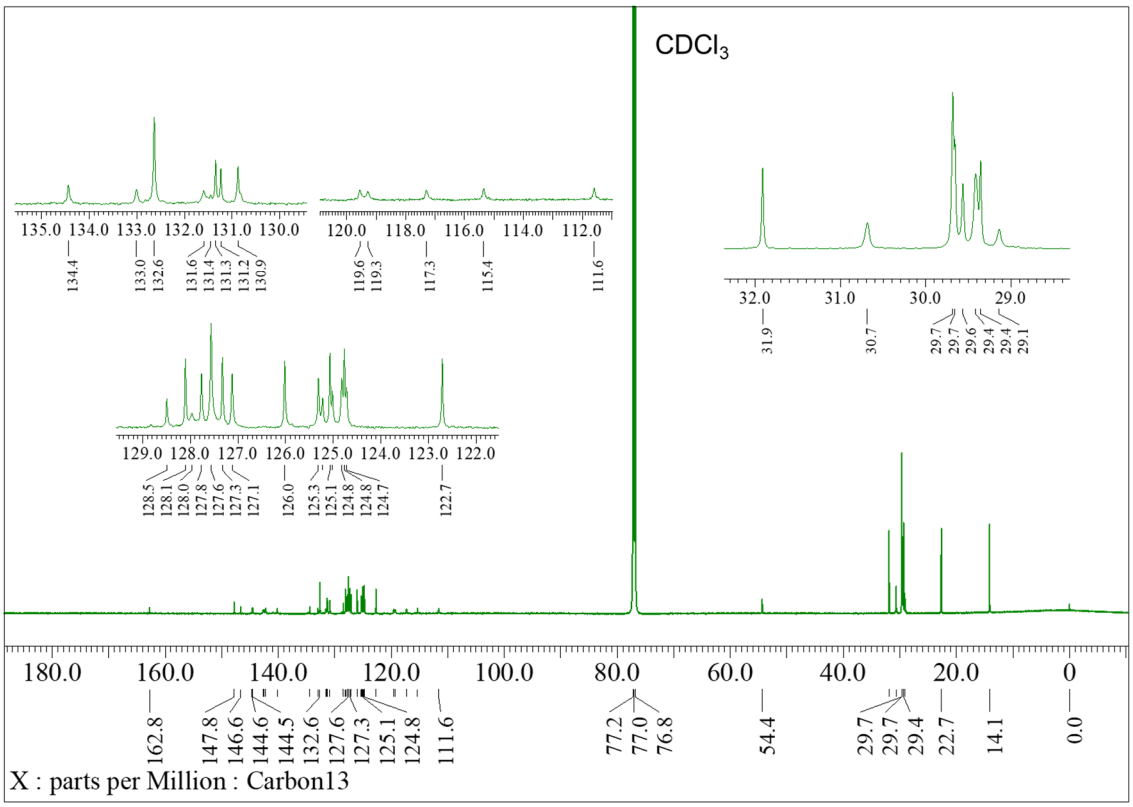


Chart S10. $^{13}C\{^{1}H\}$ NMR spectrum of **P-py-BT** in $CDCl_3$, 151 MHz.

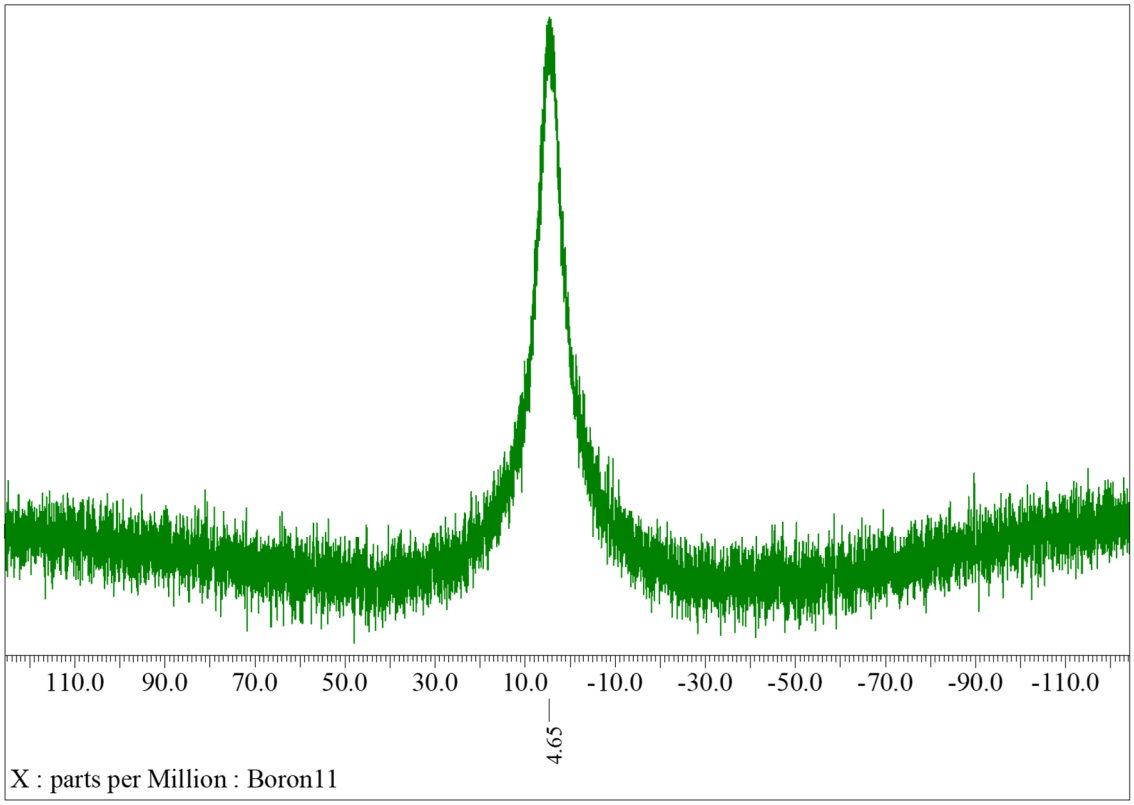
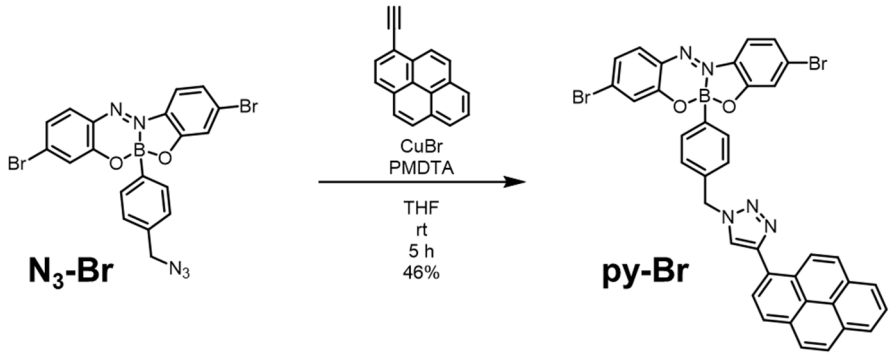


Chart S11. ^{11}B NMR spectrum of **P-py-BT** in $CDCl_3$, 128 MHz.

Synthesis of py-Br



A mixture of **N3-Br** (48.2 mg, 0.10 mmol), 1-ethynylpyrene (30.9 mg, 0.12 mmol), and copper(I) bromide (CuBr) (2.3 mg, 0.012 mmol) were placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing and filling N_2 three times, THF (2.5 mL) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDTA) (0.025 mL, 0.012 mmol) were added to the mixture. After stirring for 5 h at room temperature, the mixture was quenched by 28% aqueous NH_3 solution and extracted with EtOAc. The organic layer was washed with brine dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified with column chromatography on SiO_2 (CH_2Cl_2/hexane = 1/1 v/v to CH_2Cl_2 as eluents) and following HPLC ($CHCl_3$ as an eluent). The concentrated fraction was reprecipitated from MeOH to afford **py-Br** (34 mg, 0.046 mmol 46%) as a red solid.

R_f = 0.56 (hexane/CH_2Cl_2 = 1/1 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.63 (d, J = 9.2 Hz, 1H), 8.19–8.15 (m, 4H), 8.09–7.98 (m, 4H), 7.77 (s, 1H), 7.62 (d, J = 8.7 Hz, 1H), 7.56 (d, J = 8.7 Hz, 1H), 7.40 (d, J = 1.8 Hz, 1H), 7.38 (d, J = 1.8 Hz, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.21–7.17 (m, 4H), 5.58 (s, 2H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ 162.8, 147.8, 146.0, 139.3, 134.9, 132.8, 132.6, 132.5, 132.3, 132.0, 131.3, 131.2, 130.9, 128.5, 128.1, 127.8, 127.6, 127.3, 127.1, 126.1, 125.8, 125.4, 125.3, 125.1, 125.1, 125.0, 124.8, 124.8, 124.7, 123.3, 122.7, 119.9, 117.8, 54.2 ppm; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 6.02 ppm. HRMS (ESI) calcd. for $C_{37}H_{22}BBr_2N_5O_2Na$ $[M+Na]^+$: 760.0126, found: 760.0152. Elemental analysis calcd. for $C_{37}H_{22}BBr_2N_5O_2$: C 60.12 H 3.00 N 9.47, found: C 59.97 H 2.94 N 9.34.

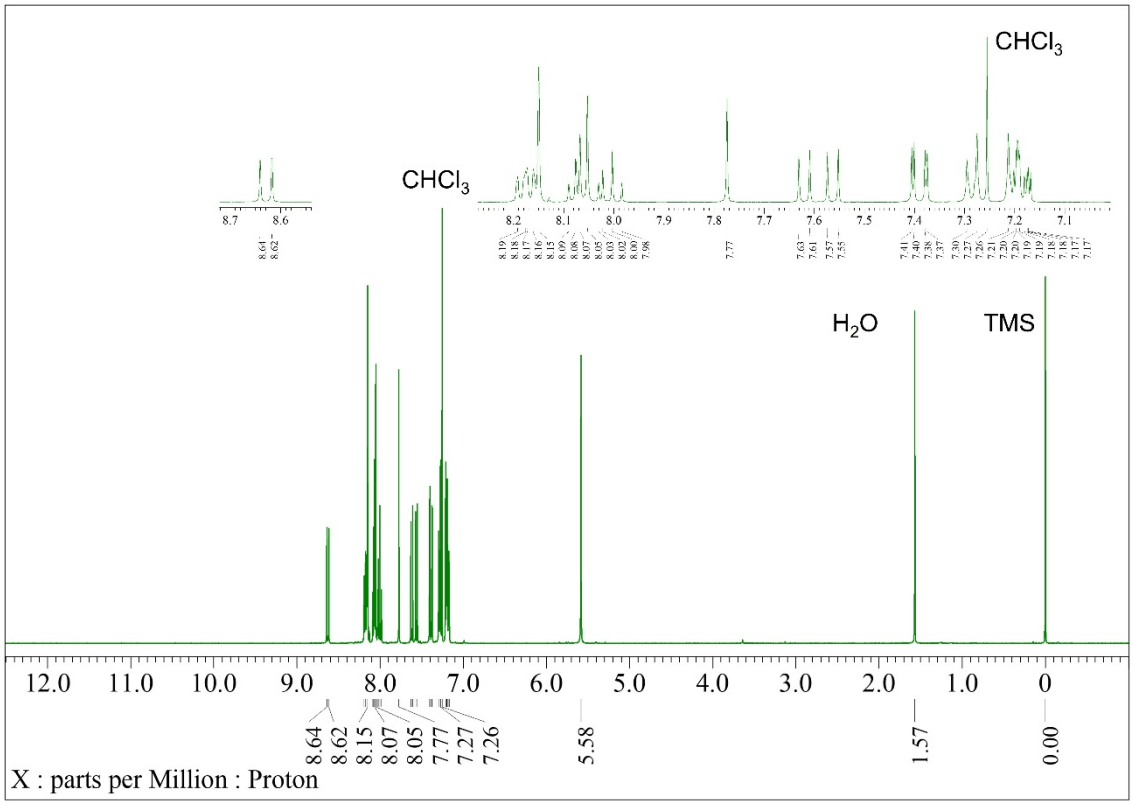


Chart S12. ^{1}H NMR spectrum of **py-Br** in $CDCl_3$, 400 MHz.

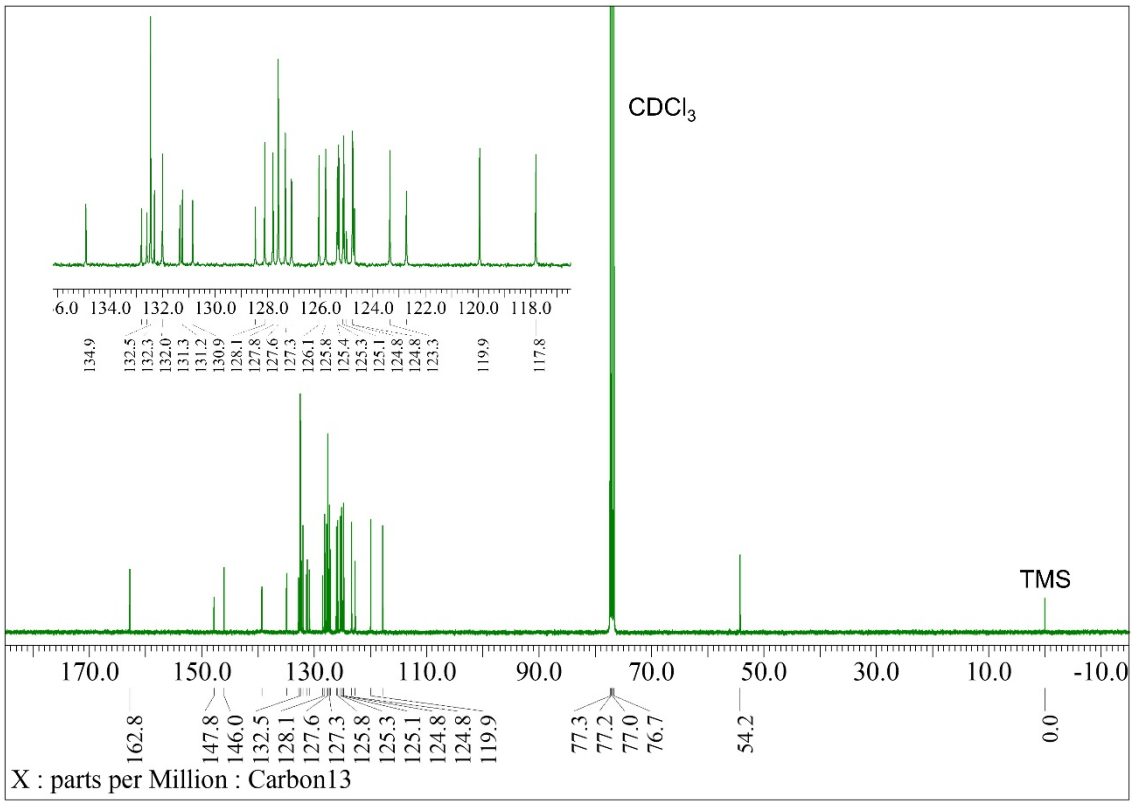


Chart S13. $^{13}C\{^{1}H\}$ NMR spectrum of **py-Br** in $CDCl_3$, 100 MHz.

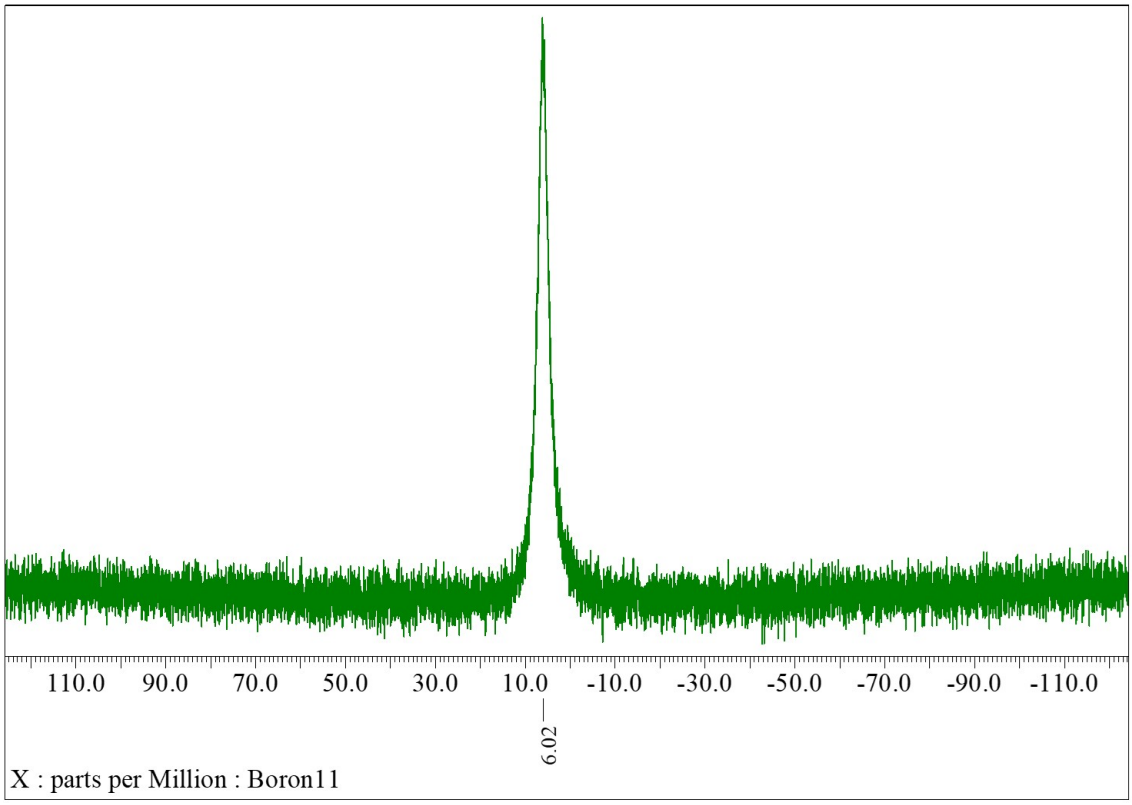
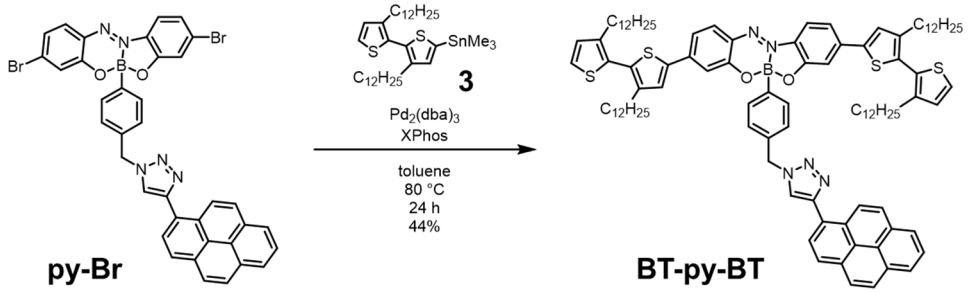


Chart S14. ^{11}B NMR spectrum of **py-Br** in $CDCl_3$, 128 MHz.

Synthesis of BT-py-BT



A mixture of **py-Br** (8.4 mg, 0.011 mmol), 5-trimethylstannyl-3,3′-didodecyl-2,2′-bithiophene (**3**) (16.6 mg, 0.025 mmol), $Pd_2(dba)_3$ (3.1 mg, 0.0033 mmol), and XPhos (3.3 mg, 0.0066 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing and filling N_2 three times, toluene (2.0 mL) was added to the mixture. The reaction was carried out at 80 °C for 24 h. After the reaction, the solution was purified by column chromatography on basic alumina ($CHCl_3$ as an eluent), HPLC ($CHCl_3$ as an eluent), and column chromatography on SiO_2 (CH_2Cl_2 as an eluent) to afford **BT-py-BT** (8.0 mg, 0.0050 mmol, 44%) as a dark blue oil.

R_f = 0.55 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.64 (d, J = 9.2 Hz, 1H), 8.19–8.16 (m, 4H), 8.09–8.04 (m, 3H), 8.00 (t, J = 7.6 Hz, 1H), 7.77 (s, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.44 (d, J = 1.9 Hz, 1H), 7.41–7.39 (m, 4H), 7.36 (s, 1H), 7.33–7.30 (m, 4H), 7.21 (d, J = 8.3 Hz, 1H), 6.98 (d, J = 5.3 Hz, 1H), 5.59 (s, 2H), 2.56–2.50 (m, 8H), 1.58–1.54 (m, 8H), 1.30–1.21 (br, 72H), 0.88–0.84 (m, 12H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz) δ 162.7 (1C), 147.8 (1C), 146.6 (1C), 144.3 (1C), 144.1 (1C), 142.8 (3C), 142.5 (1C), 142.0 (1C), 141.6 (1C), 140.9 (1C), 140.1 (1C), 134.3 (1C), 132.8 (1C), 132.7 (2C), 132.5 (1C), 131.9 (1C), 131.5 (1C), 131.4 (1C), 131.2 (1C), 130.9 (1C), 128.8 (2C), 128.5 (1C), 128.1 (1C), 127.9–127.7 (4C), 127.6 (2C), 127.3 (2C), 127.2 (1C), 126.0 (1C), 125.9–125.8 (2C), 125.3 (2C), 125.1–125.0 (2C), 124.9 (1C), 124.8–124.7 (2C), 122.7 (1C), 119.5 (1C), 119.2 (1C), 117.2 (1C), 115.2 (1C), 111.4 (1C), 54.4 (1C), 31.9 (4C), 30.7–30.7 (4C), 29.7–29.7 (12C), 29.6–29.5 (4C), 29.4–29.4 (12C), 29.0–28.9 (4C), 22.7 (4C), 14.1 (4C) ppm; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 0.97 ppm. HRMS (ESI) calcd. for $C_{101}H_{128}BN_5O_2S_4Na$ $[M+Na]^+$: 1604.8936, found: 1604.8973.

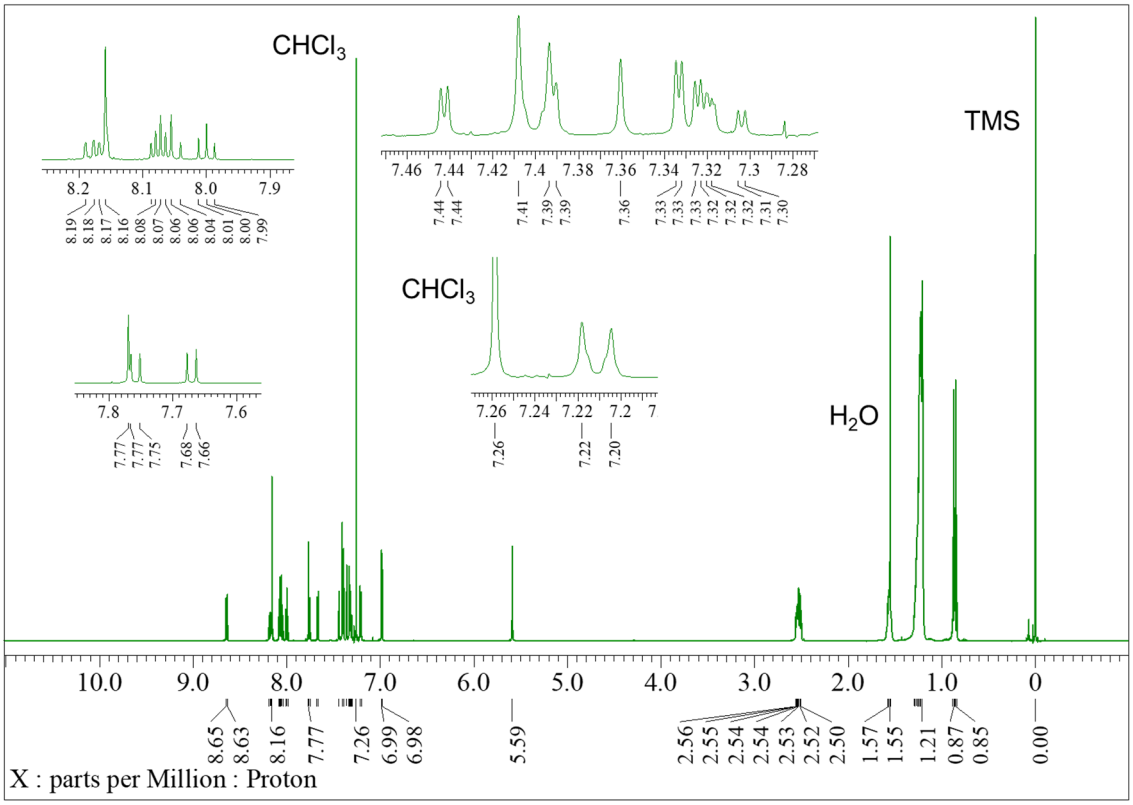


Chart S15. ^{1}H NMR spectrum of **BT-py-BT** in $CDCl_3$, 600 MHz.

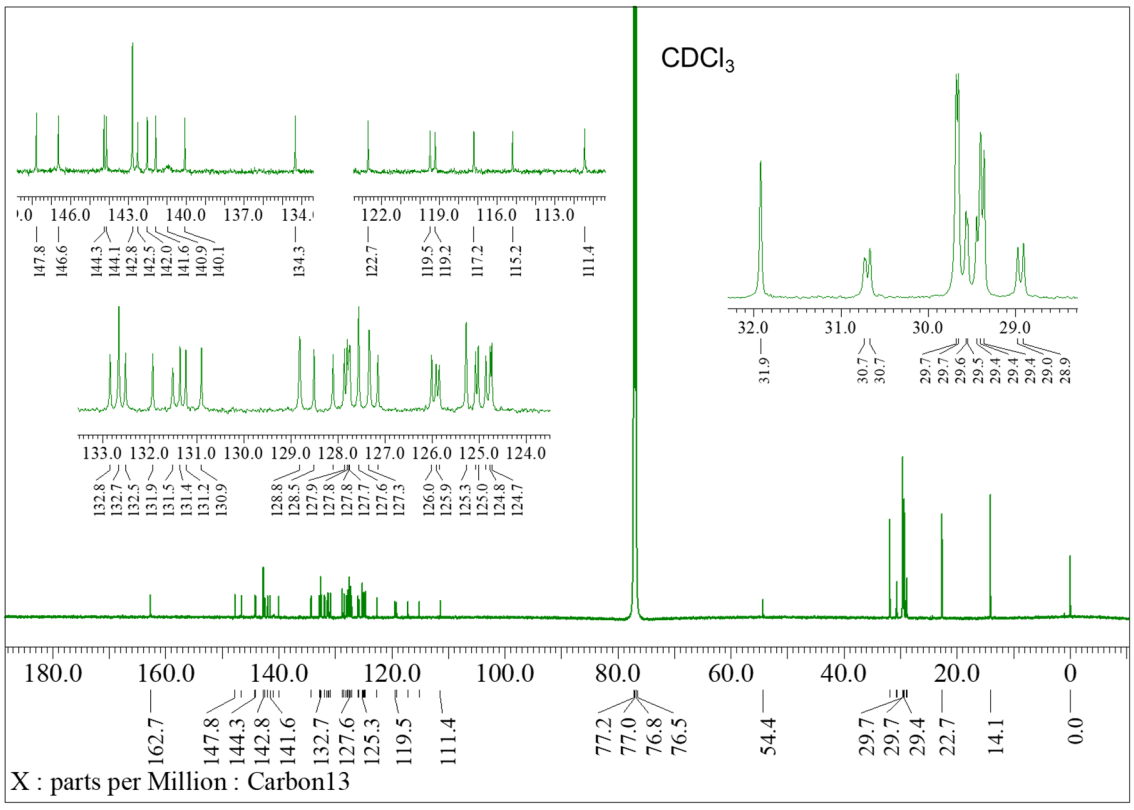


Chart S16. $^{13}C\{^{1}H\}$ NMR spectrum of **BT-py-BT** in $CDCl_3$, 151 MHz with inverse gated decoupling.

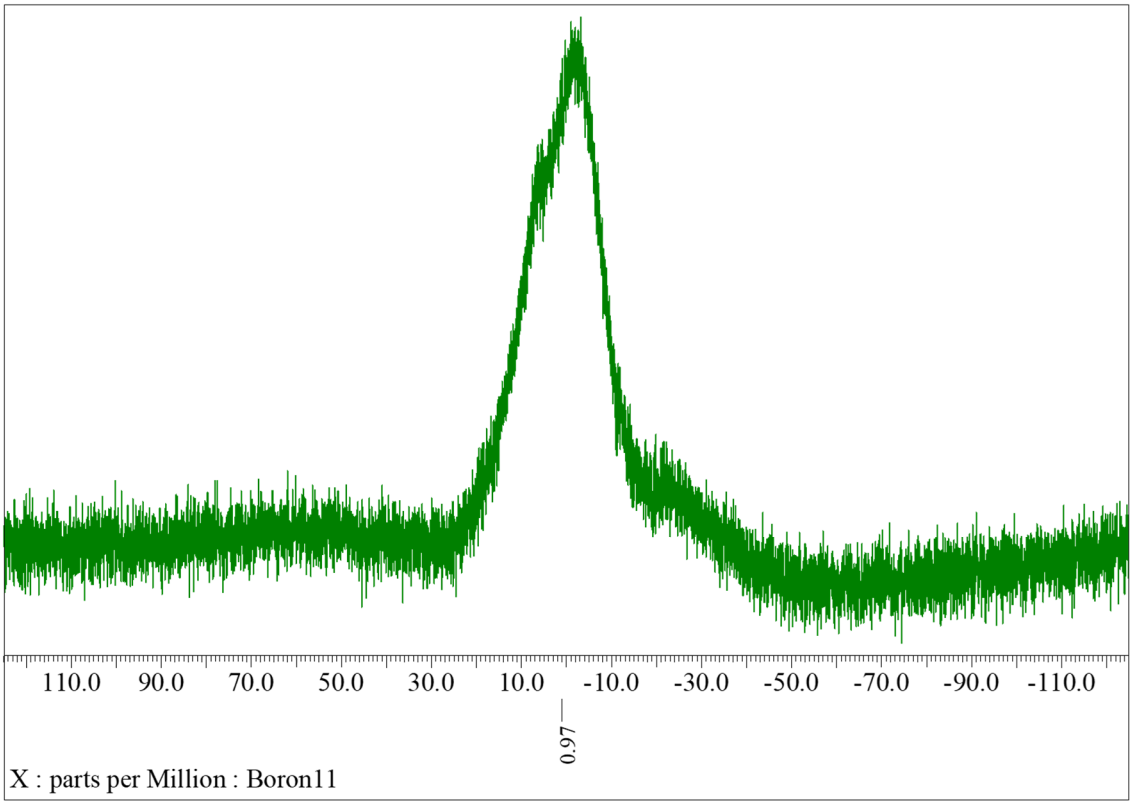
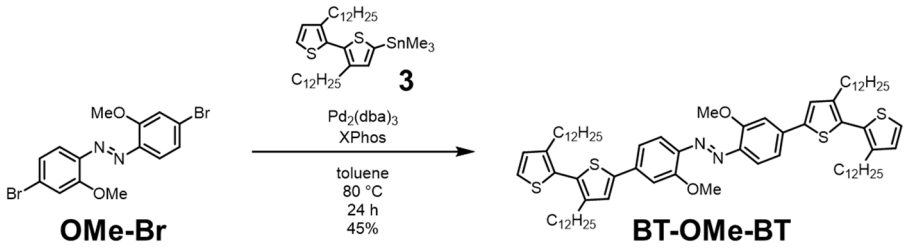


Chart S17. ^{11}B NMR spectrum of **BT-py-BT** in $CDCl_3$, 128 MHz.

Synthesis of BT-OMe-BT



A mixture of **OMe-Br** (40.0 mg, 0.10 mmol), 5-trimethylstannyl-3,3′-didodecyl-2,2′-bithiophene (**3**) (147 mg, 0.22 mmol), $Pd_2(dba)_3$ (2.7 mg, 0.0030 mmol), and XPhos (2.9 mg, 0.0060 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing and filling N_2 three times, toluene (2.0 mL) was added to the mixture. The reaction was carried out at 80 °C for 24 h. After the reaction, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on SiO_2 (hexane/CH_2Cl_2 = 1/1 v/v as an eluent) and further purification was carried out by HPLC ($CHCl_3$ as an eluent) to afford **BT-OMe-BT** (64 mg, 0.045 mmol, 45%) as an orange solid.

R_f = 0.66 (hexane/CH_2Cl_2 = 1/1 v/v). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 7.64 (d, J = 8.2 Hz, 2H), 7.35 (s, 2H), 7.35 (d, J = 5.5 Hz, 2H), 7.31 (d, J = 1.8 Hz, 2H), 7.27 (dd, J = 8.7, 1.8 Hz, 2H), 7.02 (d, J = 5.5 Hz, 2H), 4.09 (s, 6H), 2.60–2.51 (m, 8H), 1.60–1.56 (m, 8H), 1.25–1.23 (br, 72H), 0.88 (t, J = 6.4 Hz, 6H), 0.86 (t, J = 6.9 Hz, 6H) ppm; ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz) δ 157.9, 144.3, 143.2, 143.0, 142.4, 138.5, 130.2, 129.2, 128.6, 126.3, 126.0, 118.4, 117.9, 109.9, 56.8, 32.3, 31.1, 31.0, 30.1, 30.0, 29.8, 29.8, 29.4, 29.3, 23.1, 14.3 ppm. HRMS (ESI) calcd. for $C_{78}H_{118}N_2O_2S_4Na$ $[M+Na]^+$: 1265.7968, found: 1265.7969.

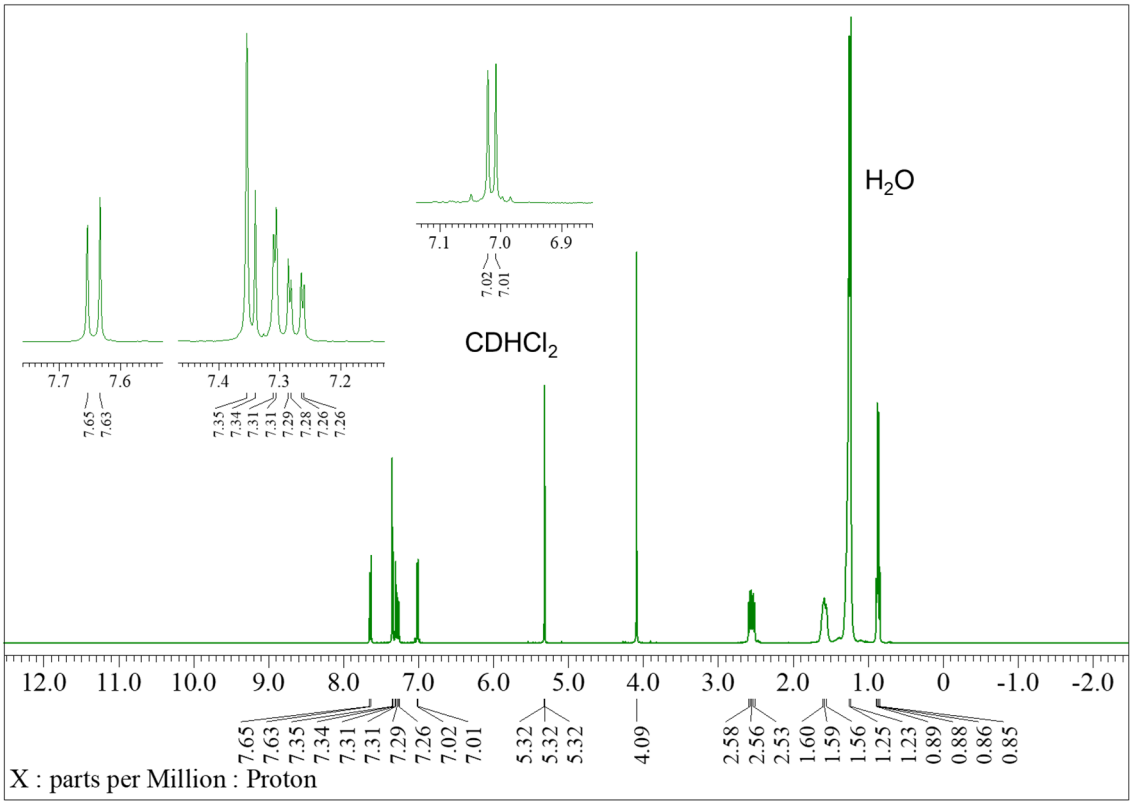


Chart S18. ^{1}H NMR spectrum of **BT-OMe-BT** in CD_2Cl_2, 400 MHz.

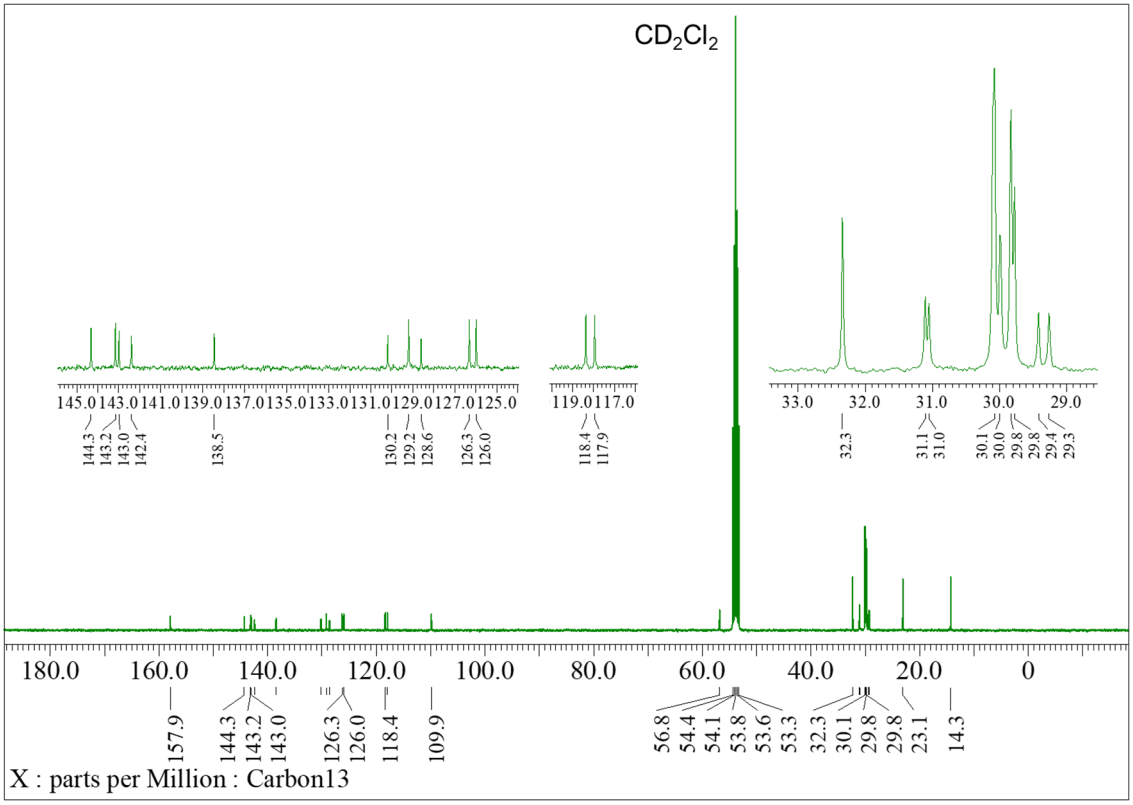
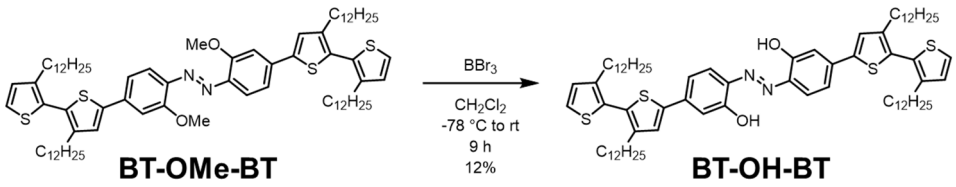


Chart S19. $^{13}C\{^{1}H\}$ NMR spectrum of **BT-OMe-BT** in CD_2Cl_2, 100 MHz.

Synthesis of BT-OH-BT



BT-OMe-BT (54.0 mg, 0.043 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing and filling N_2 three times, CH_2Cl_2 (5.0 mL) was added to the flask. After cooling the mixture to −78 °C, BBr_3 (1 M in CH_2Cl_2, 0.17 mL, 0.17 mmol) was dropwisely added. The reaction was carried out at room temperature for 9 h. After the reaction, MeOH was carefully added at 0 °C for quenching the reaction. Since the target compound was not precipitated, the solvent was evaporated. Then, the residue was extracted with CH_2Cl_2 and purified by column chromatography on SiO_2 (hexane/CH_2Cl_2 = 2/1 v/v as an eluent) to afford **BT-OH-BT** (6.0 mg, 0.0049 mmol, 12%) as an orange solid.

R_f = 0.76 (hexane/CH_2Cl_2 = 2/1 v/v). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 12.43 (s, 2H), 7.71 (d, J = 8.8 Hz, 2H), 7.40 (s, 2H), 7.35 (d, J = 5.4 Hz, 2H), 7.33 (dd, J = 8.3, 2.0 Hz, 2H), 7.26 (d, J = 1.4 Hz, 2H), 7.01 (d, J = 5.4 Hz, 2H), 2.59–2.51 (m, 8H), 1.61–1.55 (m, 8H), 1.25–1.22 (br, 72H), 0.87 (t, J = 6.8 Hz, 6H), 0.86 (t, J = 6.8 Hz, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.5, 143.9, 142.7, 141.8, 134.5, 131.4, 130.9, 128.8, 128.1, 126.7, 125.7, 117.6, 114.4, 31.9, 30.7, 30.7, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 29.0 ,28.9, 22.7, 14.1 ppm. HRMS (ESI) calcd. for $C_{76}H_{113}N_2O_2S_4$ $[M-H]^-$: 1213.7690, found: 1213.7698.

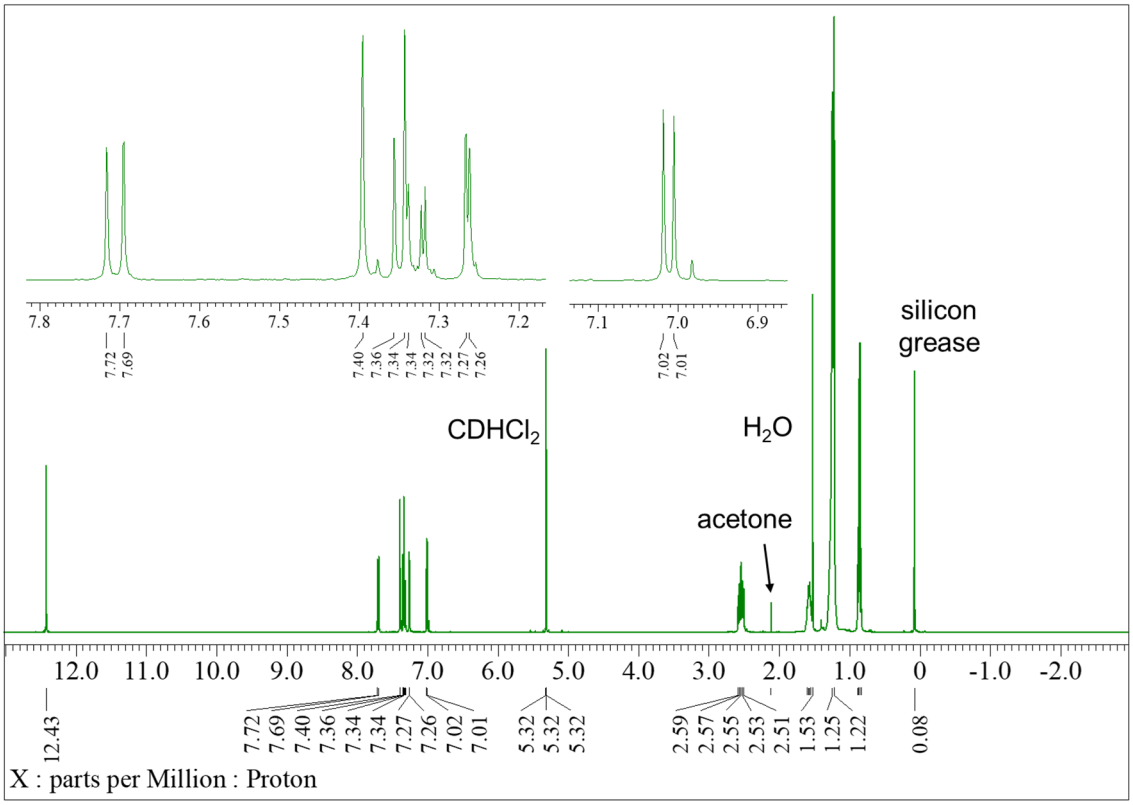


Chart S20. ^{1}H NMR spectrum of **BT-OH-BT** in $CDCl_3$, 400 MHz.

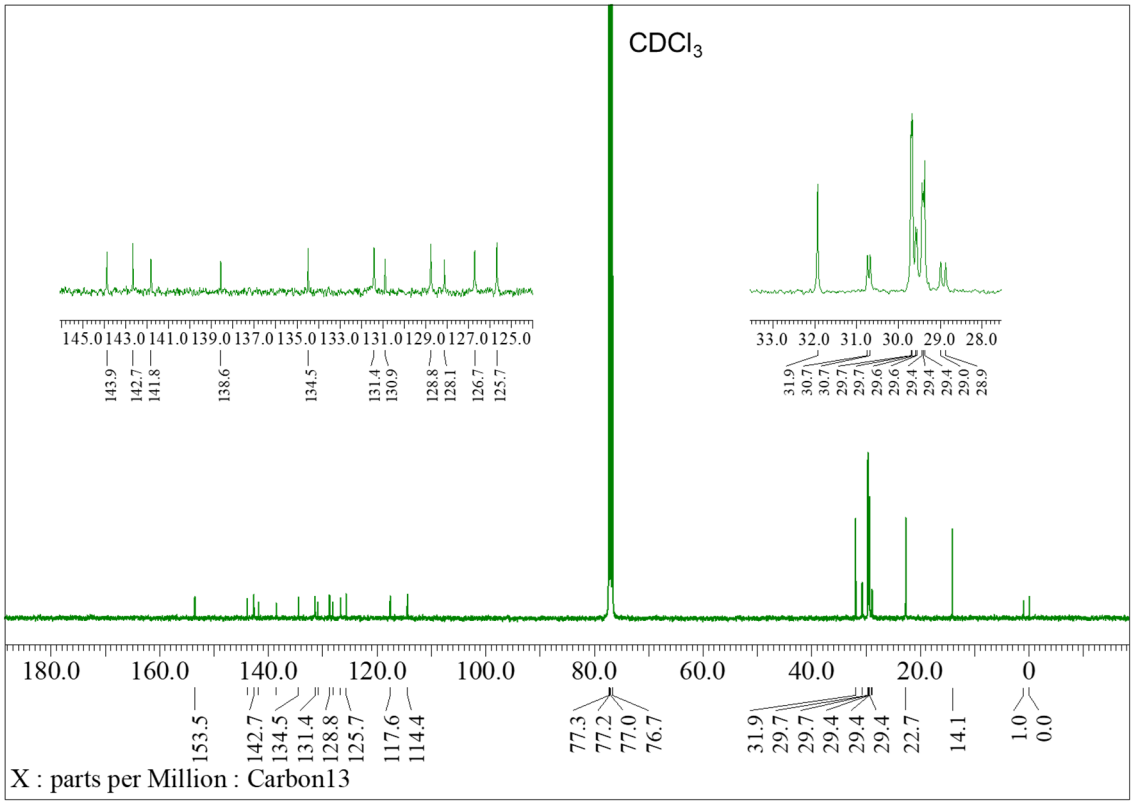


Chart S21. $^{13}C\{^{1}H\}$ NMR spectrum of **BT-OH-BT** in $CDCl_3$, 100 MHz.

FL lifetime measurements

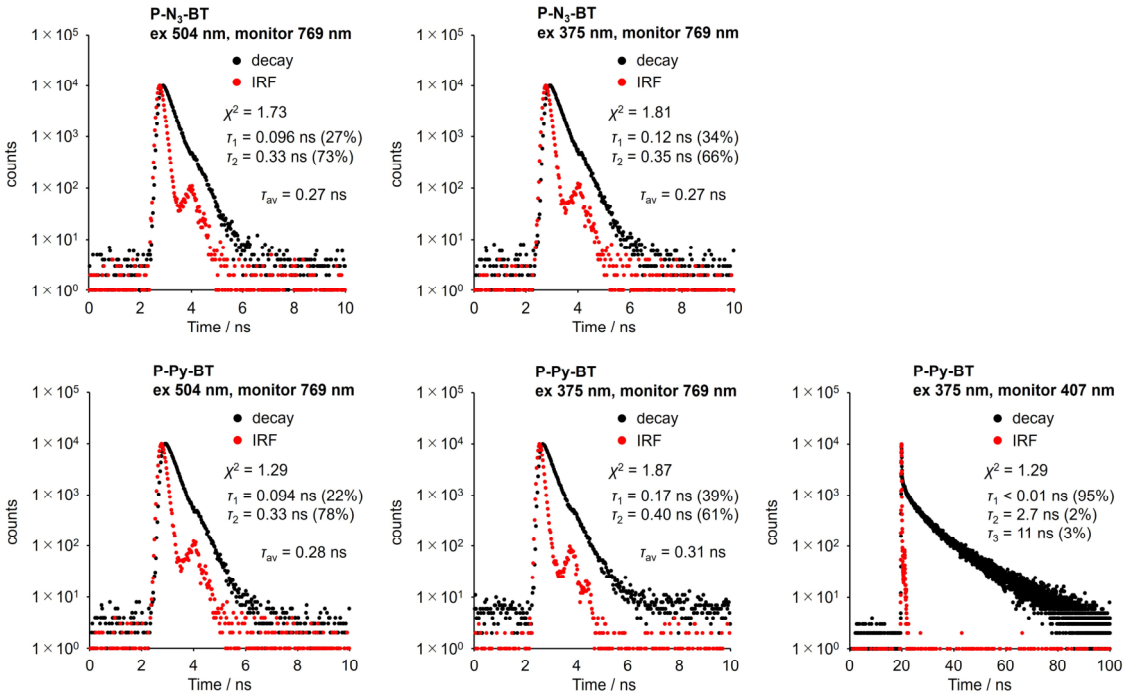


Figure S1. FL lifetime decay curves of **P-N3-BT**, and **P-py-BT** in THF (1.0×10^{-5} M), excited at 375 nm or 504 nm. $\tau_{av} = \Sigma\alpha_i\tau_i$, α: relative amplitude shown in parentheses. IRF: Instrument Response Function

GPC chromatograms

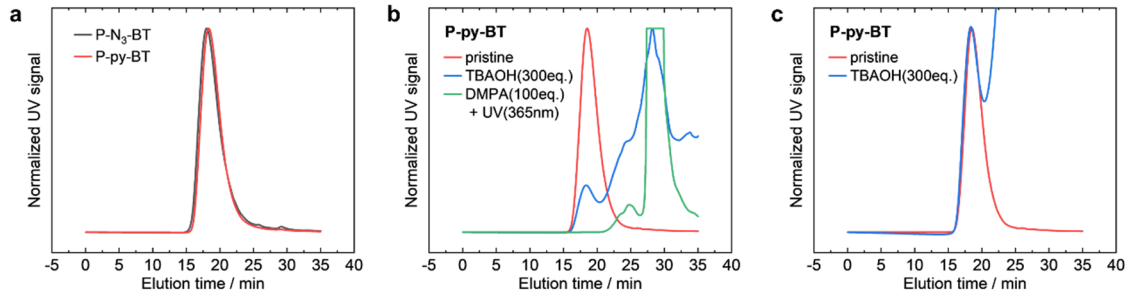


Figure S2. Gel permeation chromatography (GPC) profiles of (a) the pristine polymers **P-N3-BT** and **P-py-BT**, (b) **P-py-BT** before and after treatments with base or radical, and (c) enlarged view of (b). Molecular weights were evaluated with $CHCl_3$ as an eluent (1.0 mL / min) at 40 °C.

Preparation methods of NPs

A mixture of **P-py-BT**, DSPE-PEG(2000)-amine, DMPA (weight ratio; 1:9:24 for with DMPA (100 eq.) and 1:9:0 for without DMPA), and THF (1 mL / 0.1 mg of polymer, 100 ppm) was sonicated (55 W output, US-101, SND Co, Ltd.) to obtain a clear solution. The mixture (1 mL) was quickly injected into deionized water (10 mL), which was sonicated vigorously in water for 2 min. THF was then removed with a rotary evaporator (30 °C, 250 rpm, 100 mbar) and the resulting solution was still clear. The obtained solution was passed through 0.45 μm PTFE filter (Toyo Roshi Kaisha, Ltd.) and was ready for use. Polymer aggregates that do not form NPs were hardly observed. This means that the NP formation efficiency is almost quantitative.

Characterization of NPs

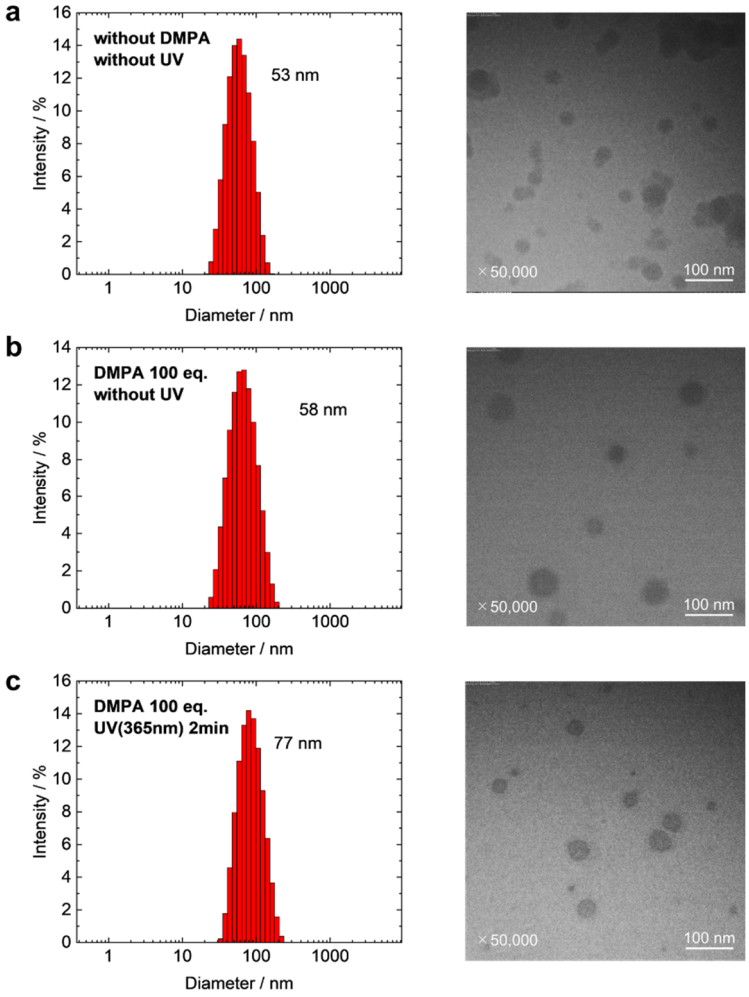


Figure S3. Dynamic light scattering profile (left) and transmission electron microscopy images (right) of the NPs.

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