Supporting Information

Effect of Alkyl Chain Lengths on Red-to-Near-Infrared Emission of Boron-Fused Azomethine Conjugated Polymers and Their Film-State Stimuli-Responsivities

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General

^1H (400 MHz), ^{13}C (100 MHz) and ^{11}B (128 MHz) NMR spectra were recorded on a JEOL JNM or a AL400 spectrometer. Samples were analyzed in $CDCl_3$ and CD_2Cl_2. The chemical shift values were expressed relative to tetramethylsilane (TMS) for ^1H NMR in $CDCl_3$. For ^1H NMR in CD_2Cl_2 and ^{13}C NMR, internal standards were used. $BF_3 \cdot OEt_2$ was used as a capillary standard for ^{11}B NMR. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel C-300 silica gel. UV–vis–NIR absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Photoluminescence (PL) spectra were measured on a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer. Absolute PL quantum efficiency was measured on a HAMAMATSU Quantaurus-QY Plus. 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 JEOL JMS-MS700 spectrometer for electron ionization (EI), a Thermo Fisher Scientific EXACTIVE spectrometer for electrospray ionization (ESI) and a Thermo Fisher Scientific EXACTIVE spectrometer for atmospheric pressure chemical ionization (APCI) and a Bruker Daltonics ultrafleXtreme for Matrix Assisted Laser Desorption ionization (MALDI). Gel permeation chromatography (GPC) was carried out on a TOSOH G3000HXI system equipped with three consecutive polystyrene gel columns (TOSOH gels: α-4000, α-3000, α-2500) using chloroform as an eluent after calibration with standard polystyrene samples. Polymer fractionation was carried out on a Recycling Preparative HPLC (LC-9204, Japan Analytical Industry Co., Ltd.). Film fabrication was performed by spray-coating method. The polymer solutions (1.0×10^{-3} M in chloroform) were loaded into the GSI Creos airbrush PS–270 with a nozzle size of 0.2 mm and sprayed onto the quartz substrate (0.9 cm×5 cm) using air pressure of 0.3 mbar provided by air compressor (Mr. Linear Compressor L5) using air pressure of 0.3 mbar provided by air compressor to ensure a fine atomization while preventing blowing off the already deposited droplets.

Materials

Commercially available compounds used without purification:

Magnesium (Turnings) (Wako Pure Chemical Industries, Ltd.)

n-Ethyl bromide (Wako Pure Chemical Industries, Ltd.)

n-Dodecyl bromide (Sigma-Aldrich Co, LLC.)

5-Bromo anthranilate (Tokyo Chemical Industry Co, Ltd.)

4-Bromo-2-hydoxybenzaldehyde (Combi-Blocks, Inc.)

$Pd_2(dba)_2$ (dba = dibenzylideneacetone) (Tokyo Chemical Industry Co, Ltd.)

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

1 M HCl for Volumetric Analysis (Wako Pure Chemical Industries, Ltd.)

$BF_3 \cdot OEt_2$ (≥46% BF_3 basis) (Sigma-Aldrich Co. LLC.)

5,5-Bis(trimethylstannyl)-2,2-bithiophene (**BTH**) (Sigma-Aldrich Co, LLC.)

3,3′-Dibromo-2,2′-bithiophene (Tokyo Chemical Industry Co, Ltd.)

(1,3-Bis(diphenylphosphino)propane)nickel(II) dichloride (Tokyo Chemical Industry Co, Ltd.)

Commercially available solvents:

MeOH (Wako Pure Chemical Industries, Ltd.), EtOH (Wako Pure Chemical Industries, Ltd.), $CHCl_3$ (Wako Pure Chemical Industries, Ltd.), hexane (Wako Pure Chemical Industries, Ltd.), EtOAc (Wako Pure Chemical Industries, Ltd.), CH_2Cl_2 (Wako Pure Chemical Industries, Ltd.), toluene (deoxidized grade, Wako Pure Chemical Industries, Ltd.), acetone (deoxidized grade, Wako Pure Chemical Industries, Ltd.), chlorobenzene (Wako Pure Chemical Industries, Ltd.) used without further purification. THF (Kanto Chemical Co., Inc.), Et_3N (Kanto Chemical Co., Inc.) purified by passage through solvent purification columns under nitrogen pressure.

Compounds prepared as described in the literatures

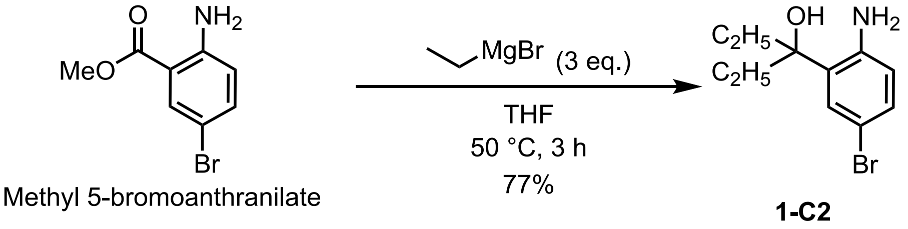
BAm8 and **BAm8BT12**[1]

5,5′-Bis(trimethylstannyl)-3,3′-dihexyl-2,2′-bithiophene (**BT6**)[2]

5,5′-Bis(trimethylstannyl)-3,3′-didodecyl-2,2′-bithiophene (**BT12**)[3],[4]

Synthetic Procedures and Characterization

Synthesis of 1-C2



Scheme S1. Synthesis of compound **1-C2**.

1.0 M *n*-Ethylmagnesium bromide in THF was prepared prior to use. Mg (1.41 g, 58.7 mmol) was stirred with I_2 under nitrogen atmosphere for 1h and dry THF (39 mL) was added to the mixture. *n*-Ethyl bromide (3.4 mL, 39.1 mmol) was added slowly into the solution. After addition was complete, the mixture was stirred at room temperature for 1 h. 1.0 M *n*-Ethylmagnesium bromide in THF was added slowly into a solution of methyl 5-bromoanthranilate (3.0 g, 13.0 mmol) in THF (12 mL) at 0 °C. The mixture was heated to 50 °C for 3 h. After cooling to room temperature, the mixture was quenched by 1 M HCl aqueous solution. Then, the product was extracted with EtOAc. Organic layer was washed with brine, dried over $MgSO_4$ and evaporated to afford a brown solid. The solid was further purified by chromatography on silica gel with hexane and EtOAc (v/v =4/1) to afford **1-C2** (2.61 g, 10.1 mmol, 77%) as a black oil.

R_f = 0.25 (hexane/EtOAc = 4/1 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.11 (dd, J = 2.2, 8.3 Hz, 1H), 7.05 (d, J = 2.2 Hz, 1H), 6.49 (d, J = 8.5 Hz, 1H), 4.74 (s, 2H), 2.04–1.83 (m, 5H), 0.88–0.84 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm):145.5, 130.5, 130.3, 129.2, 119.2, 109.1, 79.6, 31.3, 8.1. HRMS (ESI): Calcd for $[M+H]^+$, 258.0488; found, m/z 258.0484. Elemental analysis calcd. for $C_{11}H_{16}BrNO$: C, 51.18; H, 6.25; N, 5.43. Found: C, 51.41; H, 6.32; N, 5.56.

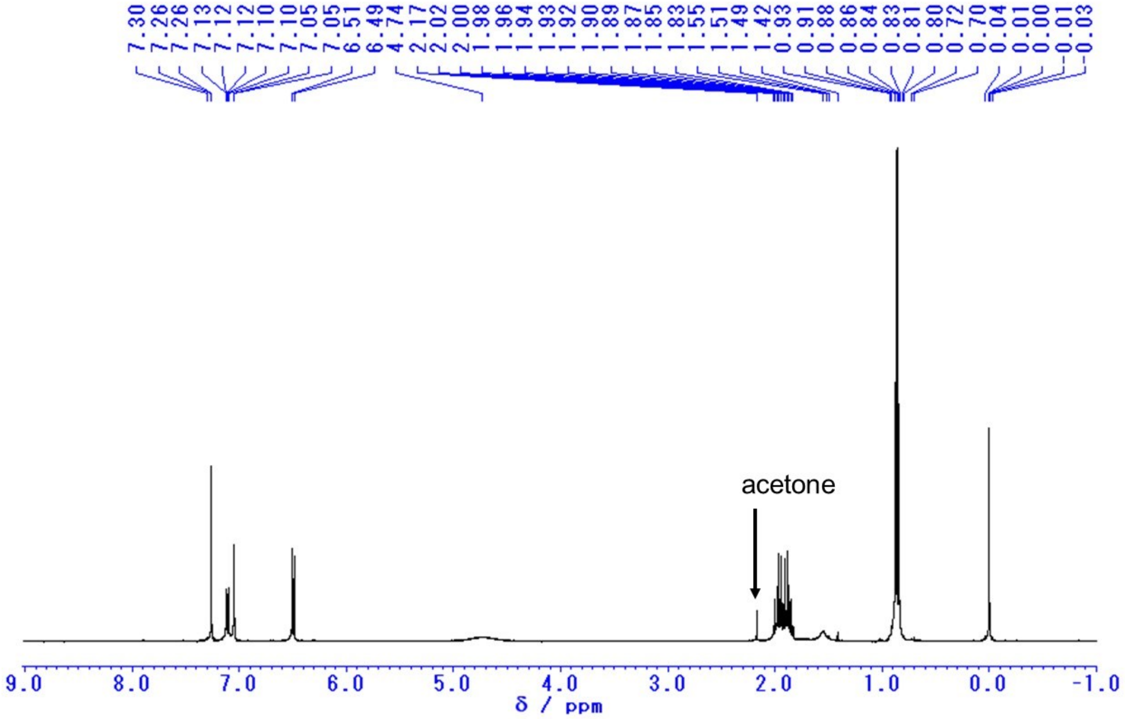


Figure S1. ^{1}H NMR spectrum of **1-C2**, $CDCl_3$, 400 MHz.

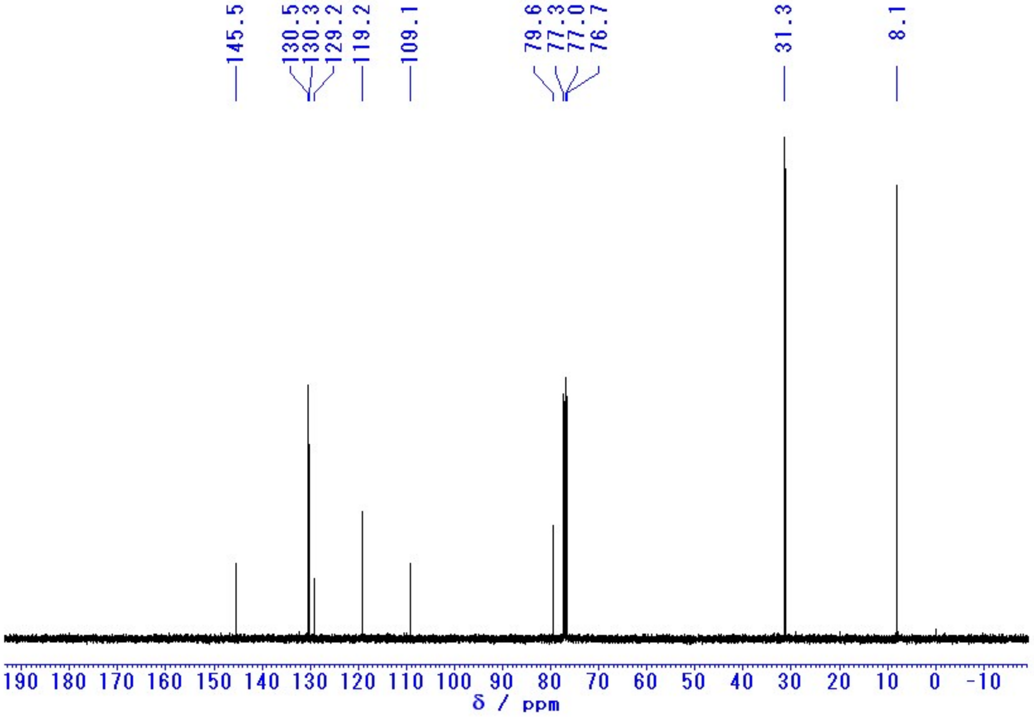
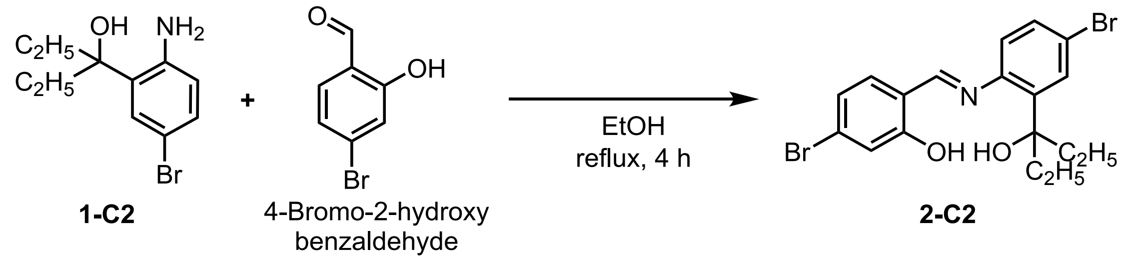
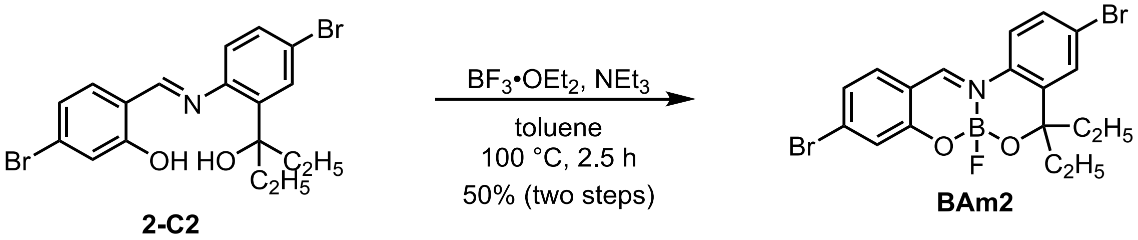


Figure S2. ^{13}C NMR spectrum of **1-C2**, $CDCl_3$, 100 MHz.

Synthesis of 2-C2 and BAm2



Scheme S2. Synthesis of compound **2-C2**.



Scheme S3. Synthesis of **BAm2**.

1-C2 (1.30 g, 5.04 mmol) and 4-bromo-2-hydroxybenzaldehyde (1.01 g, 5.04 mmol) were dissolved in deoxidized EtOH (20 mL) under nitrogen atmosphere and refluxed for 4 h. Then, the mixture was cooled to room temperature and the solvent was removed by a rotary evaporator. The residue was purified by chromatography on silica gel with hexane and CH_2Cl_2 (v/v = 7/3) to afford a yellow oil. The crude product was used in the next step without any further purification (1.17 g, 2.66 mmol). $R_f = 0.25$ (hexane/CH_2Cl_2 = 7/3 v/v).

2-C2 (0.70 g, 1.59 mmol) was dissolved in dry toluene (47 mL) under nitrogen atmosphere and triethylamine (0.4 mL, 3.17 mmol) was then added to the reaction mixture. $BF_3 \cdot OEt_2$ (0.6 mL, 4.76 mmol) was added and stirred for 2.5 h at 100 °C. After cooling to room temperature, the reaction mixture was quenched by EtOH and concentrated by a rotary evaporator to give a yellow powder. The yellow residue was purified by chromatography on silica gel with hexane and EtOAc (v/v =4/1) and recrystallization with $CHCl_3$ and hexane (good and poor solvent, respectively) to afford **BAm2** (0.37 g, 50%, 2 steps from **1**) as a yellow powder.

$R_f = 0.05$ (hexane/EtOAc = 4/1 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.48 (s, 1H), 7.50–7.29 (m, 5H), 7.13–7.10 (m, 1H), 2.18–1.58 (m, 4H), 1.08 (dd, J = 7.3 Hz, 3H), 0.61 (dd, J = 7.3 Hz, 3H). ^{11}B

NMR ($CDCl_3$, 128 MHz), δ (ppm): 0.98 (d J = 3.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 160.4, 153.7, 142.3, 135.9, 134.0, 132.4, 130.9, 130.8, 123.8, 123.2, 119.2, 115.0, 79.2, 50.6, 36.0, 35.0, 8.1, 8.0. HRMS (ESI): Calcd for $[M+Na]^+$, 489.9595; found, m/z 489.9595. Elemental analysis calcd. for $C_{18}H_{17}BBr_2FNO_2$: C, 46.10; H, 3.65; N, 2.99. Found: C, 45.90; H, 3.69; N, 3.03.

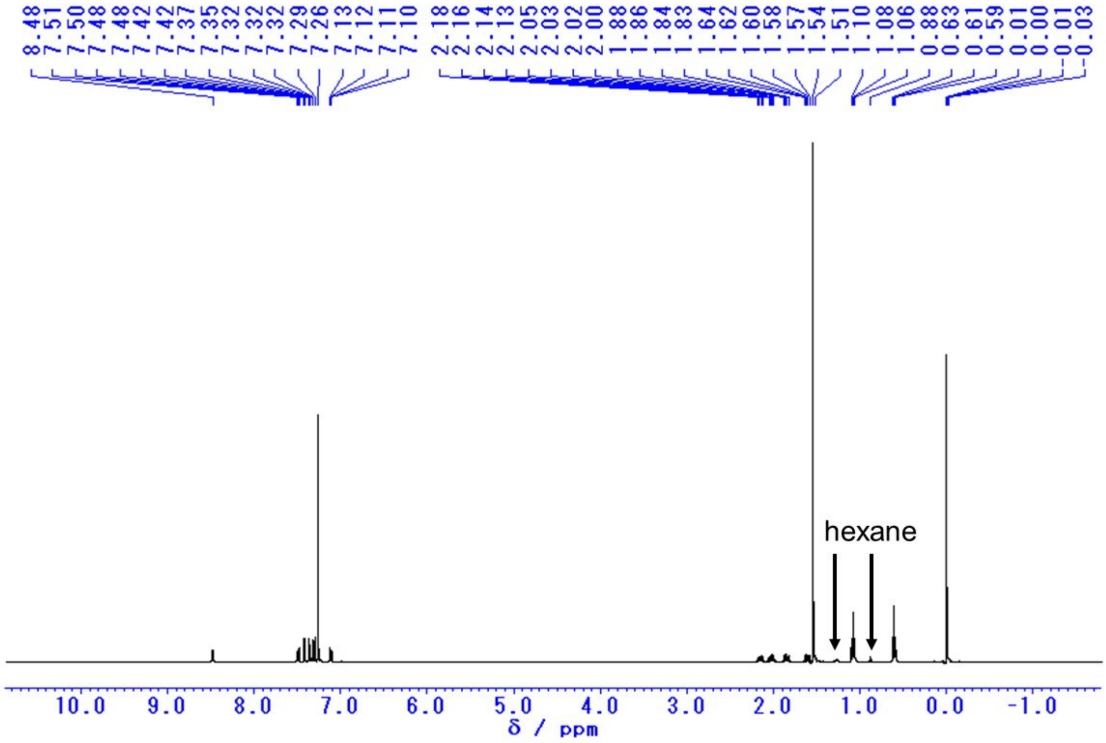


Figure S3. ^{1}H NMR spectrum of **BAm2**, $CDCl_3$, 400 MHz.

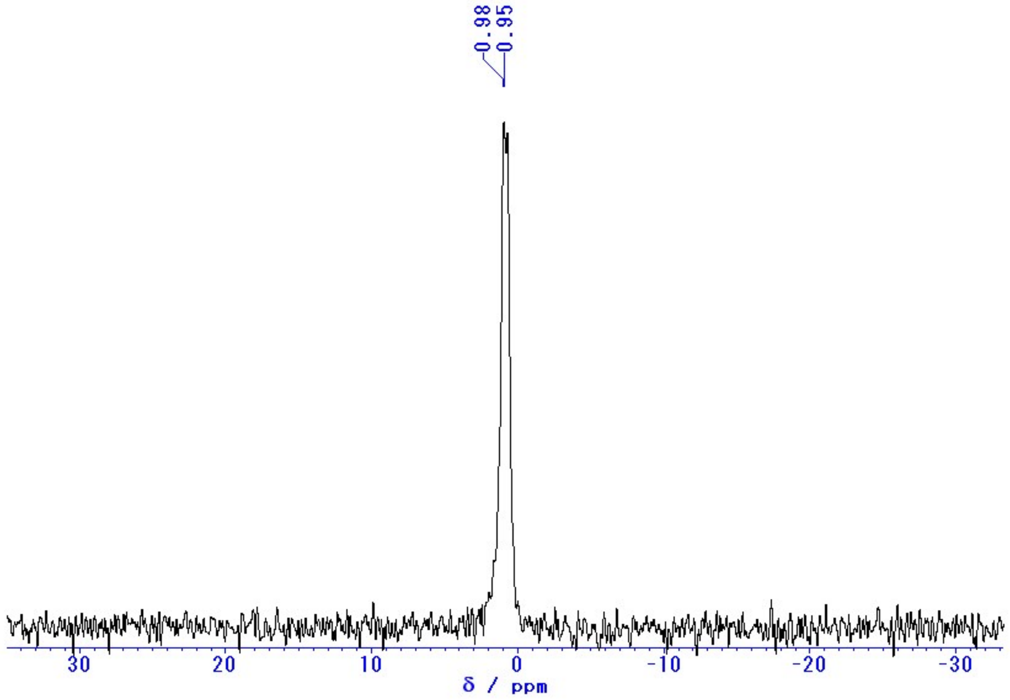


Figure S4. ^{11}B NMR spectrum of **BAm2**, $CDCl_3$, 128 MHz.

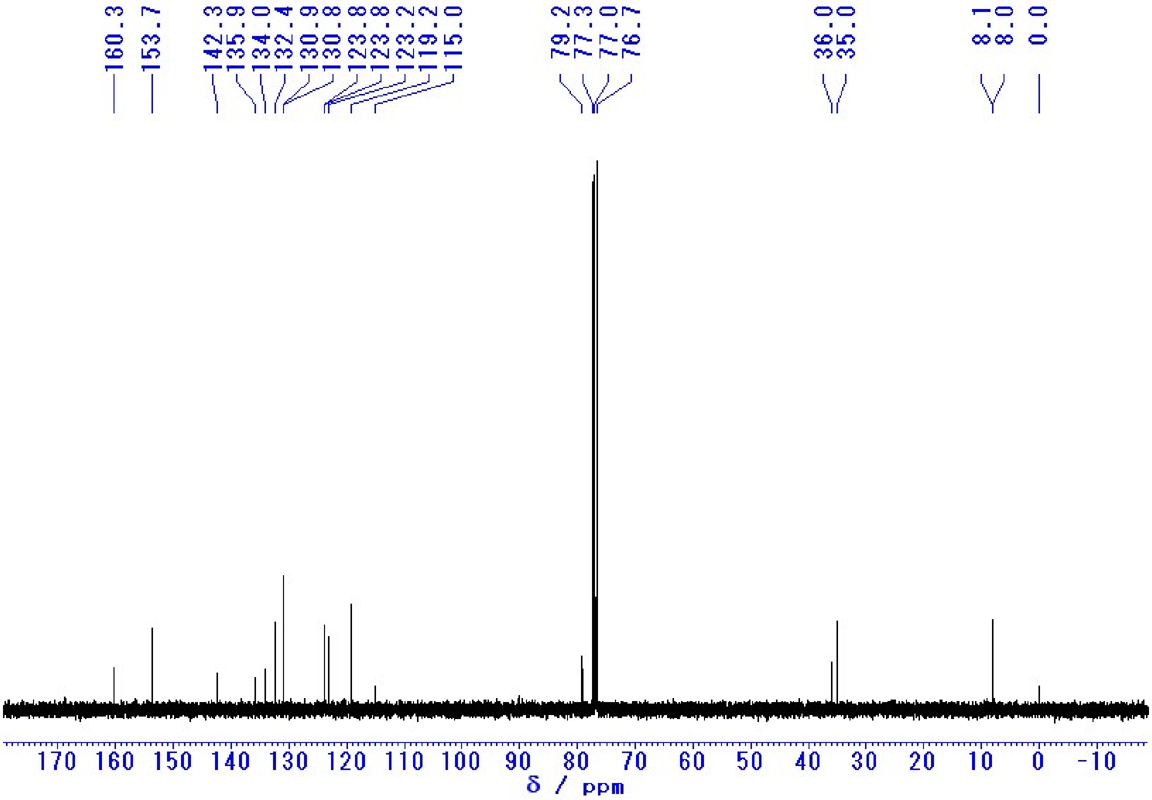
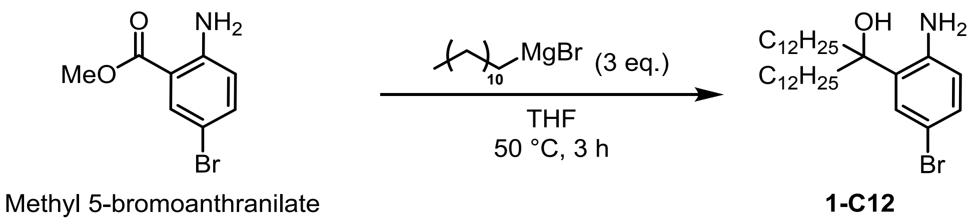
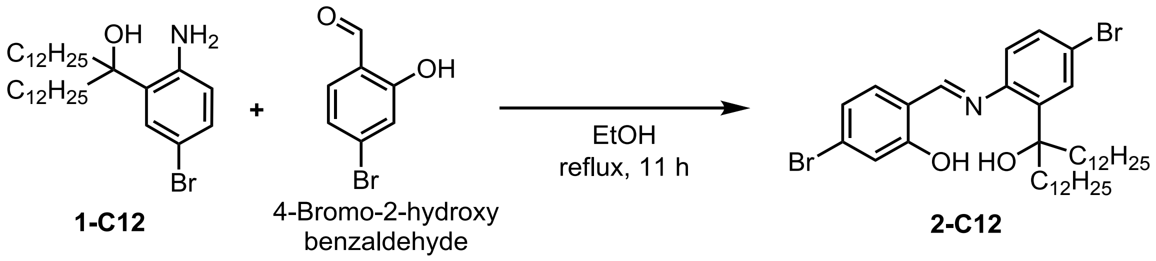


Figure S5. ^{13}C NMR spectrum of **BAm2**, $CDCl_3$, 100 MHz.

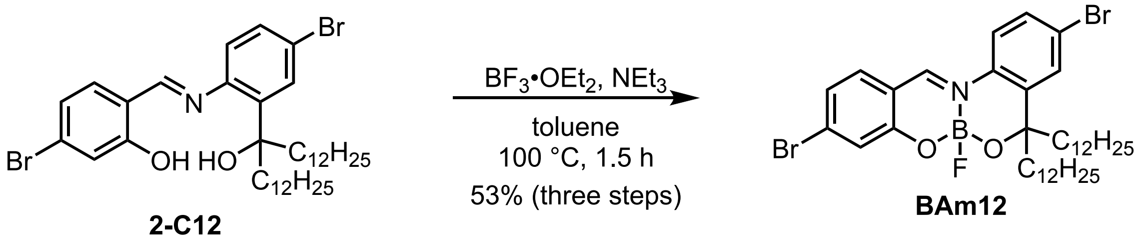
Synthesis of BAm12



Scheme S4. Synthesis of compound **1-C12**.



Scheme S5. Synthesis of compound **2-C12**.



Scheme S6. Synthesis of **BAm12**.

1.0 M *n*-Dodecylmagnesium bromide in THF was prepared prior to use. Mg (1.41g, 58.7 mmol) was stirred with I_2 under nitrogen atmosphere for 1h and dry THF (39 mL) was added to the mixture. *n*-Dodecyl bromide (7.7 mL, 39.1 mmol) was added slowly into the solution. After addition was complete, the mixture was stirred at room temperature for 1 h. 1.0 M *n*-Dodecylmagnesium bromide in THF was added slowly into a solution of methyl 5-bromoanthranilate (3.0 g, 13.0 mmol) in THF (12 mL) at 0 °C. The mixture was heated to 50 °C for 3 h. After cooling to room temperature, the mixture was quenched by 1 M HCl aqueous solution. Then, the product was extracted with EtOAc. Organic layer was washed with brine, dried over

$MgSO_4$ and evaporated. The residue was further purified by chromatography on silica gel with hexane and EtOAc (v/v =4/1) to afford a yellow solid. The crude product was used in the next step without any further purification (2.34 g, 5.49 mmol). R_f = 0.63 (hexane/EtOAc = 4/1 v/v).

1-C12 (2.00 g, 3.71 mmol) and 4-bromo-2-hydroxybenzaldehyde (0.75 g, 3.71 mmol) were dissolved in dry EtOH (14 mL) under nitrogen atmosphere and refluxed for 11 h. Then, the mixture was cooled to room temperature and the solvent was removed by a rotary evaporator. The residue was purified by chromatography on silica gel with hexane and EtOAc (v/v = 3/2) to afford a yellow oil. The crude product was used in the next step without any further purification (2.16 g, 2.99 mmol). R_f = 0.60 (hexane/EtOAc = 3/2 v/v).

2-C12 (1.00 g, 1.39 mmol) was dissolved in dry toluene (41 mL) under nitrogen atmosphere and triethylamine (0.4 mL, 2.77 mmol) was then added to the reaction mixture. $BF_3 \cdot OEt_2$ (0.5 mL, 4.16 mmol) was added and stirred for 1.5 h at 100 °C. After cooling to room temperature, the reaction mixture was quenched by EtOH and concentrated by a rotary evaporator to give a yellow powder. The yellow residue was purified by chromatography on silica gel with hexane and EtOAc (v/v =4/1) and recrystallization with $CHCl_3$ and hexane (good and poor solvent, respectively) to afford **BAm12** (0.55 g, 53%) as a yellow solid.

R_f = 0.48 (hexane/EtOAc = 4/1 v/v). ^{1}H NMR (CD_2Cl_2, 400 MHz), δ (ppm): 8.53 (s, 1H), 7.52 (dd, J = 8.8, 2.2 Hz, 1H), 7.45 (d, J = 2.2 Hz, 1H), 7.38 (dd, J = 8.8, 6.4 Hz, 2H), 7.28 (d, J = 1.7 Hz, 1H), 7.15 (dd, J = 8.3, 2.0 Hz, 1H), 2.02 (dt, J = 13, 4.4 Hz, 1H), 1.88–1.73 (m, 3H), 1.61–1.10 (m, 36H) 0.87 (q, J = 7.8 Hz, 9H), 0.75 (bs, 1H).^{11}B NMR ($CDCl_3$, 128 MHz), δ (ppm): 0.79. ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm):160.3, 153.5, 143.1, 135.5, 133.9, 132.4, 130.8, 130.8, 123.8, 123.7, 123.2, 119.1, 115.0, 78.7. HRMS (ESI): Calcd for $[M+Na]^+$, 770.2725; found, m/z 770.2731. Elemental analysis calcd. for $C_{38}H_{57}BBr_2FNO_2$: C, 60.90; H, 7.67; N, 1.87. Found: C, 61.03; H, 7.54; N, 1.92.

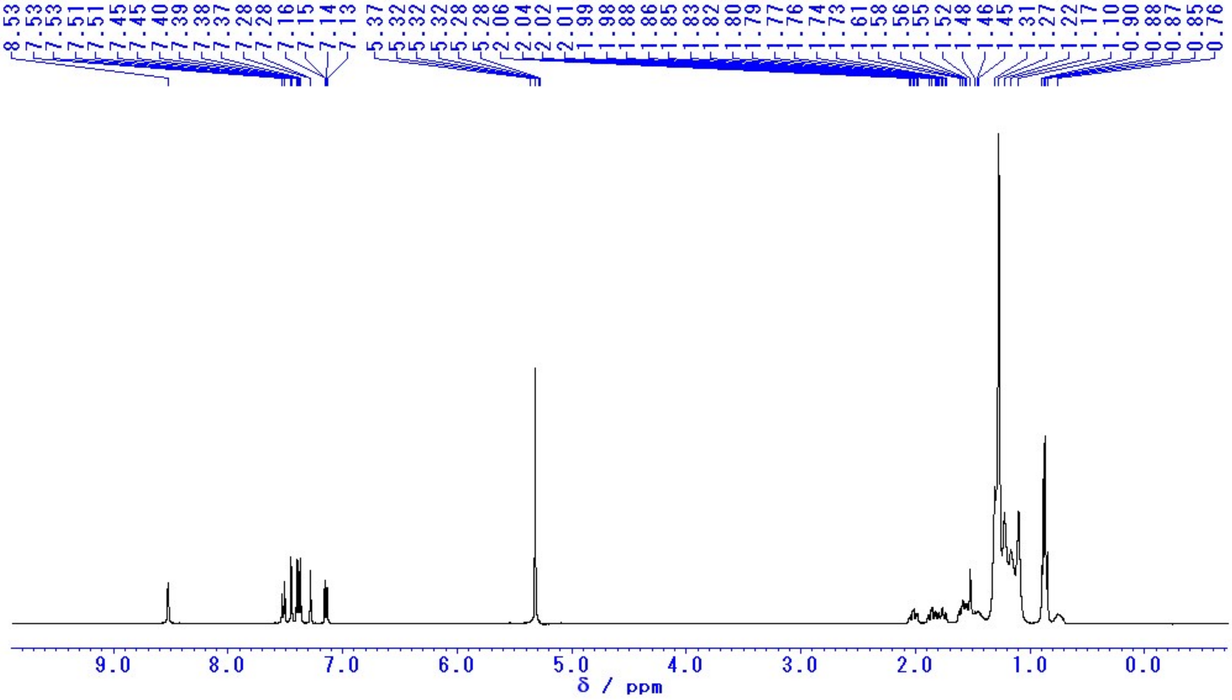


Figure S6. ^{1}H NMR spectrum of **BAm12**, CD_2Cl_2, 400 MHz.

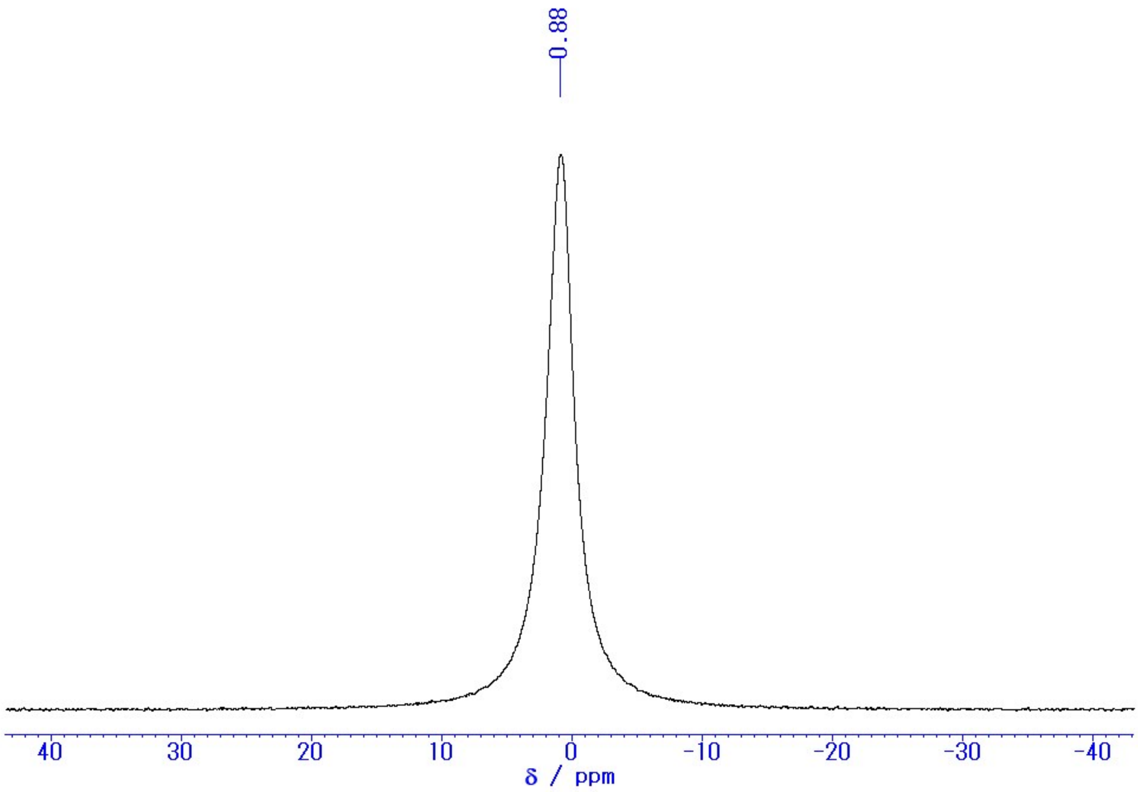


Figure S7. ^{11}B NMR spectrum of **BAm12**, $CDCl_3$, 128 MHz.

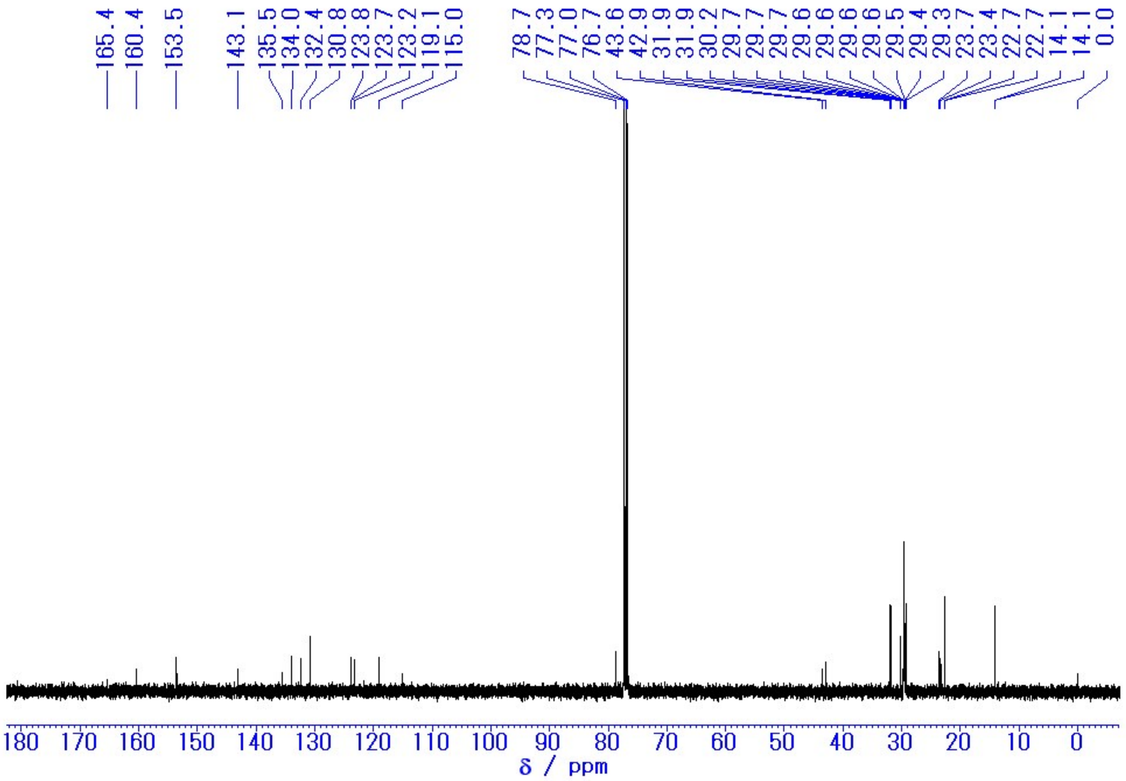
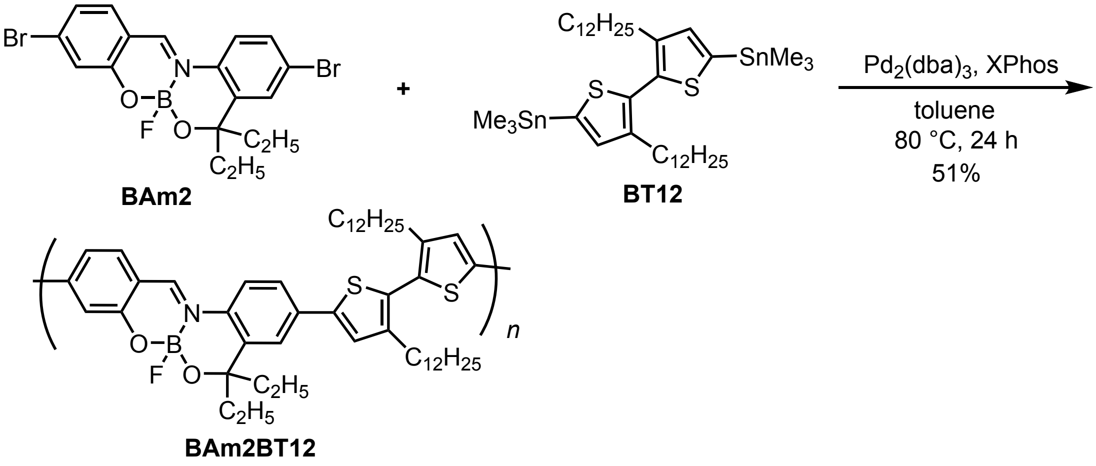


Figure S8. ^{13}C NMR spectrum of **BAm12**, $CDCl_3$, 100 MHz.

Synthesis of BAm2T12



Scheme S7. Synthesis of **BAm2BT12**.

The mixture of **BAm2** (63.8 mg, 0.13 mmol), 3,3′-didodecyl-(2,2′-bithiophene)-5,5′-diyl)bis(trimethylstannane) (106 mg, 0.13 mmol), $Pd_2(dba)_3$ (3.5 mg, 0.0039 mmol), X-Phos (3.7 mg, 0.0077 mmol) in toluene (2 mL) was stirred at 80 °C for 24 h under nitrogen atmosphere. After cooling to room temperature, the solution was purified by alumina column chromatography and poured into a large amount of methanol to collect the polymer by filtration. The polymer collected by filtration was dried *in vacuo* to afford **BAm2BT12** as a red solid (55.1 mg, 51%).

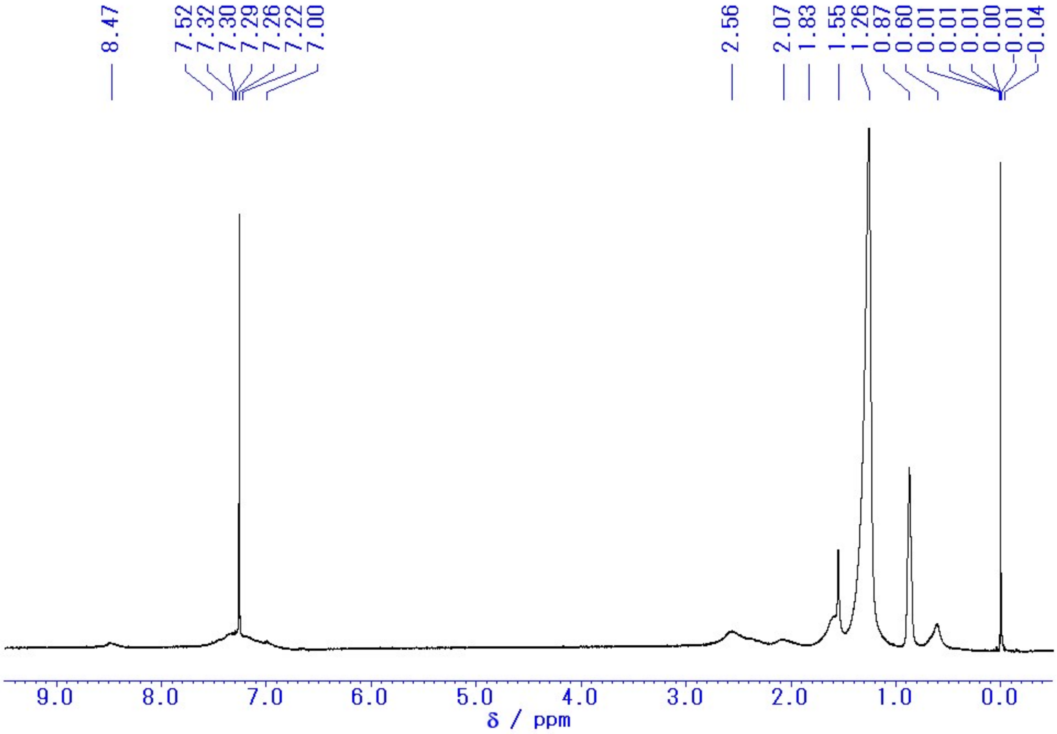


Figure S9. ^{1}H NMR spectrum of **BAm2BT12**, $CDCl_3$, 400 MHz.

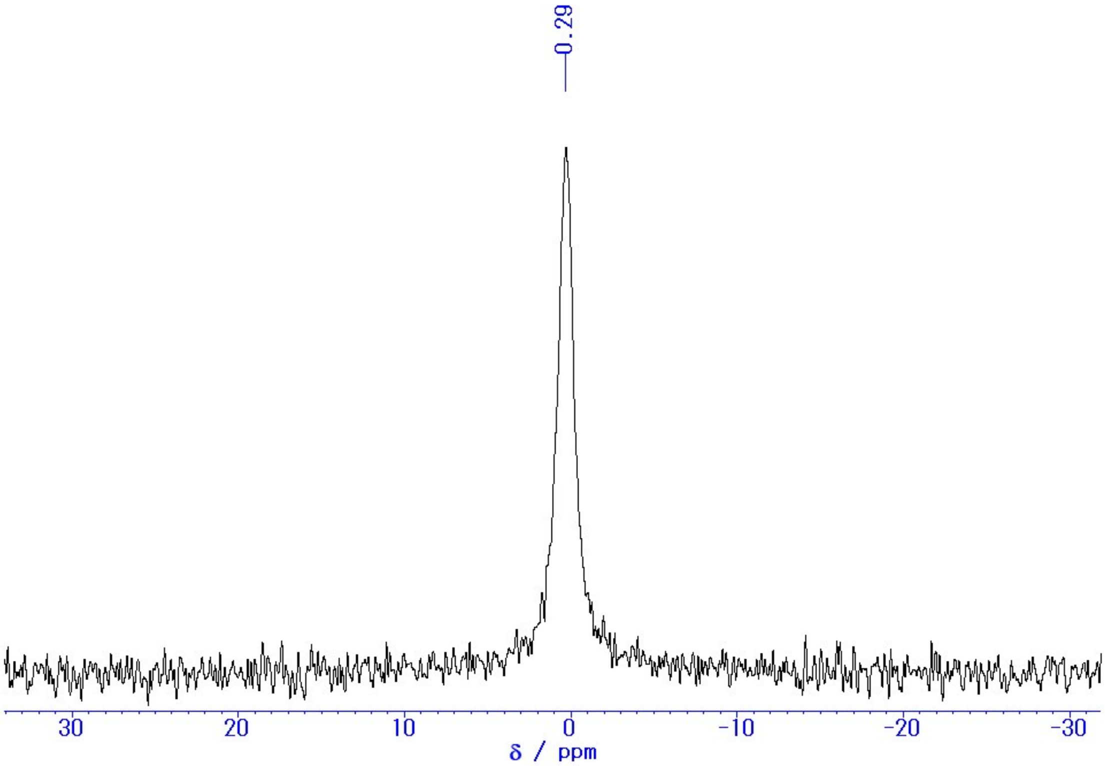


Figure S10. ^{11}B NMR spectrum of **BAm2BT12**, $CDCl_3$, 128 MHz.

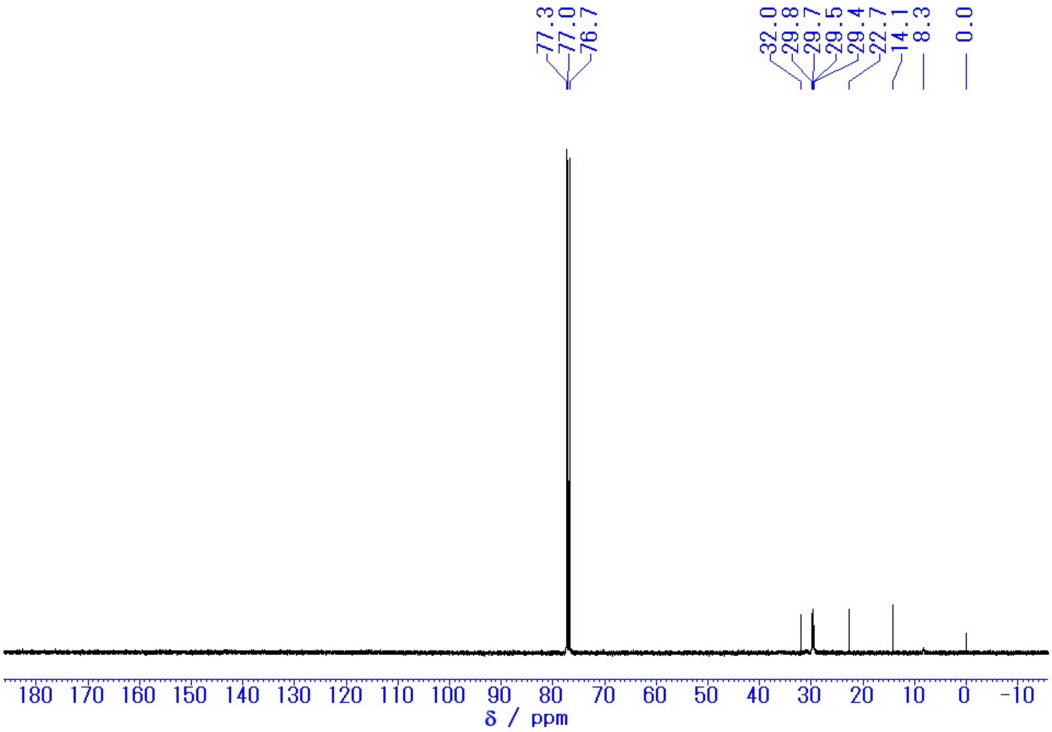


Figure S11. ^{13}C NMR spectrum of **BAm2BT12**, $CDCl_3$, 100 MHz.

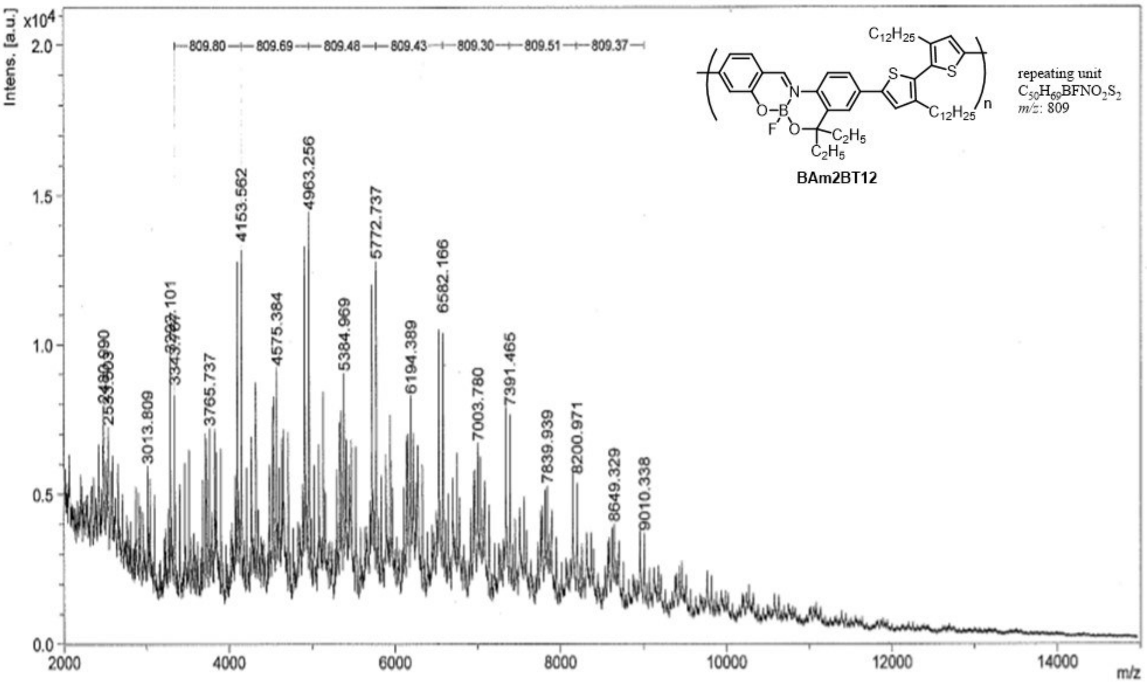
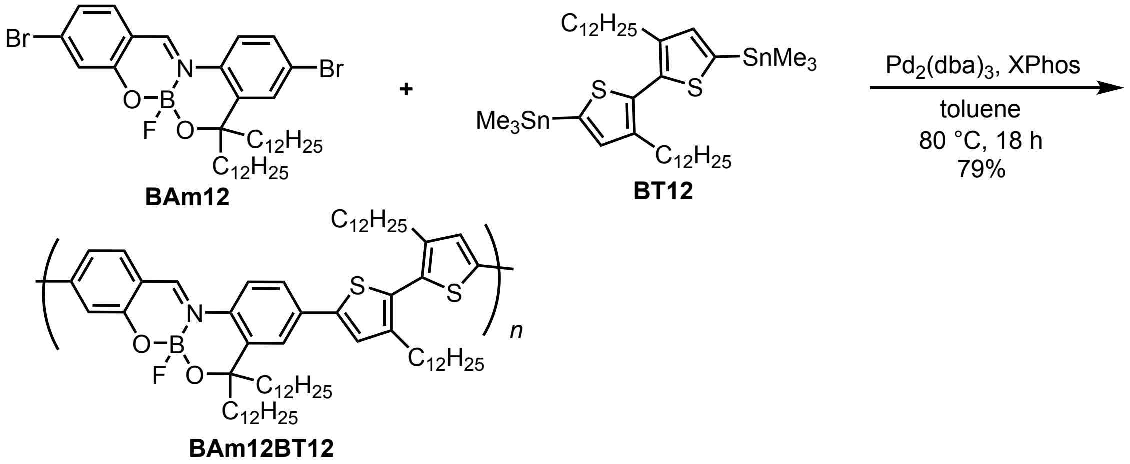


Figure S12. MALDI-TOF mass spectrum of **BAm2BT12**.

Synthesis of BAm12BT12



Scheme S8. Synthesis of **BAm12BT12**.

The mixture of **BAm12** (91.1 mg, 0.12 mmol), 3,3′-didodecyl-(2,2′-bithiophene)-5,5′-diyl)bis(trimethylstannane) (**BT12**) (101 mg, 0.12 mmol), $Pd_2(dba)_3$ (3.3 mg, 0.0036 mmol), X-Phos (3.5 mg, 0.0073 mmol) in toluene (2 mL) was stirred at 80 °C for 18 h under nitrogen atmosphere. After cooling to room temperature, the solution was purified by alumina column chromatography and poured into a large amount of methanol to collect the polymer by filtration. The polymer collected by filtration was dried *in vacuo* to afford **BAm12BT12** as a red solid (107 mg, 79%).

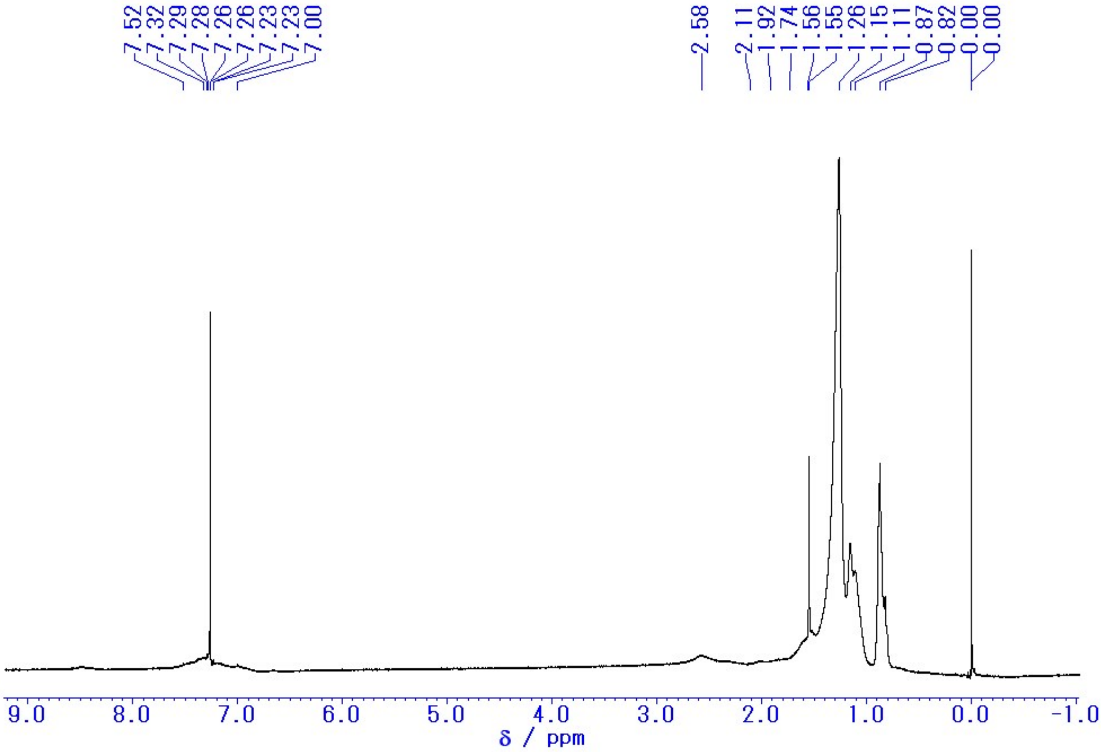


Figure S13. ^{1}H NMR spectrum of **BAm12BT12**, CDCl$_3$, 400 MHz.

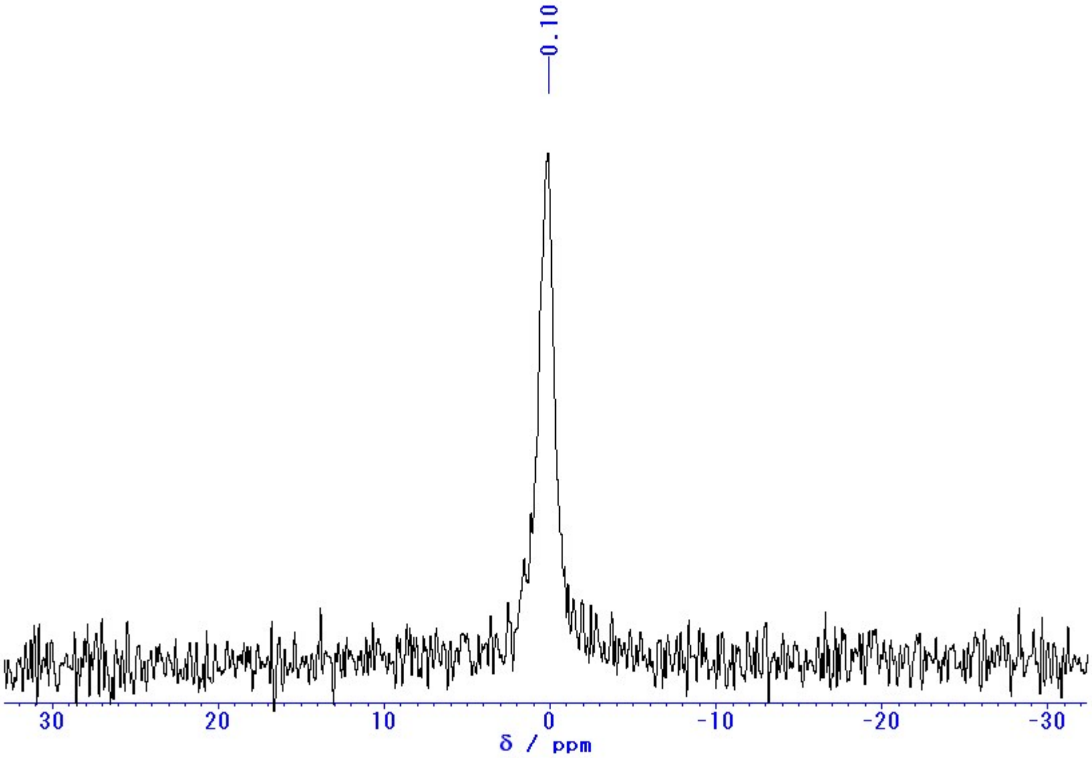


Figure S14. ^{11}B NMR spectrum of **BAm12BT12**, CDCl$_3$, 128 MHz.

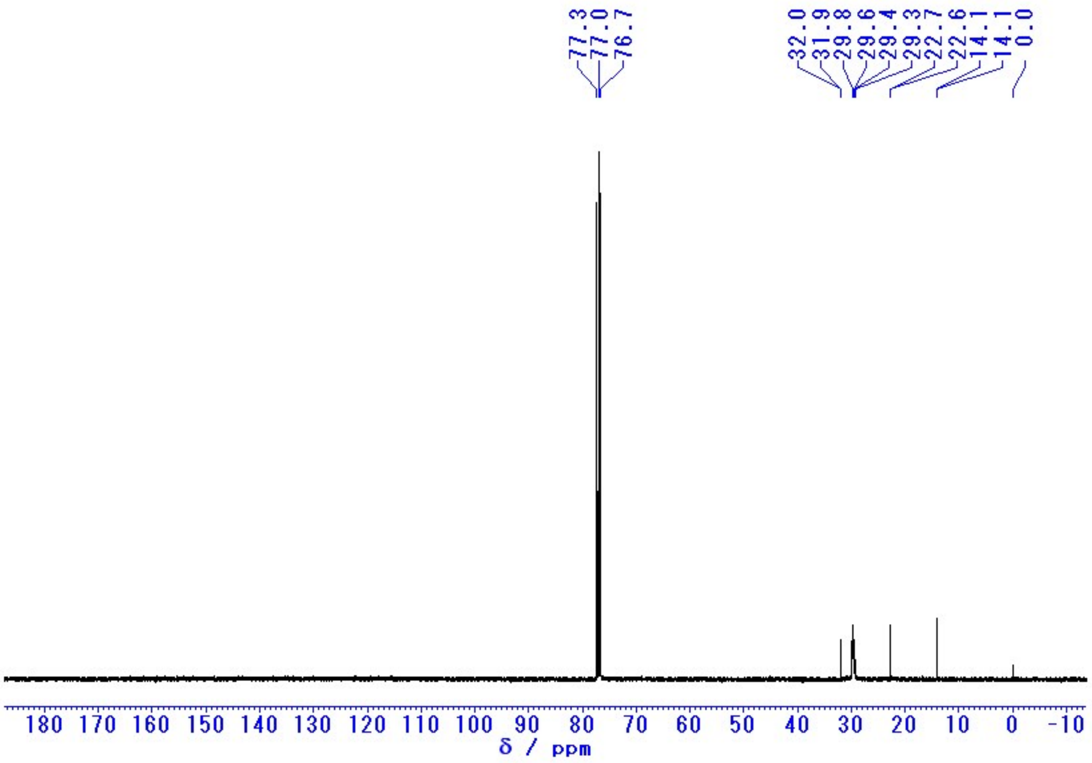


Figure S15. ^{13}C NMR spectrum of **BAm12BT12**, CDCl$_3$, 100 MHz.

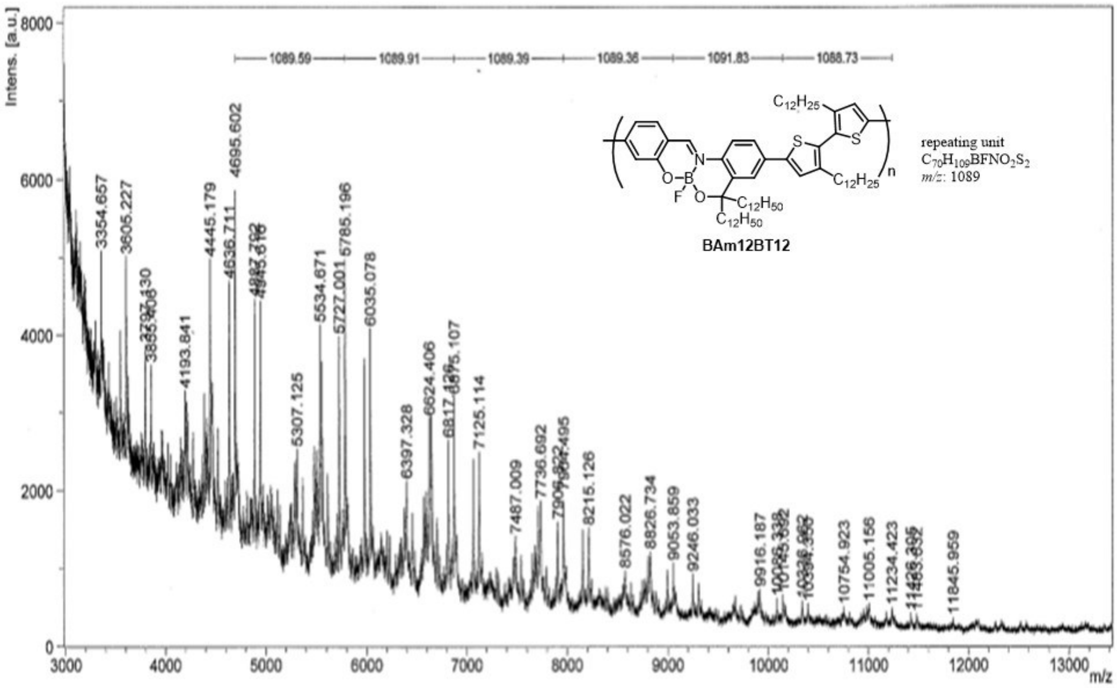
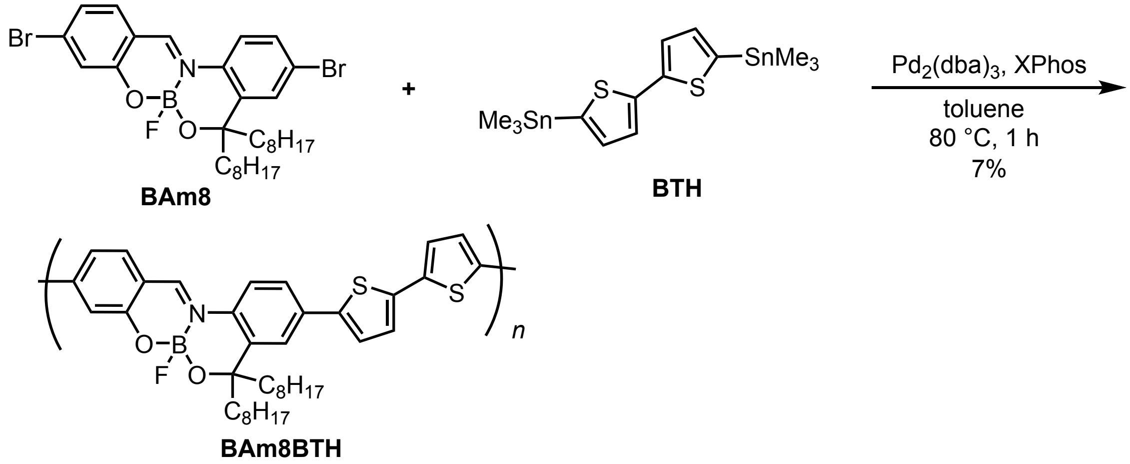


Figure S16. MALDI-TOF mass spectrum of **BAm12BT12**.

Synthesis of BAm8BTH



Scheme S9. Synthesis of **BAm8BTH**.

The mixture of **BAm8** (63.8 mg, 0.10 mmol), 3,3′-didodecyl-(2,2′-bithiophene)-5,5′-diyl)bis(trimethylstannane) (**BTH**) (43.2 mg, 0.10 mmol), $Pd_2(dba)_3$ (2.8 mg, 0.0030 mmol), X-Phos (2.9 mg, 0.0060 mmol) in toluene (2 mL) was stirred at 80 °C for 1 h under nitrogen atmosphere. After cooling to room temperature, the solution was purified by alumina column chromatography and poured into a large amount of methanol to collect the polymer by filtration. After the polymer was washed with MeOH, hexane, EtOAc and acetone, it was extracted with $CHCl_3$ using a Soxhlet extractor to afford **BAm8BTH** as a reddish-purple solid (5.3 mg, 7%). Due to poor solubility, the peaks corresponding to the target polymer structure were not obtained in ^1H and ^{13}C NMR.

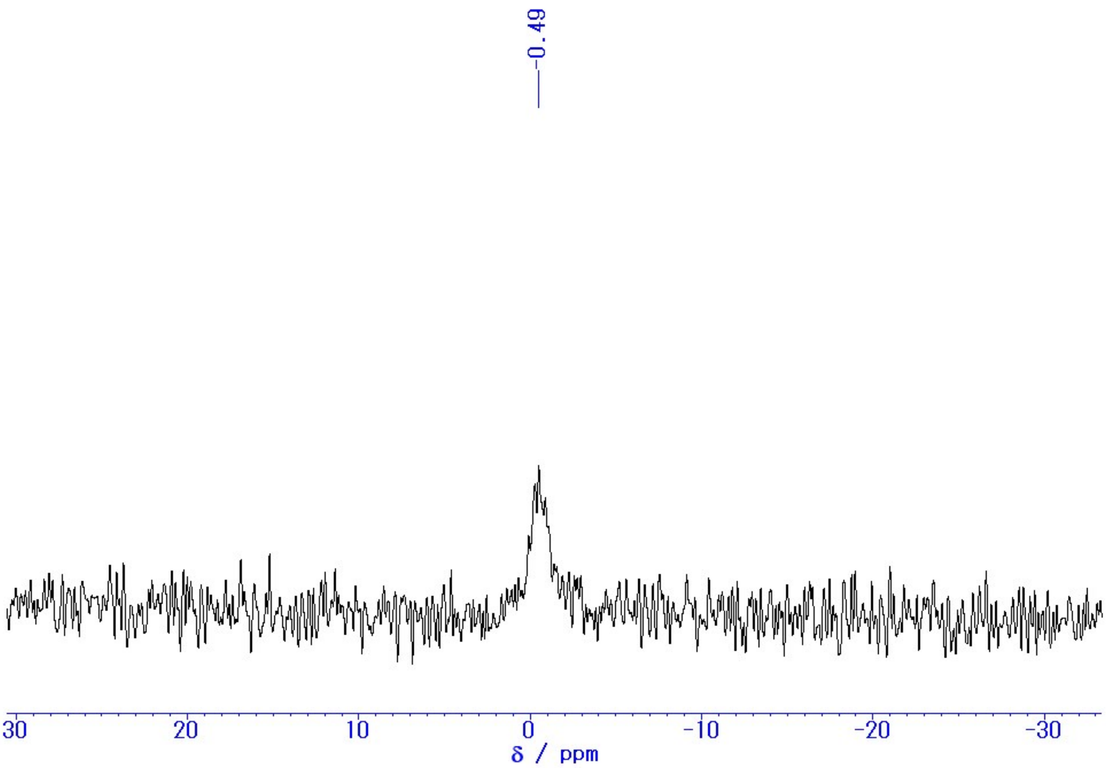


Figure S17. ^{11}B NMR spectrum of **BAm8BTH**, $CDCl_3$, 128 MHz.

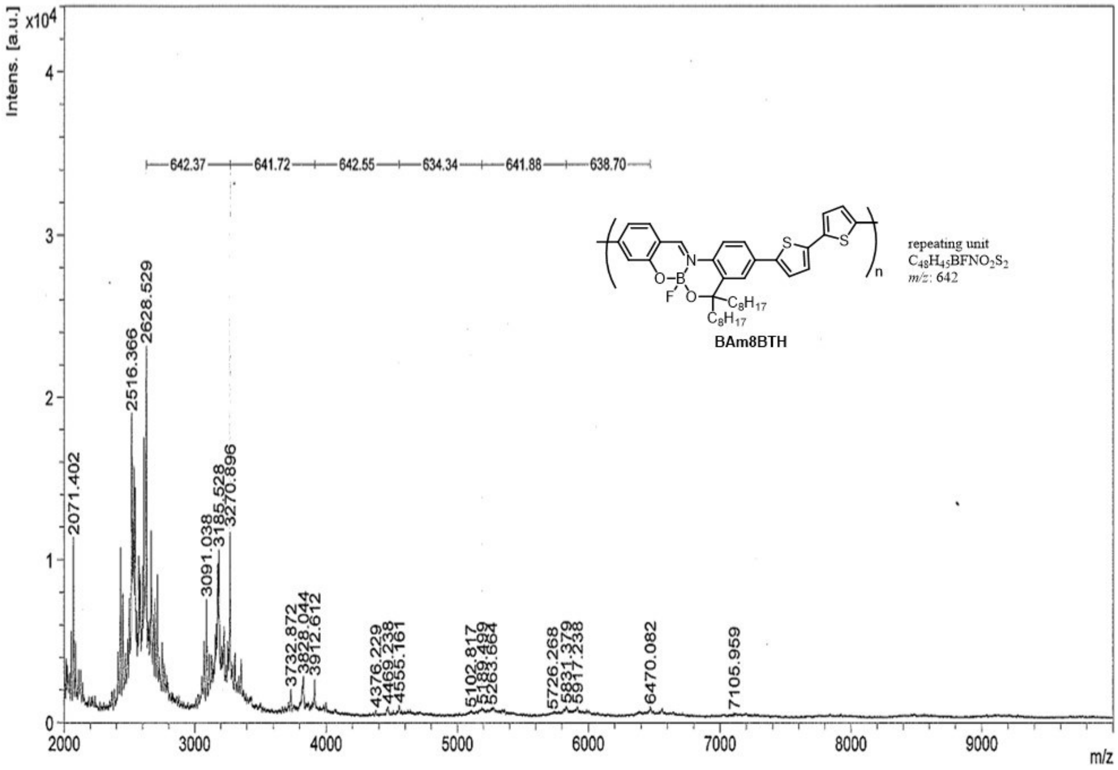
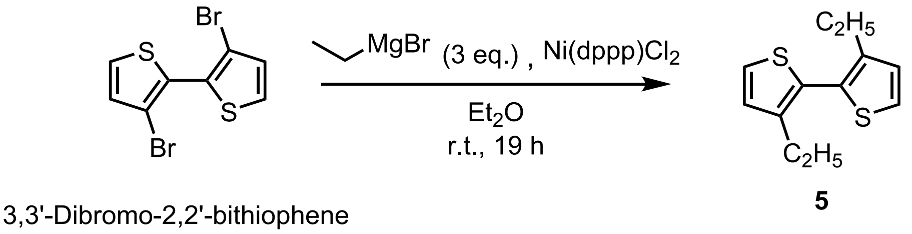
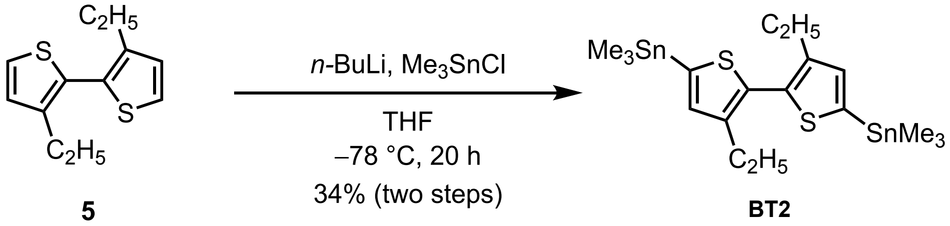


Figure S18. MALDI-TOF mass spectrum of **BAm8BTH**.

Synthesis of BT2



Scheme S10. Synthesis of compound **5**.



Scheme S11. Synthesis of compound **BT2**.

2.0 M *n*-Ethylmagnesium bromide in Et_2O was prepared prior to use. Mg (0.67 g, 27.8 mmol) was stirred with I_2 under nitrogen atmosphere for 1h and dry Et_2O (9 mL) was added to the mixture. *n*-Ethyl bromide (1.6 mL, 18.5 mmol) was added slowly into the solution. After addition was complete, the mixture was stirred at room temperature for 1 h. 2.0 M *n*-Ethylmagnesium bromide in Et_2O was added slowly into a solution of 3,3′-dibromo-2,2′-bithiophene (2.0 g, 6.17 mmol) and (1,3-bis(diphenylphosphino)propane)nickel(II) dichloride in Et_2O (19 mL) at 0 °C. The mixture was stirred at room temperature for 19 h and quenched by saturated NH_4Cl aqueous solution at 0 °C. Then, the white precipitation was removed by filtration and the resulting solution was extracted with Et_2O. Organic layer was washed with brine, dried over $MgSO_4$ and the solvent was removed by a rotary evaporator. The residue was further purified by chromatography on silica gel with hexane to afford **5** (0.55 g, 2.46 mmol) as a colorless oil. The crude product was used in the next step without any further purification. ($R_f = 0.45$ for hexane).

5 (0.53 g, 2.39 mmol) was solubilized in dry THF (60 mL) and cooled to −78 °C. A solution of 1.6 M *n*-BuLi (3.6 mL, 5.75 mmol) was added to the mixture with a dropping funnel and then the solution was stirred at this temperature for 2 h. Me_3SnCl (10.6 mL, 10.6 mmol) was added to the mixture at −78 °C and stirred overnight and allowed to reach room temperature. The reaction was quenched by the addition of water and extracted with Et_2O. Organic layer was washed with brine, dried over Na_2SO_4 and the solvent was removed by a rotary evaporator. The yellow oil product **BT2** was used without further purification (1.15 g, yield 34% for two steps).

^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.05 (s, 1H), 2.56 (q, J = 7.6 Hz, 2H), 1.17 (t, J = 7.6 Hz, 3H), 0.37 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm):144.1, 137.6, 136.4, 134.9, 22.0, 15.4, −8.2 (t, J = 1.6 Hz). HRMS (ESI): Calcd for $[M\bullet]^+$, 549.9827; found, 549.9835. Elemental analysis calcd. for $C_{18}H_{30}S_2Sn_2$: C, 39.45; H, 5.52. Found: C, 39.28; H, 5.41.

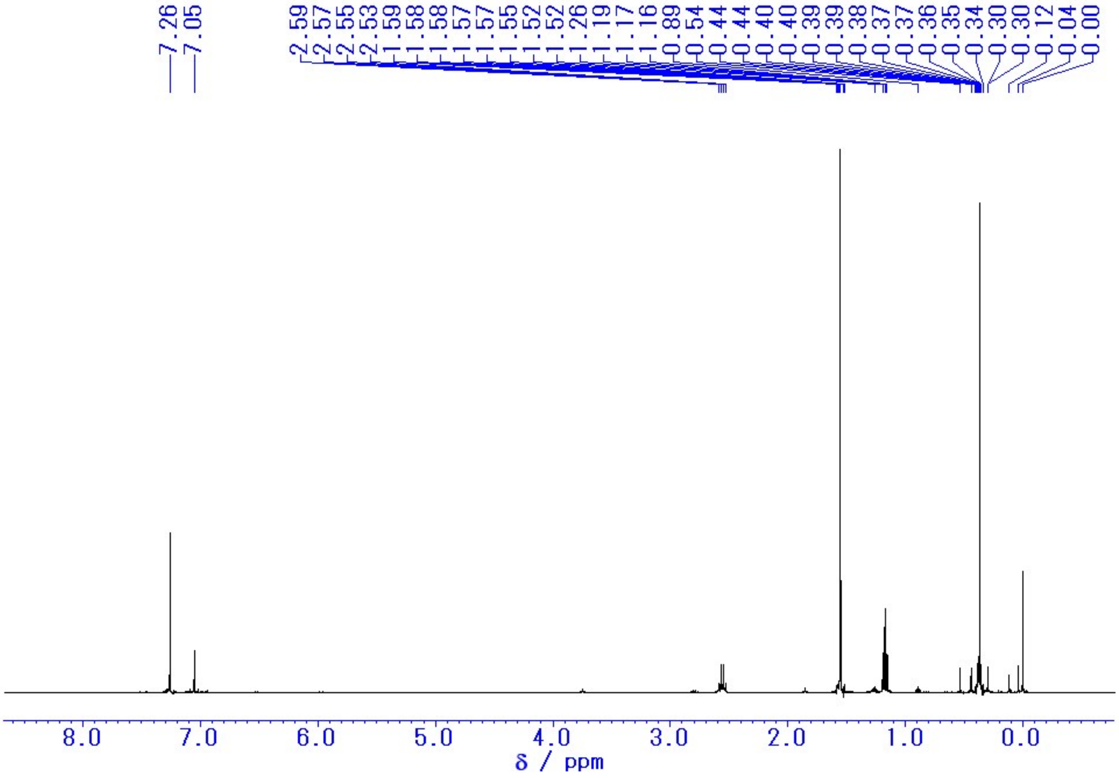


Figure S19. ^{1}H NMR spectrum of **BT2**, $CDCl_3$, 400 MHz.

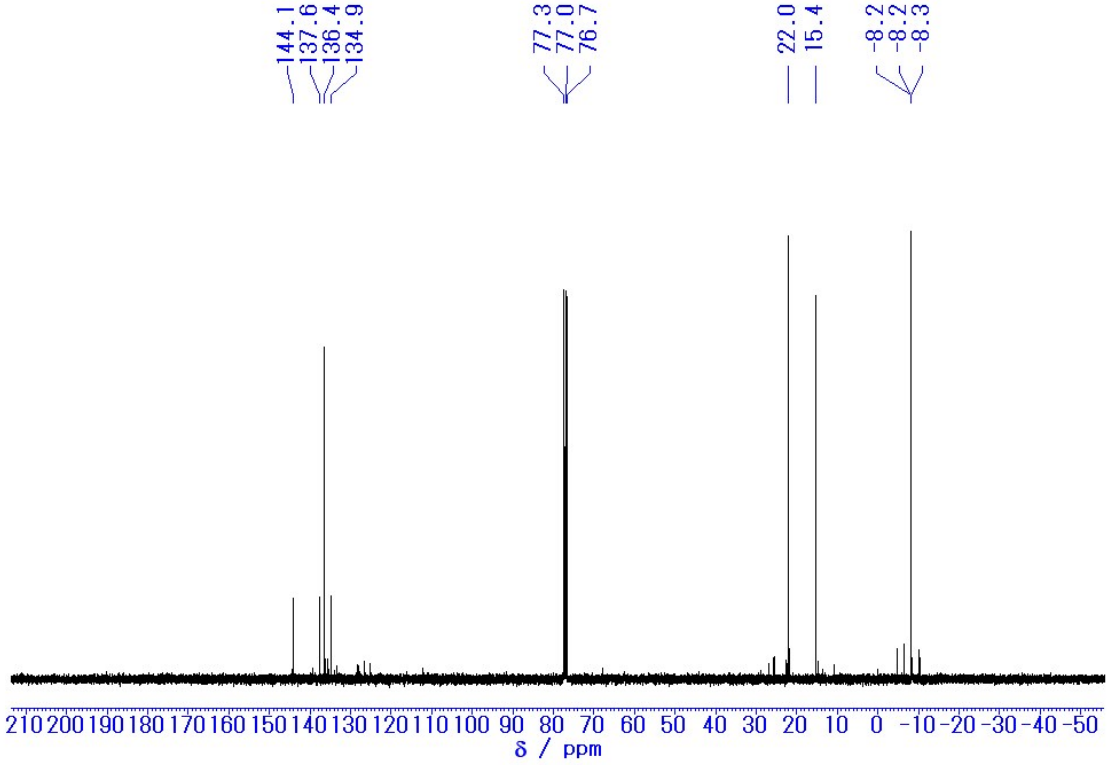
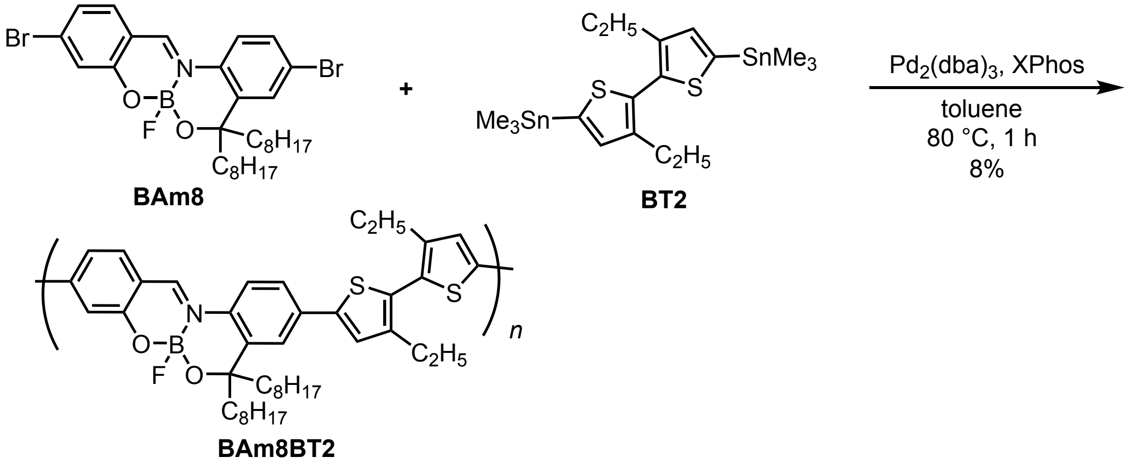


Figure S20. ^{13}C NMR spectrum of **BT2**, $CDCl_3$, 100 MHz.

Synthesis of BAm8BT2



Scheme S12. Synthesis of **BAm8BT2**.

The mixture of **BAm8** (88.1 mg, 0.14 mmol), 3,3′-diethyl-(2,2′-bithiophene)-5,5′-diyl)bis(trimethylstannane) (75.8 mg, 0.14 mmol) (**BT2**), $Pd_2(dba)_3$ (3.8 mg, 0.0041 mmol), X-Phos (4.0 mg, 0.0083 mmol) in toluene (2 mL) was stirred at 80 °C for 24 h under nitrogen atmosphere. After cooling to room temperature, the solution was purified by alumina column chromatography and poured into a large amount of methanol to collect the polymer by filtration. Additionally, the part of high molecular weight was fractionated by HPLC to afford **BAm8BT2** as a red solid (7.8 mg, 8%).

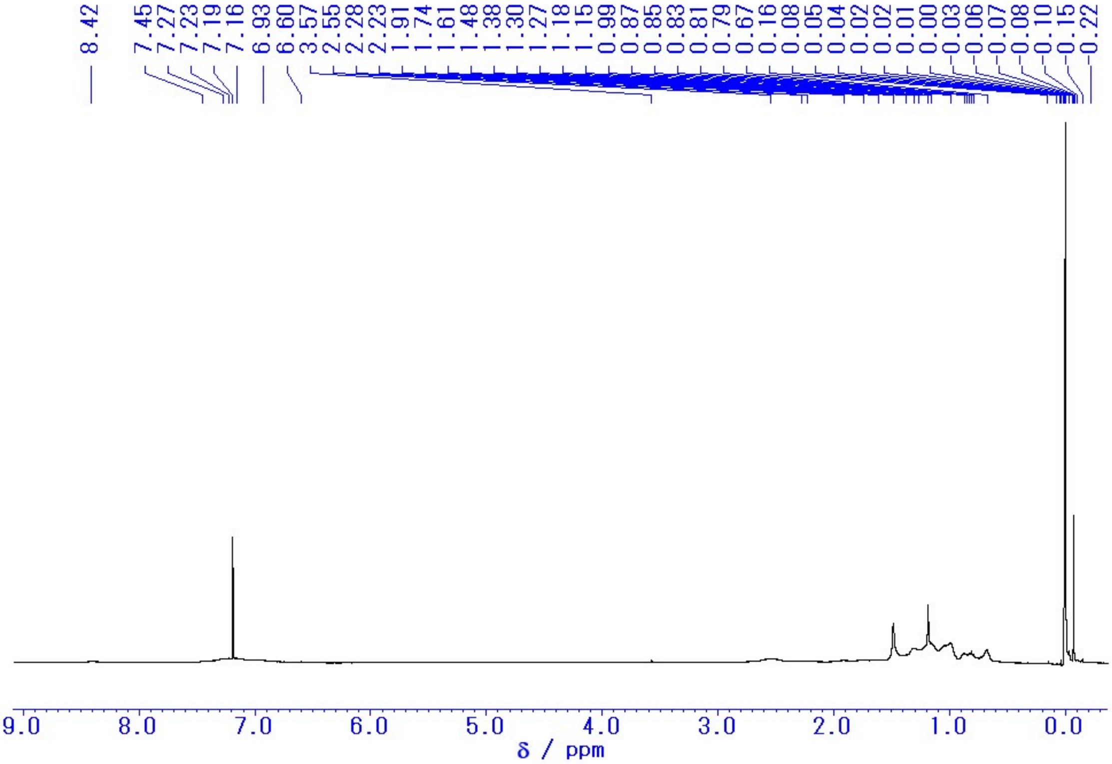


Figure S21. ^{1}H NMR spectrum of **BAm8BT2**, $CDCl_3$, 400 MHz.

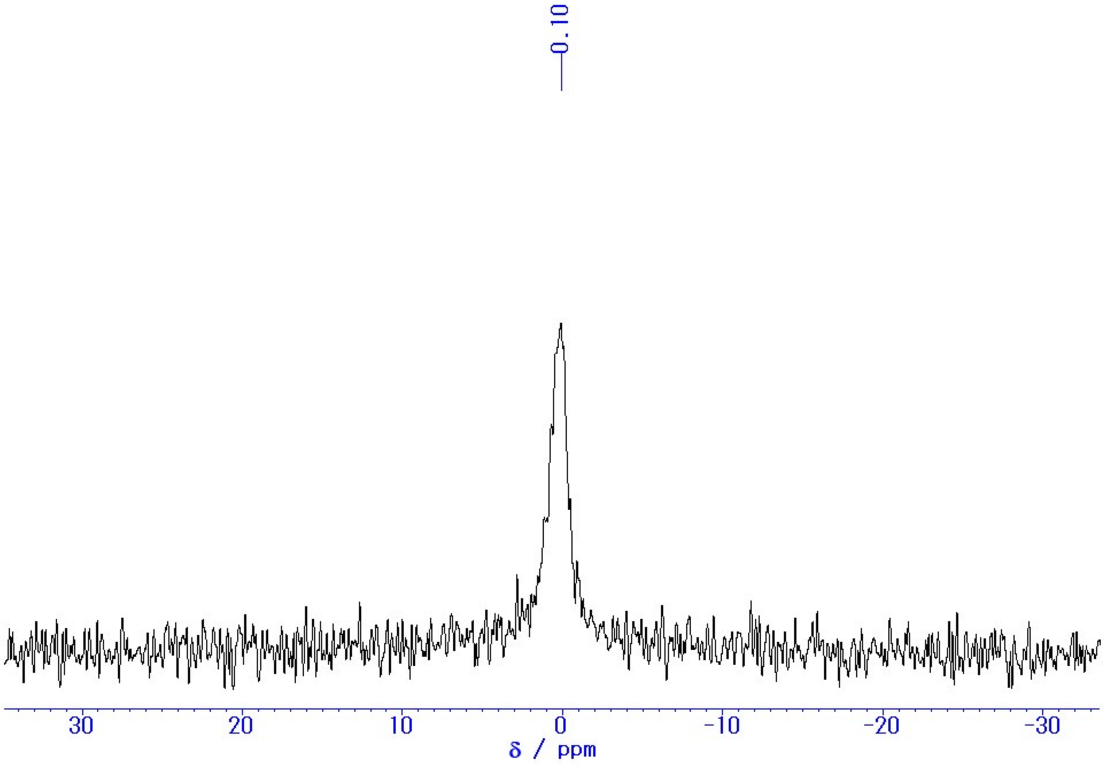


Figure S22. ^{11}B NMR spectrum of **BAm8BT2**, $CDCl_3$, 128 MHz.

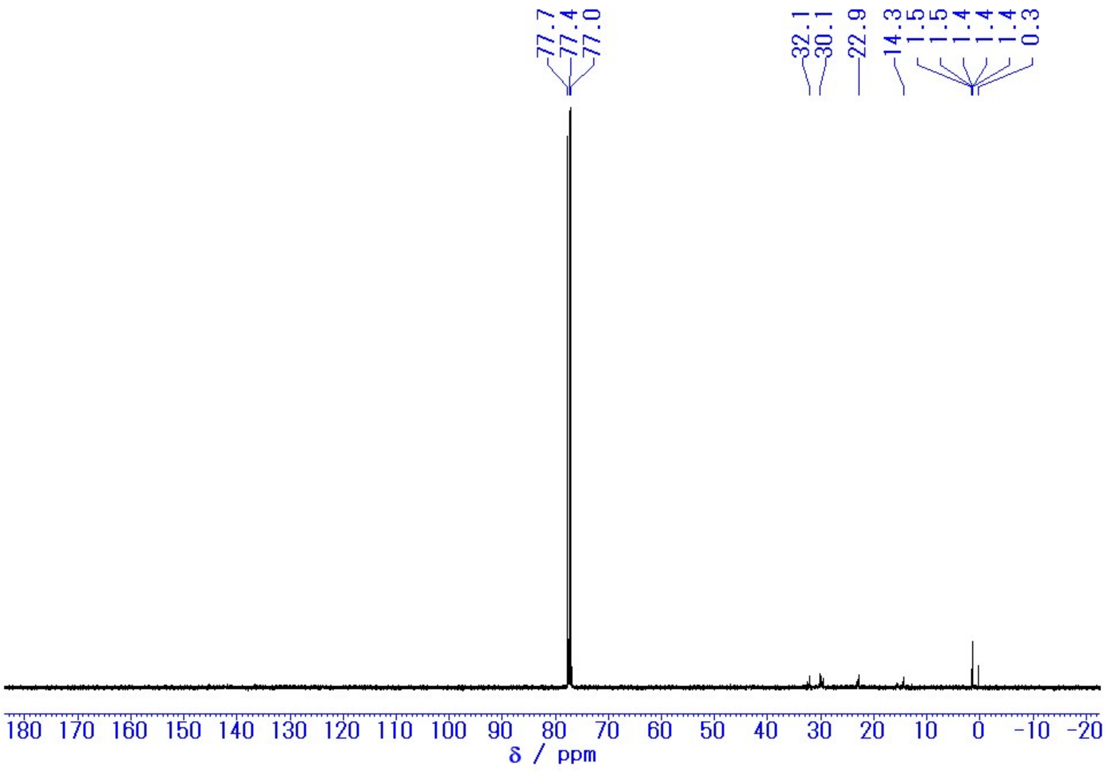


Figure S23. ^{13}C NMR spectrum of **BAm8BT2**, $CDCl_3$, 100 MHz.

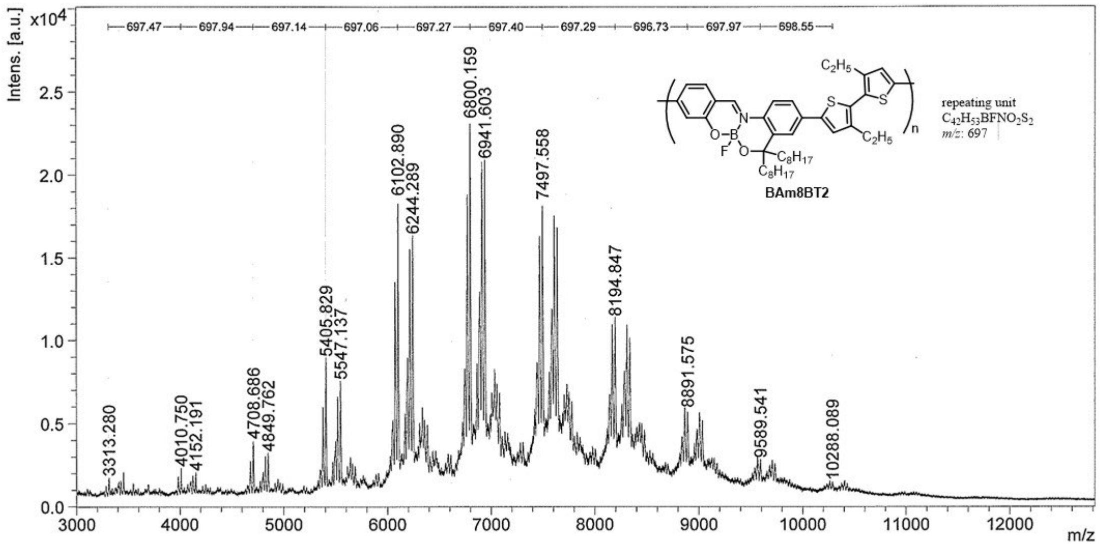
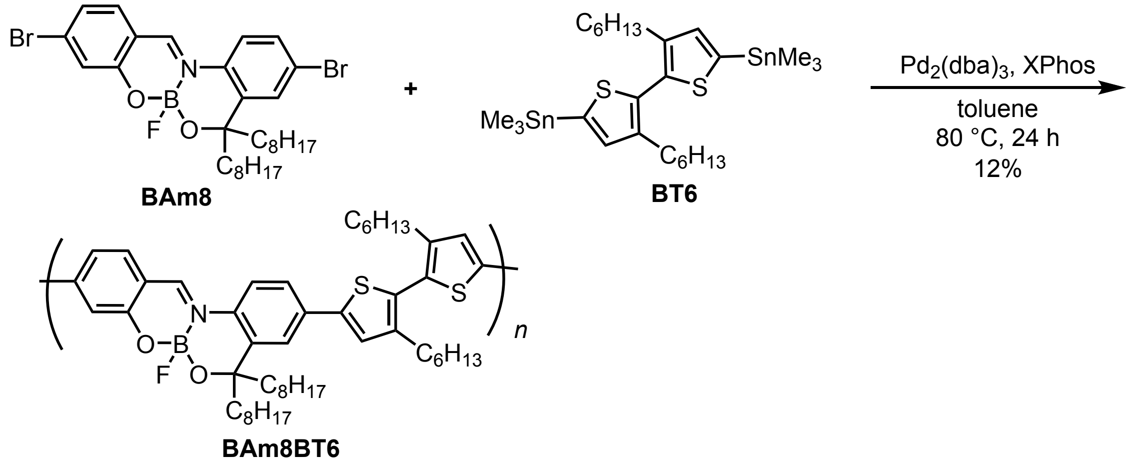


Figure S24. MALDI-TOF mass spectrum of **BAm8BTH**.

Synthesis of BAm8BT6



Scheme S13. Synthesis of **BAm8BT6**.

The mixture of **BAm8** (68.6 mg, 0.11 mmol), 3,3′-dihexyl-(2,2′-bithiophene)-5,5′-diyl)bis(trimethylstannane) (**BT6**) (71.1 mg, 0.11 mmol), $Pd_2(dba)_3$ (2.9 mg, 0.0032 mmol), X-Phos (3.1 mg, 0.0065 mmol) in toluene (2 mL) was stirred at 80 °C for 24 h under nitrogen atmosphere. After cooling to room temperature, the solution was purified by alumina column chromatography and poured into a large amount of methanol to collect the polymer by filtration. Additionally, the part of high molecular weight was fractionated by HPLC and to afford **BAm8BT6** as a red solid (11 mg, 12%).

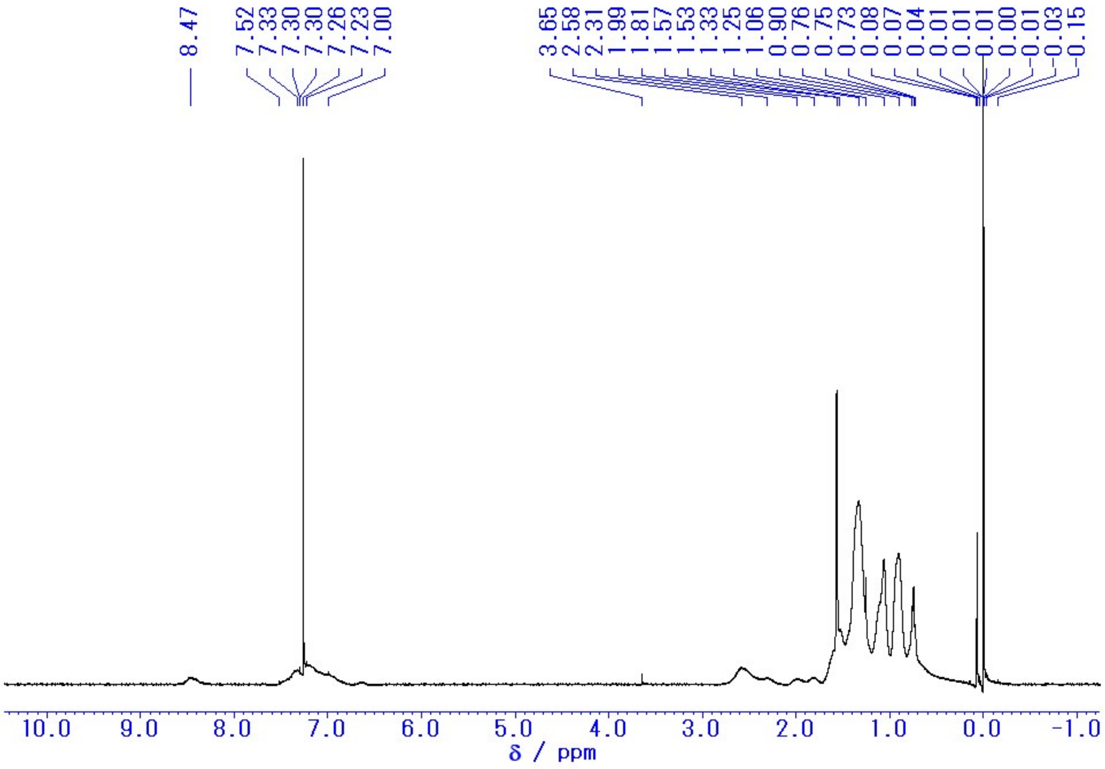


Figure S25. ^{1}H NMR spectrum of **BAm8BT6**, $CDCl_3$, 400 MHz.

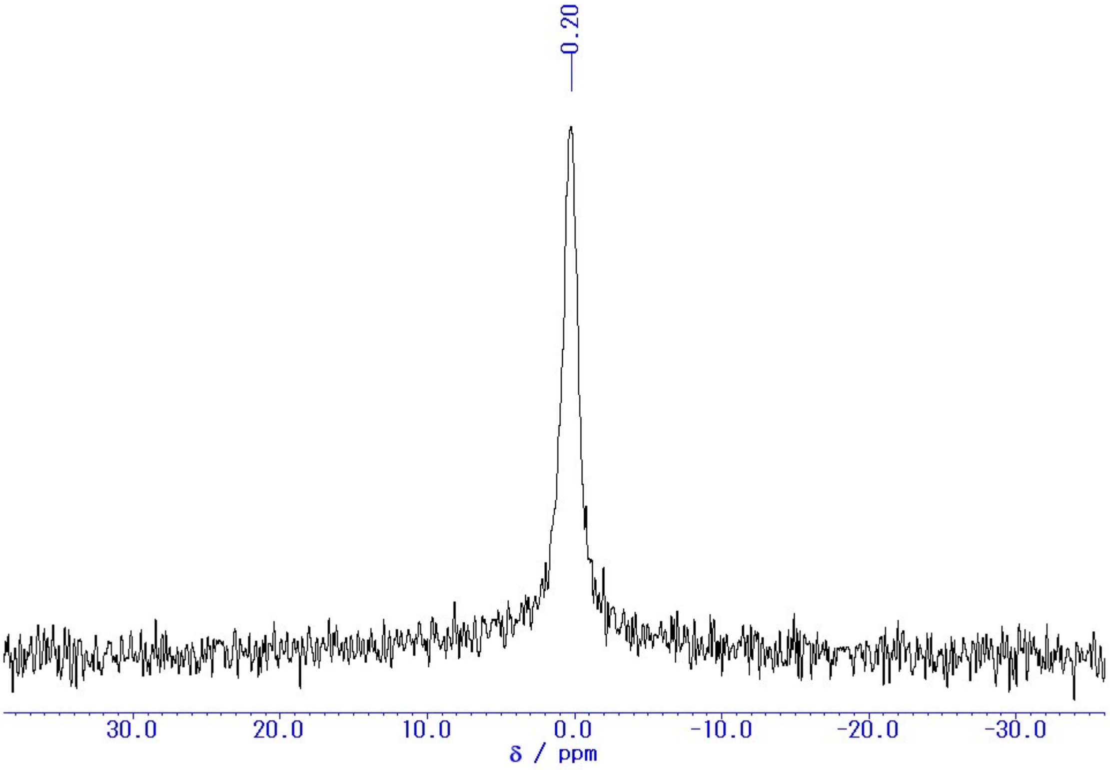


Figure S26. ^{11}B NMR spectrum of **BAm8BT6**, $CDCl_3$, 128 MHz.

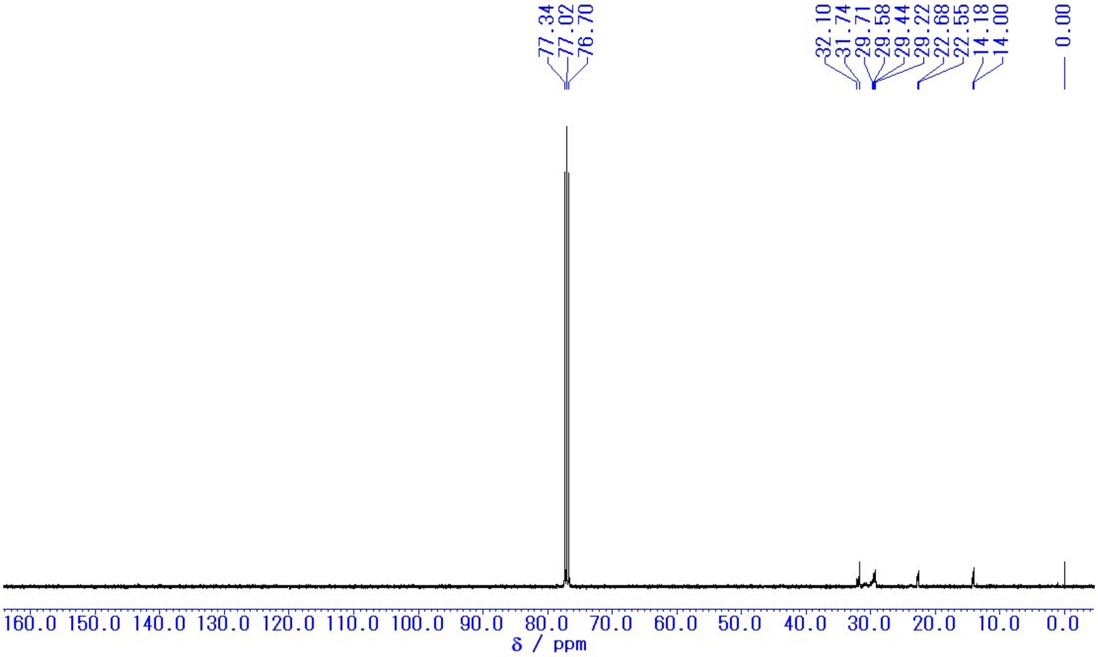


Figure S27. ^{13}C NMR spectrum of **BAm8BT6**, CDCl$_3$, 100 MHz.

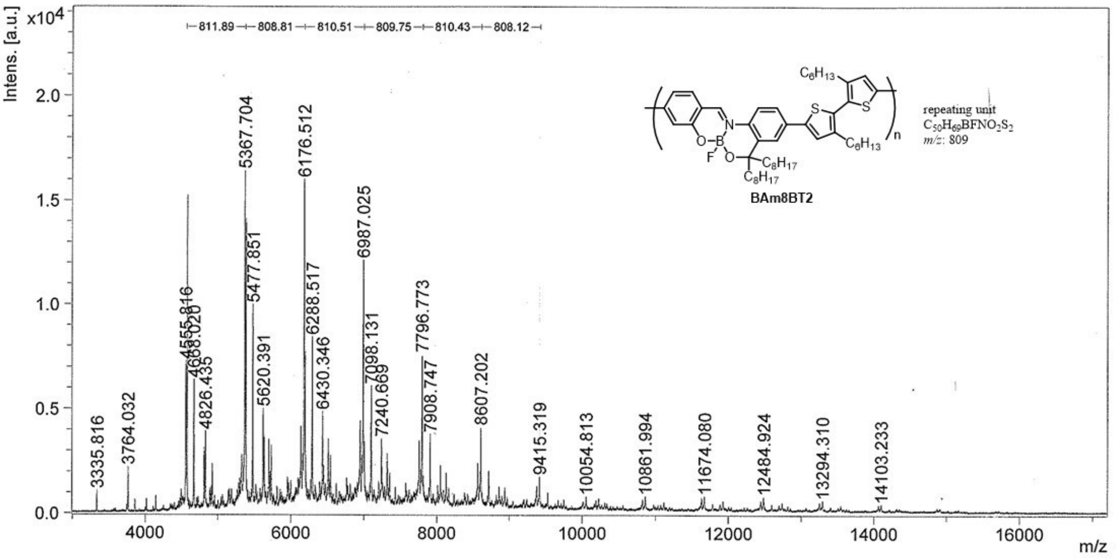


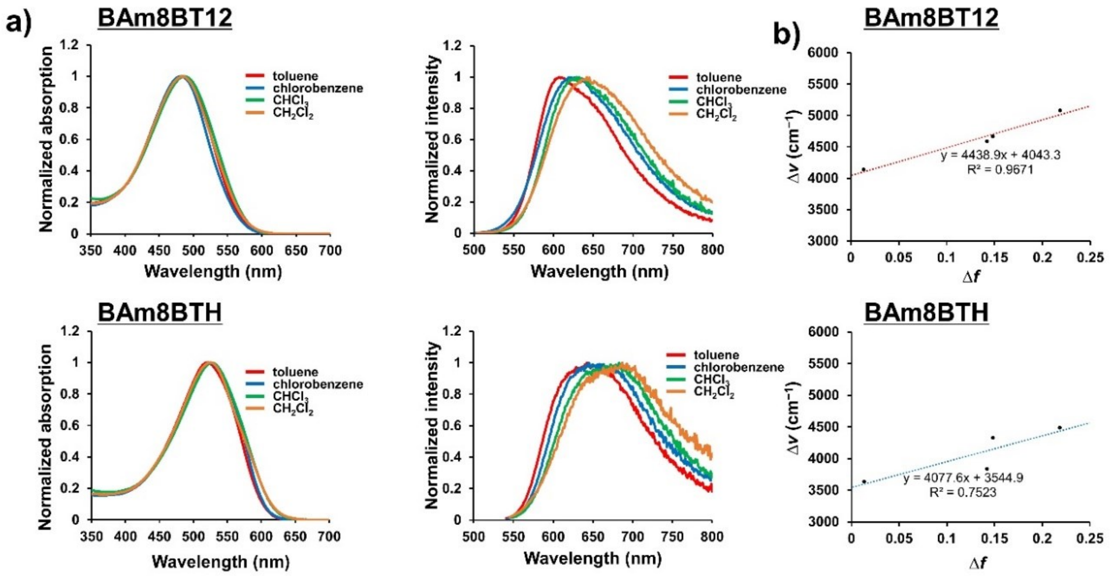
Figure S28. MALDI-TOF mass spectrum of **BAm8BT6**.

Table S1. Polymerization results[a]

	Yield (%)[b]	M_n	M_w	M_w/M_n	n[c]
BAm12BT12	79	22,000	72,800	3.3	20
BAm8BT12	67	33,100	93,000	2.8	34
BAm2BT12	51	17,000	50,500	3.0	20
BAm8BT6	12	27,500	38,600	1.4	33
BAm8BT2	8	20,100	30,600	1.5	28
BAm8BTH	7	9,100	12,700	1.4	14

[a]Estimated by SEC with the polystyrene standards in $CHCl_3$. [b]Isolated yield. [c]Average number of repeating units calculated from M_n and molecular weights of repeating units.

Lippert–Mataga plots



BAm8BT12	Δf^{a}	$\lambda_{\mathrm{abs,max}}$ (nm)^{b}	λ_{em} (nm)^{c}	Δv (cm^{-1})^{d}	$\Phi_{\mathrm{F}}{}^{e}$
toluene	0.013	485	607	4144	0.45
chlorobenzene	0.14	482	619	4592	0.40
$CHCl_3$	0.15	488	632	4669	0.38
CH_2Cl_2	0.22	484	642	5085	0.30

BAm8BTH	Δf^{a}	$\lambda_{\mathrm{abs,max}}$ (nm)^{b}	λ_{em} (nm)^{c}	Δv (cm^{-1})^{d}	$\Phi_{\mathrm{F}}{}^{e}$
toluene	0.013	521	643	4144	0.36
chlorobenzene	0.14	524	645	3840	0.33
$CHCl_3$	0.15	527	683	4334	0.27
CH_2Cl_2	0.22	525	687	4492	0.16

[a] Orientation polarizability. [b] The wavelength of the longest absorption maximum. [c] The wavelength of a fluorescence peak top excited at $\lambda_{\mathrm{abs,max}}$. [d] The Stokes shift: The difference between the absorption and emission peak top. [e] Absolute fluorescence quantum efficiency excited at $\lambda_{\mathrm{abs,max}}$.

Figure S29. a) UV–vis absorption (left) and PL spectra (right), b) Lippert–Mataga plots and c) Sumary of the spectroscopic data of **BAm8BT12** and **BAm8BTH**.

Computational Details

The Gaussian 16 program package[5] was used for computation. We optimized the structures of **BAm8BT12′** and **BAm8BTH′** in the ground S_0 states and calculated their molecular orbitals. The DFT was applied for the optimization of the structures in the S_0 states at B3LYP/6-311G(d,p) level (Table S2 and S3). We also confirmed that the optimized structures had no imaginary frequency by the frequency calculations at B3LYP/6-311G(d,p) level. Finally, we investigated the transition characters related to $S_0 \rightarrow S_1$ transitions by time-dependent (TD)-DFT calculation at B3LYP/6-311G(d,p) level (Table S4).

Table S2. Cartesian coordinates of DFT-optimized geometry for **BAm8BT12′**

Tag	Symbol	X	Y	Z
1	C	4.82612	−0.49177	−0.14659
2	C	3.50365	−0.07576	−0.34198
3	C	2.54246	−1.02118	−0.79781
4	C	2.946703	−2.35058	−1.04416
5	C	4.24388	−2.74897	−0.82746
6	C	5.209511	−1.81514	−0.36918
7	O	3.191764	1.189565	−0.14787
8	B	1.814315	1.705023	−0.11724
9	N	0.822699	0.626931	−0.7755
10	C	1.216196	−0.5829	−1.05586
11	O	1.73498	2.873114	−0.91195
12	C	0.481723	3.513402	−1.11671
13	C	−0.67241	2.495844	−1.20407
14	C	−0.48538	1.111232	−1.03507
15	C	−1.96898	2.943658	−1.46435
16	C	−3.07325	2.086563	−1.54406
17	C	−2.85637	0.714846	−1.32895
18	C	−1.58342	0.240597	−1.07797
19	F	1.388996	1.841013	1.211315
20	C	−4.42012	2.589362	−1.82918
21	C	6.592346	−2.22492	−0.12466
22	C	−5.4699	1.922046	−2.41013
23	C	−6.66352	2.690506	−2.54786

24	C	−6.51767	3.969464	−2.05672
25	S	−4.89872	4.222002	−1.43082
26	C	−7.48352	5.071631	−2.03403
27	S	−7.79151	5.991164	−3.49862
28	C	−8.90828	7.021464	−2.67357
29	C	−9.02475	6.684032	−1.35878
30	C	−8.21168	5.569058	−0.97613
31	C	7.519247	−1.63837	0.703423
32	C	8.783511	−2.29108	0.741493
33	C	8.819995	−3.40183	−0.07655
34	S	7.29263	−3.62445	−0.90448
35	C	9.926912	−4.3262	−0.32738
36	S	11.31454	−3.79985	−1.26577
37	C	12.07007	−5.34642	−1.10504
38	C	11.29816	−6.2095	−0.38658
39	C	10.06492	−5.64021	0.064339
40	C	3.853408	10.88126	5.224087
41	C	2.772045	9.838166	4.927542
42	C	2.993907	9.091642	3.607132
43	C	1.915997	8.045574	3.301714
44	C	2.139024	7.298869	1.981654
45	C	1.059281	6.254466	1.676458
46	C	1.295553	5.499986	0.362237
47	C	0.190373	4.477418	0.072791
48	C	2.4261	3.302289	−11.2141
49	C	2.158567	4.167262	−9.979
50	C	1.912235	3.348868	−8.70636
51	C	1.642799	4.206153	−7.46465
52	C	1.397613	3.386769	−6.19252
53	C	1.125597	4.243941	−4.95106
54	C	0.890292	3.419056	−3.6801
55	C	0.621256	4.289464	−2.44891
56	C	−18.4249	−7.13157	−1.29624
57	C	−17.7451	−6.04655	−2.1363
58	C	−16.4646	−5.49719	−1.49706
59	C	−15.7773	−4.41048	−2.33135

60	C	−14.497	−3.86097	−1.69194
61	C	−13.8104	−2.77478	−2.52786
62	C	−12.5304	−2.22374	−1.88939
63	C	−11.8449	−1.13842	−2.72738
64	C	−10.5653	−0.58502	−2.09004
65	C	−9.88209	0.499264	−2.93118
66	C	−8.60386	1.054711	−2.294
67	C	−7.93138	2.142791	−3.15223
68	C	−15.9356	−1.68192	10.16251
69	C	−14.6243	−1.01263	9.741176
70	C	−14.6474	−0.4846	8.302174
71	C	−13.3387	0.187028	7.871418
72	C	−13.3629	0.715725	6.432707
73	C	−12.0539	1.387568	6.002598
74	C	−12.0786	1.918371	4.564685
75	C	−10.7694	2.590538	4.135513
76	C	−10.7949	3.124887	2.698871
77	C	−9.48525	3.797253	2.271679
78	C	−9.51373	4.336376	0.837381
79	C	−8.19077	5.007821	0.42307
80	C	19.86559	8.131451	2.949796
81	C	19.15618	6.884015	3.484357
82	C	18.01778	6.398627	2.579674
83	C	17.30233	5.149659	3.106558
84	C	16.16393	4.664757	2.201664
85	C	15.45051	3.414303	2.728313
86	C	14.3118	2.92905	1.824042
87	C	13.6018	1.67623	2.349671
88	C	12.4628	1.190645	1.44589
89	C	11.75827	−0.06577	1.97026
90	C	10.62066	−0.55011	1.065132
91	C	9.928763	−1.81859	1.600027
92	C	−0.59223	−16.7121	0.295054
93	C	0.164945	−15.6513	1.098994
94	C	1.178875	−14.864	0.260951
95	C	1.942539	−13.8	1.057246

96	C	2.955153	−13.0128	0.217643
97	C	3.720853	−11.9501	1.014013
98	C	4.731234	−11.1618	0.172736
99	C	5.500251	−10.1012	0.968725
100	C	6.507179	−9.31143	0.124671
101	C	7.280455	−8.25384	0.920524
102	C	8.280632	−7.46281	0.070639
103	C	9.055622	−6.40634	0.880955
104	H	5.543459	0.257341	0.161271
105	H	2.210707	−3.06634	−1.39612
106	H	4.527577	−3.78094	−0.98982
107	H	0.520558	−1.27062	−1.53059
108	H	−2.12526	4.001601	−1.63471
109	H	−3.69428	0.029046	−1.31703
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112	H	−9.40933	7.814015	−3.20824
113	H	−9.66996	7.212696	−0.66831
114	H	7.289239	−0.77399	1.313473
115	H	13.04019	−5.52218	−1.54434
116	H	11.5969	−7.22673	−0.16594
117	H	3.665982	11.39489	6.171224
118	H	4.842882	10.41757	5.288068
119	H	3.896246	11.64102	4.437233
120	H	1.790273	10.32676	4.904644
121	H	2.730067	9.112482	5.748887
122	H	3.976643	8.602805	3.63031
123	H	3.036982	9.818368	2.785239
124	H	0.933676	8.53535	3.278861
125	H	1.873483	7.31985	4.124118
126	H	3.119338	6.806144	2.005284
127	H	2.184143	8.024702	1.159174
128	H	0.078635	6.748068	1.646525
129	H	1.011574	5.531591	2.500334
130	H	2.256031	4.97895	0.405369
131	H	1.367216	6.226222	−0.45553

132	H	−0.75485	4.999688	−0.11166
133	H	0.043442	3.857084	0.960559
134	H	2.597562	3.915477	−12.1032
135	H	3.308819	2.671065	−11.071
136	H	1.579325	2.641437	−11.425
137	H	1.291424	4.812324	−10.166
138	H	3.007876	4.841527	−9.81481
139	H	2.780378	2.703345	−8.51945
140	H	1.06269	2.673197	−8.8715
141	H	0.774534	4.851123	−7.6524
142	H	2.492261	4.881791	−7.30089
143	H	2.26674	2.743911	−6.0028
144	H	0.549299	2.709597	−6.35703
145	H	0.253662	4.884217	−5.13936
146	H	1.972152	4.923582	−4.78958
147	H	1.767076	2.795702	−3.48054
148	H	0.048046	2.736942	−3.84701
149	H	−0.27472	4.899376	−2.60942
150	H	1.45565	4.983966	−2.31995
151	H	−19.3334	−7.50144	−1.77945
152	H	−17.7595	−7.98682	−1.14152
153	H	−18.7056	−6.7499	−0.30954
154	H	−18.4473	−5.22075	−2.30322
155	H	−17.5084	−6.44832	−3.12904
156	H	−15.7621	−6.32405	−1.32945
157	H	−16.7017	−5.09549	−0.50322
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159	H	−15.541	−4.8131	−3.32486
160	H	−13.7935	−4.68674	−1.524
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163	H	−13.5741	−3.17844	−3.52091
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168	H	−9.86031	−1.40901	−1.91957
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172	H	−7.89655	0.23507	−2.11997
173	H	−8.83469	1.472266	−1.30721
174	H	−8.63805	2.960385	−3.31463
175	H	−7.70453	1.726135	−4.14136
176	H	−15.8861	−2.04671	11.19216
177	H	−16.7751	−0.98245	10.09825
178	H	−16.1684	−2.53595	9.518679
179	H	−13.7988	−1.72657	9.849749
180	H	−14.4008	−0.18484	10.4251
181	H	−15.4741	0.229661	8.193747
182	H	−14.8719	−1.31326	7.61787
183	H	−12.5128	−0.52788	7.979968
184	H	−13.1147	1.014705	8.55679
185	H	−14.1888	1.430677	6.324298
186	H	−13.5869	−0.11186	5.747181
187	H	−11.2282	0.672347	6.109831
188	H	−11.8294	2.214206	6.689007
189	H	−12.9043	2.633713	4.45763
190	H	−12.3029	1.091881	3.877945
191	H	−9.94394	1.874811	4.240426
192	H	−10.5442	3.415469	4.823673
193	H	−11.6202	3.84097	2.594085
194	H	−11.0198	2.300337	2.010153
195	H	−8.66006	3.080867	2.372767
196	H	−9.25873	4.619667	2.962506
197	H	−10.3371	5.052756	0.73329
198	H	−9.73166	3.519201	0.139979
199	H	−7.3764	4.284663	0.514101
200	H	−7.96747	5.817728	1.128466
201	H	20.67085	8.450935	3.617053
202	H	20.30504	7.944891	1.964825
203	H	19.16852	8.968944	2.846164

204	H	18.75771	7.091383	4.484955
205	H	19.88597	6.074999	3.610547
206	H	18.41667	6.192221	1.577878
207	H	17.28749	7.20857	2.45349
208	H	16.90439	5.356829	4.108419
209	H	18.03348	4.340572	3.232505
210	H	16.56149	4.458878	1.19942
211	H	15.43197	5.473153	2.076873
212	H	15.05338	3.619967	3.730775
213	H	16.18272	2.605947	2.852642
214	H	14.7083	2.725564	0.820917
215	H	13.5781	3.736206	1.701727
216	H	13.20577	1.879261	3.353094
217	H	14.33573	0.869053	2.471116
218	H	12.85777	0.990447	0.441727
219	H	11.72654	1.995923	1.327323
220	H	11.36284	0.133148	2.97484
221	H	12.49431	−0.8714	2.087186
222	H	11.0105	−0.75294	0.061349
223	H	9.878555	0.248718	0.949594
224	H	9.551903	−1.61873	2.610239
225	H	10.6656	−2.62077	1.694802
226	H	−1.30624	−17.2546	0.920816
227	H	−1.15112	−16.259	−0.5298
228	H	0.095199	−17.4462	−0.13691
229	H	0.685211	−16.1308	1.93702
230	H	−0.55179	−14.9525	1.547345
231	H	0.657806	−14.3843	−0.57791
232	H	1.895465	−15.5638	−0.18856
233	H	2.463736	−14.2808	1.895234
234	H	1.225375	−13.1015	1.507435
235	H	2.433564	−12.5311	−0.61954
236	H	3.671239	−13.7116	−0.23379
237	H	4.2442	−12.4321	1.849854
238	H	3.005015	−11.2521	1.467193
239	H	4.207267	−10.678	−0.66178

240	H	5.445391	−11.8601	−0.2825
241	H	6.026945	−10.5854	1.801204
242	H	4.7866	−9.40405	1.426437
243	H	5.97988	−8.82456	−0.70573
244	H	7.218629	−10.0089	−0.33595
245	H	7.812591	−8.74085	1.748022
246	H	6.570121	−7.55759	1.384341
247	H	7.752623	−6.96491	−0.75052
248	H	8.990429	−8.15453	−0.39834
249	H	9.576157	−6.90482	1.707644
250	H	8.348292	−5.70742	1.33565

Table S3. Cartesian coordinates of DFT-optimized geometry for **BAm8BTH′**

Tag	Symbol	X	Y	Z
1	H	−0.0019	−0.8425	2.921176
2	H	3.032622	−0.82987	3.35828
3	H	0.914482	1.44816	2.697804
4	H	2.18954	0.87578	1.657896
5	H	−0.65564	0.270724	0.810992
6	H	4.979973	5.198434	−2.29844
7	H	6.479805	4.608933	−0.36541
8	H	4.275153	3.429614	−0.66672
9	H	3.484702	4.646483	0.318723
10	H	0.520579	3.319825	−1.57615
11	H	1.992903	5.234921	−1.6255
12	H	2.316745	1.571493	−1.98578
13	H	2.737639	1.682945	−0.28155
14	H	2.166595	2.308238	6.608704
15	H	3.852415	1.959019	7.001649
16	H	2.616038	−1.55697	6.336398
17	H	3.120208	−0.14017	8.210224
18	H	0.743508	−0.23389	5.307186
19	H	1.905455	0.942345	4.721581
20	H	−1.71747	−3.1156	−0.6344
21	H	−4.16319	−3.59656	−0.58874
22	H	0.125946	−3.76186	−1.7389
23	H	2.497174	−4.3461	−1.51785
24	H	−14.4321	0.880774	1.084757
25	H	−9.73539	2.03225	−1.37348
26	H	4.48387	−4.79686	−0.28615
27	H	−11.3731	−2.12232	0.365038
28	H	11.09777	−0.50003	−1.79706
29	H	11.95924	−2.42001	−0.21354
30	H	7.337214	8.729712	−1.32244
31	H	6.286374	8.36774	0.05014
32	H	7.27649	6.31722	−2.02121
33	H	7.944943	6.513792	−0.41431
34	H	−6.46797	−2.75724	−0.46932

35	C	0.211448	0.931789	0.727882
36	C	1.435355	3.259323	−0.98332
37	C	5.998859	5.592285	−0.43628
38	C	7.018079	6.598943	−0.99283
39	C	6.498469	−3.92547	−0.46652
40	C	−11.118	0.01418	0.151522
41	S	−8.54652	−1.04723	0.111562
42	C	−7.79212	0.999624	−1.25283
43	C	3.122131	−2.35187	−0.97293
44	B	−1.25731	0.124348	−1.95499
45	C	−5.91926	−0.68312	−0.81338
46	O	−2.56327	0.576887	−1.39032
47	C	1.144742	0.69736	1.936226
48	C	2.500406	0.301452	7.421761
49	C	6.550586	8.058548	−0.9665
50	C	8.459295	−2.33138	−0.81261
51	H	1.928761	−2.02999	3.997157
52	H	1.186509	−1.45725	1.787925
53	H	−0.19519	1.944675	0.753602
54	C	−13.4867	0.42231	0.839545
55	H	5.738129	5.876137	0.592005
56	H	4.192432	6.41468	−1.31083
57	H	2.728642	3.955628	−2.56957
58	H	1.172829	3.564964	0.03647
59	H	2.691494	2.291167	8.290434
60	H	1.460439	0.1697	7.745516
61	H	3.766492	−0.35027	5.795527
62	S	−12.1472	1.416058	0.37284
63	H	−5.01796	1.256272	−1.1578
64	H	3.397885	−0.27402	−0.53196
65	H	−7.1956	1.688212	−1.83578
66	H	−13.8527	−1.688	1.104089
67	H	7.090497	−4.80339	−0.24311
68	H	8.498896	−0.61823	−2.13095
69	H	5.673817	8.218489	−1.59934
70	C	1.782752	−0.11623	4.971064

71	C	1.02657	−0.70119	2.56312
72	C	2.004743	−0.97219	3.716678
73	C	2.727076	−0.48687	6.122199
74	C	2.818128	1.797789	7.322768
75	C	3.7514	4.391807	−0.71585
76	C	1.916565	1.801911	−0.99253
77	C	2.468023	4.249718	−1.54463
78	C	4.714615	5.45208	−1.26349
79	C	10.94039	−2.22465	−0.50996
80	C	9.054949	−1.29899	−1.49975
81	C	10.46411	−1.23939	−1.32573
82	S	9.665549	−3.23953	0.079412
83	S	5.806476	−1.52477	−1.08213
84	C	−11.8113	−1.13661	0.450207
85	C	7.060301	−2.70295	−0.75622
86	C	5.0841	−3.92446	−0.50802
87	C	−13.1565	−0.90259	0.842085
88	C	−9.74507	0.163413	−0.28295
89	C	2.672435	−1.0332	−0.79079
90	C	0.836323	−3.00506	−1.42769
91	C	−9.16982	1.18661	−1.00487
92	C	−7.28349	−0.1697	−0.73212
93	C	4.535289	−2.70559	−0.83273
94	C	0.409172	−1.69188	−1.21433
95	C	2.175823	−3.33369	−1.30747
96	F	−1.41969	−0.09105	−3.32097
97	C	1.332766	−0.67371	−0.91025
98	C	−4.36409	−2.5391	−0.72706
99	C	0.813105	0.758397	−0.69956
100	N	−0.95283	−1.32107	−1.31256
101	C	−3.54572	−0.2777	−1.18758
102	C	−3.28815	−1.66922	−1.00903
103	C	−4.85942	0.1901	−1.06427
104	C	−5.65167	−2.06867	−0.64668
105	C	−1.94024	−2.11096	−0.98685
106	O	−0.20607	1.016677	−1.6618

Table S4. Photophysical parameters obtained by TD-DFT/B3LYP/6-311G(d,p) based on optimized geometries in the S_0 states

	Excitation energy	$S_0 \rightarrow S_1$ transition contribution	Oscillator strength
BAm8BT12′	2.80 eV (444 nm)	HOMO–LUMO (97%)	1.7789
BAm8BTH′	2.53 eV (491 nm)	HOMO–LUMO (99%)	1.5361

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