

Electronic Supplementary Information

**Synthesis of an ABC Triblock Copolymer by a Bilateral Click
Reaction Using α,ω -Bifunctionalized Poly(3-hexylthiophene)
as an Inner Segment**

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Materials.

Tetrahydrofuran (THF, Tokyo Chemical Industry Co.) was dried over sodium benzophenone and distilled before use under N₂. THF (deoxidized) for living anionic polymerization was purchased from Fujifilm Wako Chemical Co. and used as received inside glovebox (GB) under purified N₂ (O₂ < 10 ppm, H₂O < 10 ppm). Lithium chloride (LiCl) was dried in a flask by a heat gun under vacuum and stored inside GB. Methyl methacrylate (MMA) was washed with NaOH aqueous solution followed by drying over magnesium sulfate (MgSO₄). After filtration of MgSO₄, MMA was purified by distillation under reduced pressure over calcium hydride and immediately transferred into GB and stored under N₂. 1-Pheny-1-[4'-(2''-triisopropylsilylethynyl)phenyl]ethylene was synthesized according to the literature.¹ The precursor for the functionalized external initiator, 2-methyl-4-(*tert*-butyldimethylsilyloxymethyl)phenyl-bis(triphenylphosphino)nickel(II) bromide (TBSO-Ar-Ni(PPh₃)₂Br), was synthesized by the previous report.² The precursory terminating reagent of 2-bromo-5-(4-bromobutyl)thiophene was synthesized according to the previous report.³ Synthesis of *w*-chain-end-functionalized polystyrene (PS) with an alkyne group (**3**: M_n (SEC) = 5,000, M_n (¹H NMR) = 6,100, \bar{D}_M = 1.04) was synthesized according to the literature.⁴ Other reagents were purchased from Tokyo Chemical Industry Co., Fujifilm Wako Chemical Co., Kanto Chemical Co., or Aldrich, Japan, and were used without further purification.

Measurements.

¹H nuclear magnetic resonance (NMR) spectra were recorded with a JOEL JNM-ECX400 spectrometer at 25 °C using deuterated chloroform (CDCl₃). Number-average molecular weights (M_n), weight-average molecular weights (M_w), and molar-mass dispersity (\bar{D}_M) were measured by size-exclusion chromatography (SEC) on a JASCO GULLIVER 1500 equipped with a pump (JASCO PU-1580 Intelligent HPLC Pump), an absorbance detector (JASCO UV-1575 Intelligent UV/VIS Detector, λ = 254 nm), and two polystyrene gel columns (Shodex GPC KF-804L, Shodex GPC KF-805L) and one guard column (Shodex Column GPC KF-G), based on a calibration curve using polystyrene standards. THF (40 °C) was used as a carrier solvent at the flow rate of 1.0 mL/min. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG) and a TA Instruments Q-100 connected to a cooling system at a heating rate of 10 °C/min for differential scanning calorimetry (DSC). UV-Vis absorption spectra of the polymer solution and thin films (drop cast from the chloroform solution followed by annealed at 150 °C for 10 min) were recorded using a JASCO V-630BIO UV-Vis spectrophotometer. Tapping mode AFM observation was performed with an Agilent AFM 5500, using microfabricated cantilevers with a force constant of 47 N/m. The polymer thin film samples for AFM analysis were prepared by spin-coating the polymers onto Si wafers from their toluene solutions, followed by annealing at 150 °C for 10 min. Matrix-assisted laser desorption ionization time-of flight mass spectrometry (MALDI-TOF MS)

analysis was performed on a JMS-S3000 SpiralTOF™-plus (JEOL Ltd., Japan) at an acceleration voltage of 20 kV in the positive linear mode. External mass calibration was performed using a PSt standard ($M_n = 5000$, Tosoh corp. A-5000). *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propanylidene]malononitrile (DCTB) was used as the matrix. The polymer solution in THF (10 mg/mL) and the matrix solution in THF (20 mg/mL) were mixed at a volume ratio of 1:5. 1 μ L of the mixed solution was deposited on a MALDI sample plate, followed by drying in air at room temperature.

Synthesis of TBSO-P3HT-Br (1).

2-Bromo-3-hexyl-5-iodothiophene (2.1 g, 5.5 mmol) and dry THF (100 mL) were placed in a flask, and the atmosphere was then replaced with N_2 and the mixture was cooled to 0 °C. i PrMgCl·LiCl (1.3 M in THF solution \times 4.2 mL, 5.5 mmol) was then added and the reaction mixture was stirred at room temperature for 30 min to prepare the monomer solution. TBSO-Ar-Ni(PPh₃)₂Br (0.16 g, 0.19 mmol) and 1,2-bis(diphenylphosphino)propane (0.16 g, 0.38 mmol) were placed into another flask. Then dry THF (8 mL) was added via a syringe under a N_2 atmosphere. This Ni catalyst solution was then added to the monomer solution via a syringe to initiate the polymerization. The mixture was stirred at room temperature for 10 min to afford the solution of the living poly(3-hexylthiophene) (P3HT). In another flask, a THF solution of i PrMgCl·LiCl (1.3 M in THF solution \times 1.4 mL, 1.8 mmol) was added to a THF solution (10 mL) of 2-bromo-5-(4-bromobutyl)thiophene (0.54 g, 1.8 mmol) at 0 °C under a N_2 atmosphere, and the mixture was stirred at room temperature for 30 min to obtain the terminator solution. It was then added to the solution of living P3HT to terminate the polymerization. The solution was then poured into methanol to precipitate the polymer. After filtration, freeze-drying of the polymer from its benzene solution afforded **1** as a dark purple solid. M_n (SEC) = 8,400, M_n (¹H NMR) = 5,600, $D_M = 1.07$, Yield: 0.80 g, 88%.

¹H NMR (400 MHz, CDCl₃) δ 6.98 (s), 4.74 (s), 3.45 (t), 2.92-2.79 (m), 2.80 (t, $J = 7.3$ Hz), 2.49 (s), 2.01-1.83 (m), 1.70 (m), 1.39 (m), 0.96 (s), 0.91 (br), 0.12(s).

Synthesis of TBSO-P3HT-N₃ (2).

1 (0.26 g, 47 μ mol, based on M_n (calcd) = 5,500) was placed in a flask and dry THF (10 mL) was added to dissolve **1** at elevated temperature, followed by the addition of trimethylsilyl azide (0.14 ml, 1.4 mmol) and tetra(*n*-butyl)ammonium fluoride (TBAF) in a THF solution (1.0 M, 1 mL, 1 mmol). The reaction mixture was stirred at room temperature overnight and poured into methanol to precipitate the polymer. After filtration, freeze-drying of the polymer from its benzene solution afforded **2** as a dark purple solid. M_n (SEC) = 8,400, M_n (¹H NMR) = 6,000, $D_M = 1.08$, Yield: 0.23 g, 92%.

¹H NMR (400 MHz, CDCl₃) δ 6.98 (s), 4.74 (s), 3.30 (t), 2.88 (m), 2.81 (t), 2.49 (s), 1.84-1.79 (m), 1.70 (m), 1.40 (m), 0.96 (s), 0.91 (br), 0.13 (s).

Synthesis of TBSO-P3HT-*b*-PS (4).

2 (0.10 g, 17 μmol based on M_n ($^1\text{H NMR}$) = 6,000), **3** (0.22 g, 44 μmol based on M_n (SEC) = 5,000), and PMDETA (100 mg, 0.58 mmol) were placed in a flask. Dry THF 5 mL was then added to dissolve all the chemicals at elevated temperature. The solution was degassed by three freeze–pump–thaw cycles. Next, CuBr (53 mg, 0.38 mmol) was added to the solution. After stirring at 60 $^\circ\text{C}$ overnight, the resulting solution was directly passed through a short pad of Al_2O_3 column to remove the copper catalyst. It was concentrated by reduced pressure and poured into acetone to precipitate the polymer. After filtration, freeze-drying of the polymer from its benzene solution afforded **4** as a dark purple solid. M_n (SEC) = 13,000, D_M = 1.07, Yield: 0.17 g, 89%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.21-6.90 (m), 6.74-6.34 (m), 4.74 (s), 4.42 (td, J = 3.3, 1.3 Hz), 2.89-2.66 (m), 2.06-1.80 (m), 1.74-1.67 (m), 1.49-1.42 (m), 1.37-1.33 (m), 0.96 (s), 0.93-0.86 (m), 0.72-0.56 (m).

Synthesis of HO-P3HT-*b*-PS (5).

4 (0.13 g, 10 μmol based on M_n (SEC) = 13,000) and THF 20 mL were placed in a flask, followed by the addition of TBAF in a THF solution (1.0 M, 0.3 mL, 0.3 mmol). The reaction mixture was stirred at room temperature overnight. It was poured into methanol to precipitate the polymer. After filtration, freeze-drying of the polymer from its benzene solution afforded **5** as a dark purple solid. M_n (SEC) = 13,000, D_M = 1.07, Yield: 0.12 g, 95%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.18-6.91 (m), 6.71-6.47 (m), 4.71 (s), 4.43-4.41 (m), 2.82-2.65 (m), 2.51 (s), 2.05-1.87 (m), 1.74-1.67 (m), 1.45-1.34 (m), 0.93-0.86 (m), 0.71-0.56 (m).

Synthesis of N_3 -P3HT-*b*-PS (6).

5 (0.092 g, 7.1 μmol based on M_n (SEC) = 13,000) and THF 20 mL were placed in a flask, followed by the addition of diphenylphosphoryl azide (DPPA) (0.04 mL, 0.11 mmol) at 0 $^\circ\text{C}$. Next, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.03 mL, 0.19 mmol) was stepwisely added at 0 $^\circ\text{C}$. The reaction mixture was stirred at room temperature overnight, being shielded from light covered with aluminum foils. It was poured into methanol to precipitate the polymer. After filtration, freeze-drying of the polymer from its benzene solution afforded **6** as a dark purple solid. M_n (SEC) = 13,000, D_M = 1.08, Yield: 0.088 g, 96%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.19-6.92 (m), 6.73-6.35 (m), 4.37-4.51 (m), 4.34 (s), 2.81-2.65 (m), 2.51 (s), 1.96-1.80 (m), 1.64-1.76, 1.58 (s), 1.44-1.22 (m), 0.93-0.86 (m), 0.77-0.62 (m).

Synthesis of a-Chain-End-Functionalized PMMA with a Triisopropylsilylethynyl Group (TIPS-alkyne-PMMA).

THF 20 mL, LiCl (0.064 g, 1.5 mmol), and 1-phenyl-1-[4'-(2''-triisopropylsilylethynyl)phenyl]ethylene (0.13 g, 0.36 mmol) were placed in a flask and cooled to

-78 °C in GB under N₂ (O₂ <10 ppm, H₂O < 10 ppm). Next, a cyclohexane/hexane solution of *sec*-butyllithium (*sec*-BuLi, 1.2 M) was dropwisely added to the solution until getting coloration in light red. Then, *sec*-BuLi (1.2 M, 0.25 mL, 0.30 mmol) was added to the solution at -78 °C. The color of the solution immediately changed to dark red upon addition of *sec*-BuLi. After stirring for 10 min, THF (3 mL) solution of MMA (1.5 g, 0.015 mol) was added at once with vigorous mixing. After stirring at -78 °C for another 1 h, ethanol (deoxidized) was added to quench the polymerization. The obtained solution was then poured into a mixture of methanol/water (1:1, by vol.) to precipitate the polymer. It was filtrated, and freeze dried from its benzene solution to afford TIPS-alkyne-PMMA as a white solid. M_n (SEC) = 6,800, D_M = 1.03, Yield: 1.6 g, 99%.

¹H NMR (400 MHz, CDCl₃) δ 3.60 (s), 1.81 (s), 1.12 (t, J = 3.0 Hz), 1.02 (s), 0.85 (s)

Synthesis of Alkyne-PMMA (7).

TIPS-alkyne-PMMA (0.81 g, 0.12 mmol based on M_n (SEC) = 6,800), THF 50 mL, TBAF in a THF solution (1.0 M, 1.5 mL) were placed in a flask under nitrogen. After stirring at room temperature overnight, the solution was then poured into a mixture of methanol/water (1:1, by vol.) to precipitate the polymer. It was filtrated, and freeze dried from its benzene solution to afford **7** as a white solid. M_n (SEC) = 6,600, D_M = 1.03, Yield: 0.67 g, 83%.

¹H NMR (400 MHz, CDCl₃) δ 3.59 (s), 3.06 (q, J = 1.7 Hz), 1.81 (s), 1.01 (s), 0.85 (s)

Synthesis of PMMA-*b*-P3HT-*b*-PS (8).

6 (0.042 g, 3.2 μmol based on M_n (SEC) = 13,000), **7** (0.055 g, 8.3 μmol based on M_n (SEC) = 6,600), PMDETA (0.013 g, 0.075 mmol), and THF 5 mL were placed in a flask, and then the solution was degassed by three freeze-pump-thaw cycles. Next, CuBr (16 mg, 0.11 mmol) was added to the solution. After stirring at 60 °C overnight, the solution was passed through a short pad of Al₂O₃ column to remove the copper catalyst. It was concentrated by reduced pressure and poured into methanol to precipitate the polymer. After filtration, freeze-drying of the polymer from its benzene solution afforded **8** as a purple solid. M_n (SEC) = 18,000, D_M = 1.10, Yield: 0.067 g, 96%.

¹H NMR (400 MHz, CDCl₃) δ 7.19-6.91 (m), 6.64-6.39 (m), 5.58 (s), 3.60 (s), 2.91-2.78 (m), 2.72-2.64 (m), 2.06-1.90 (m), 1.81 (s), 1.74-1.69 (m), 1.62 (s), 1.44-1.25 (m), 1.02 (s), 0.91-0.86 (m), 0.75-0.57 (m). Anal. Calcd. for (C₅H₈O)_l(C₁₀H₁₄S)_n(C₈H₈)_m (%) (excluding the chain-end and joint units between polymer segments): C 73.1; H 8.08; S 5.40. Found: C 71.3; H 8.09; S 5.34.

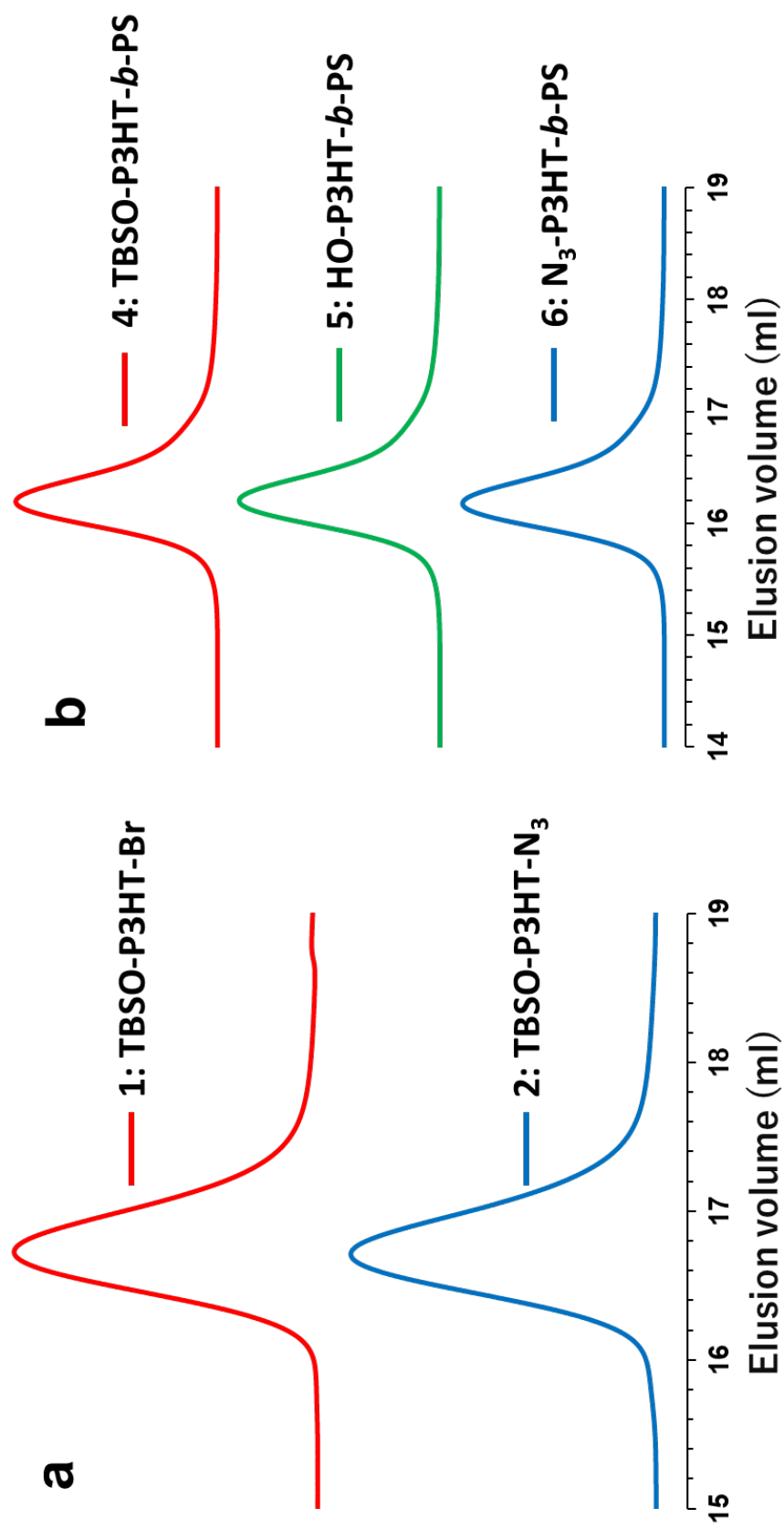


Figure S1. SEC UV curves of (a) 1, 2 and (b) 4, 5, and 6.

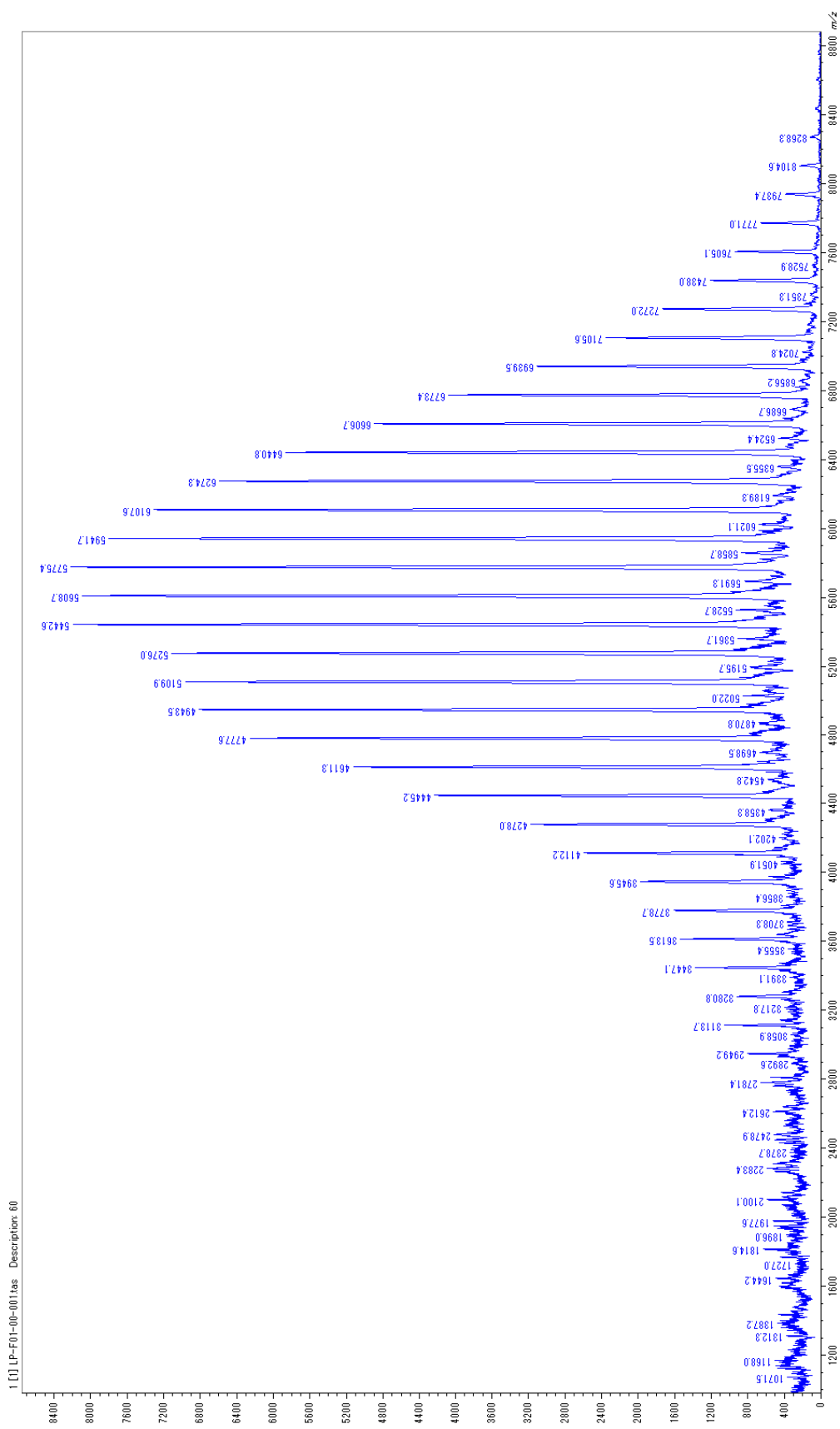


Figure S2. MALDI-TOF mass spectra of **1**.

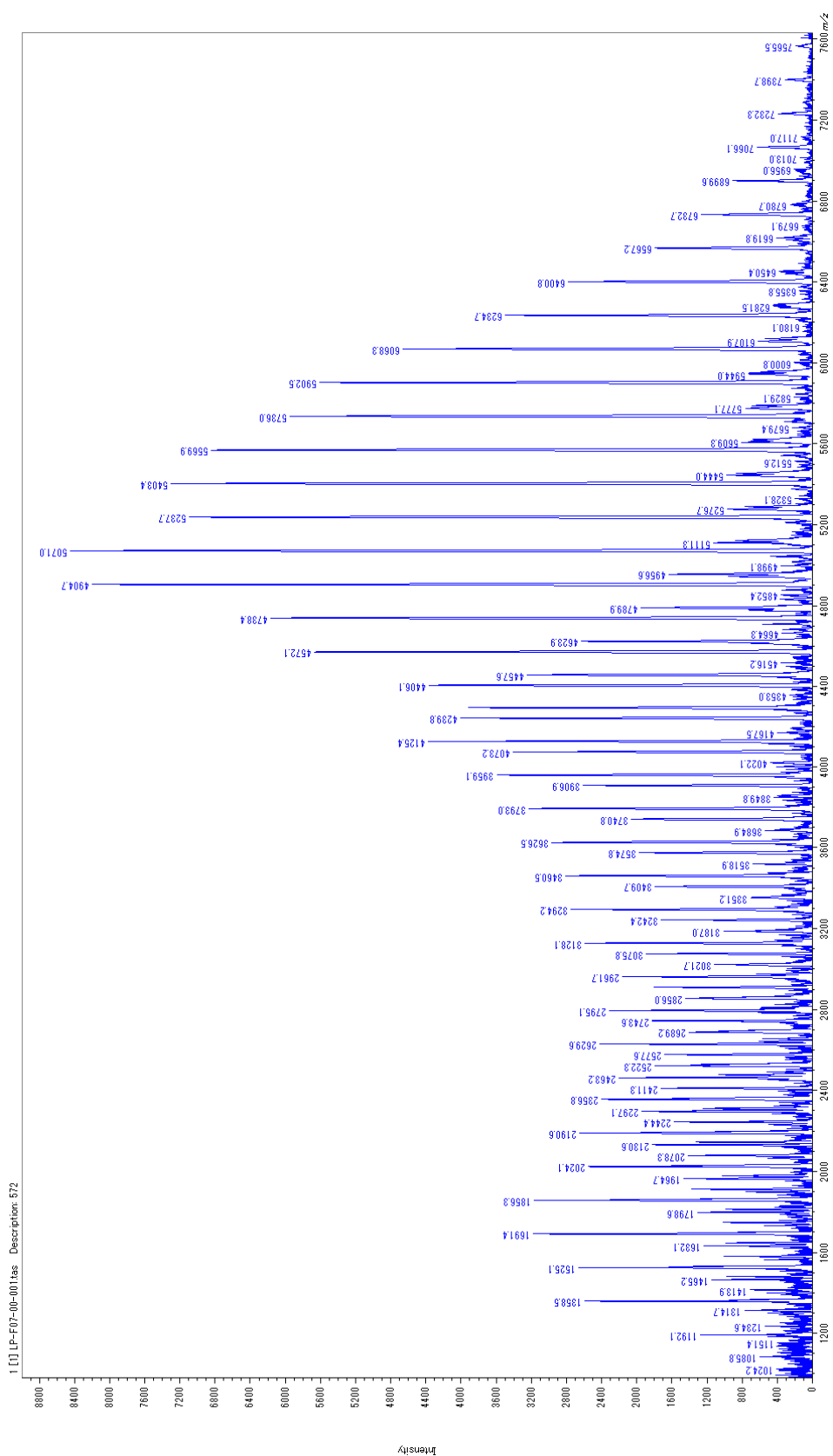


Figure S3. MALDI-TOF mass spectra of **2**.

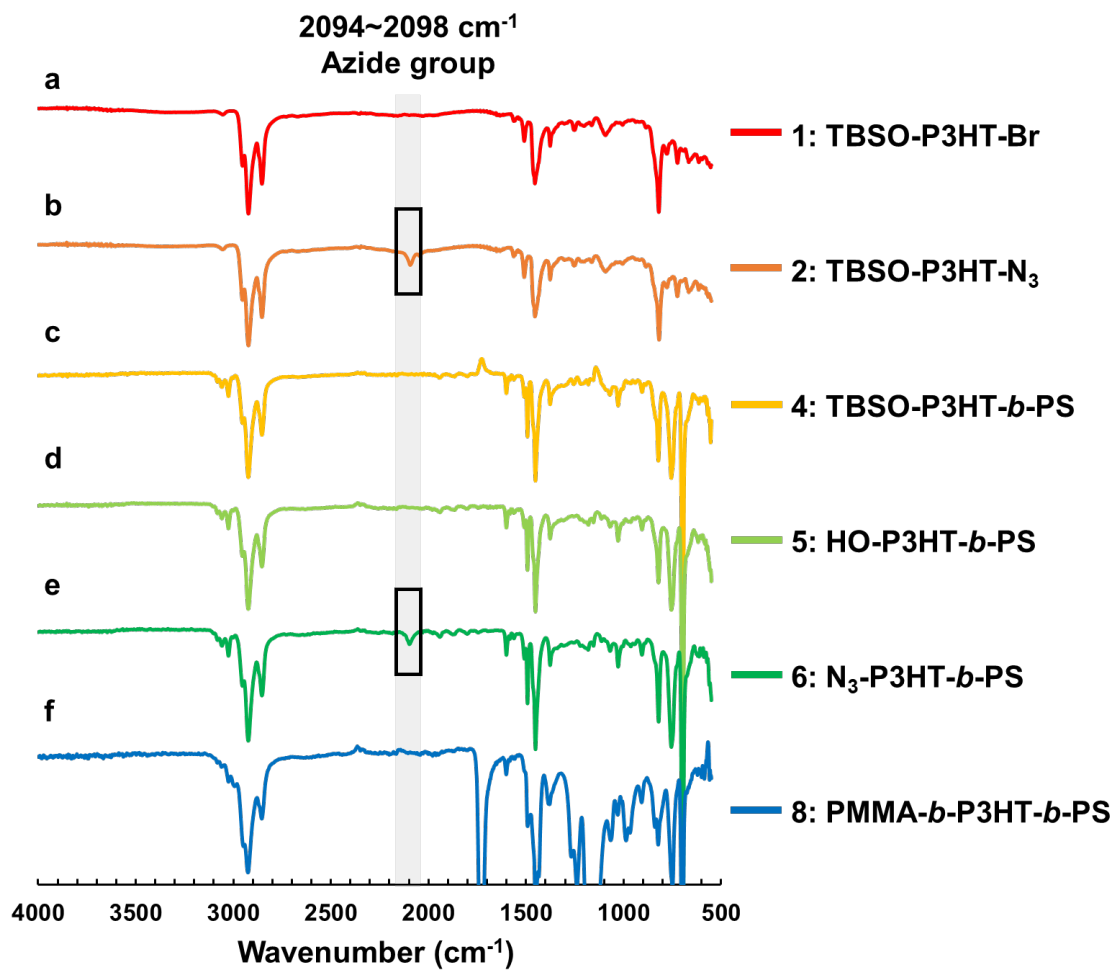


Figure S4. FT-IR spectra of (a) 1, (b) 2, (c) 4, (d) 5, (e) 6, and (f) 8.

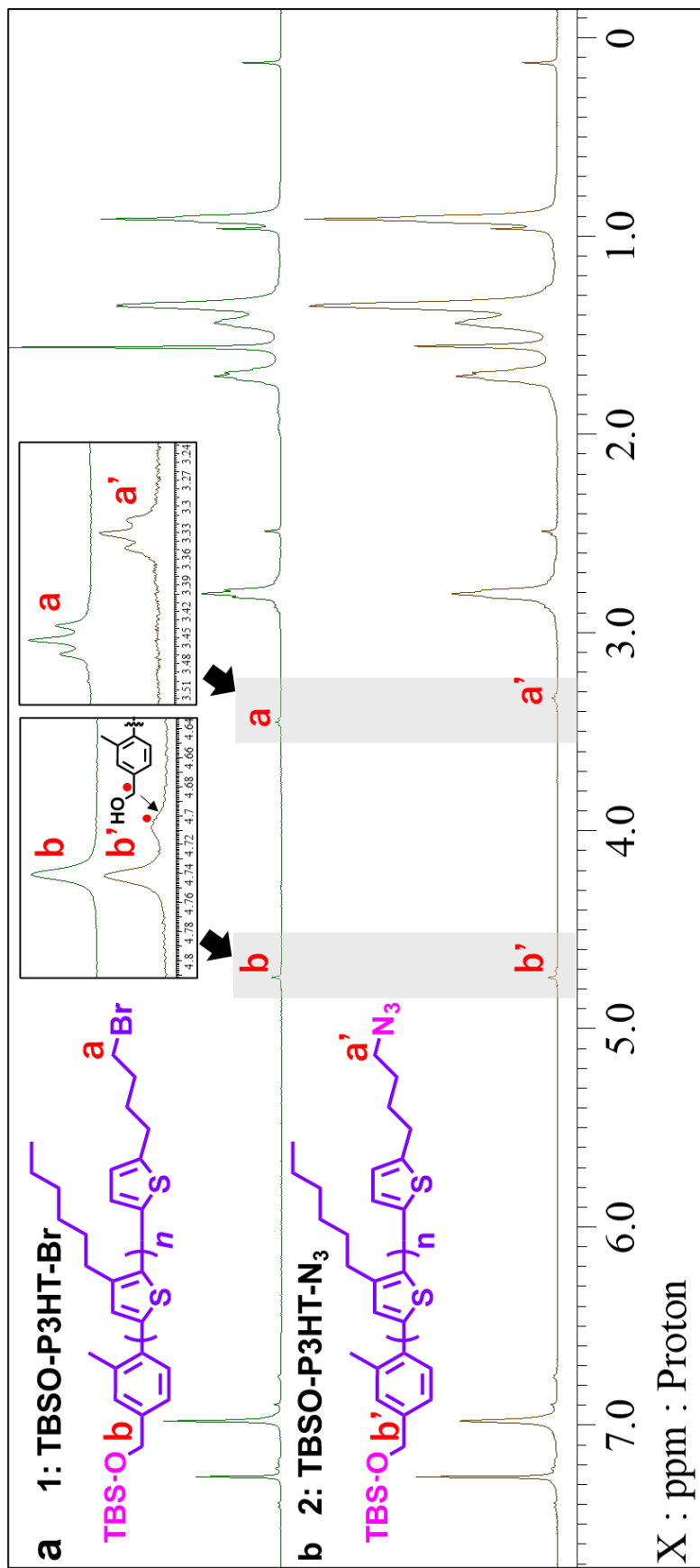


Figure S5. ¹H NMR spectra of (a) **1** and (b) **2**.

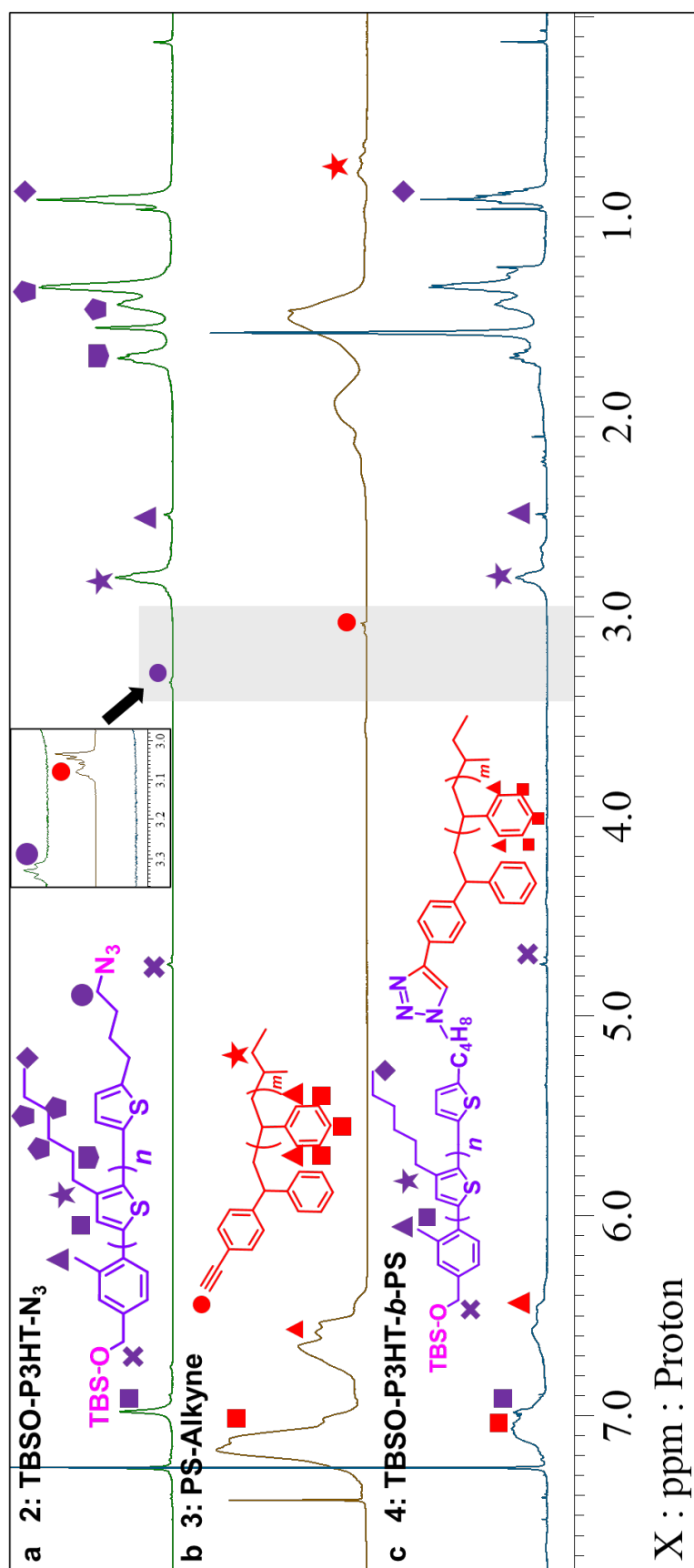


Figure S6. ¹H NMR spectra of (a) **2**, (b) **3**, and (c) **4**.

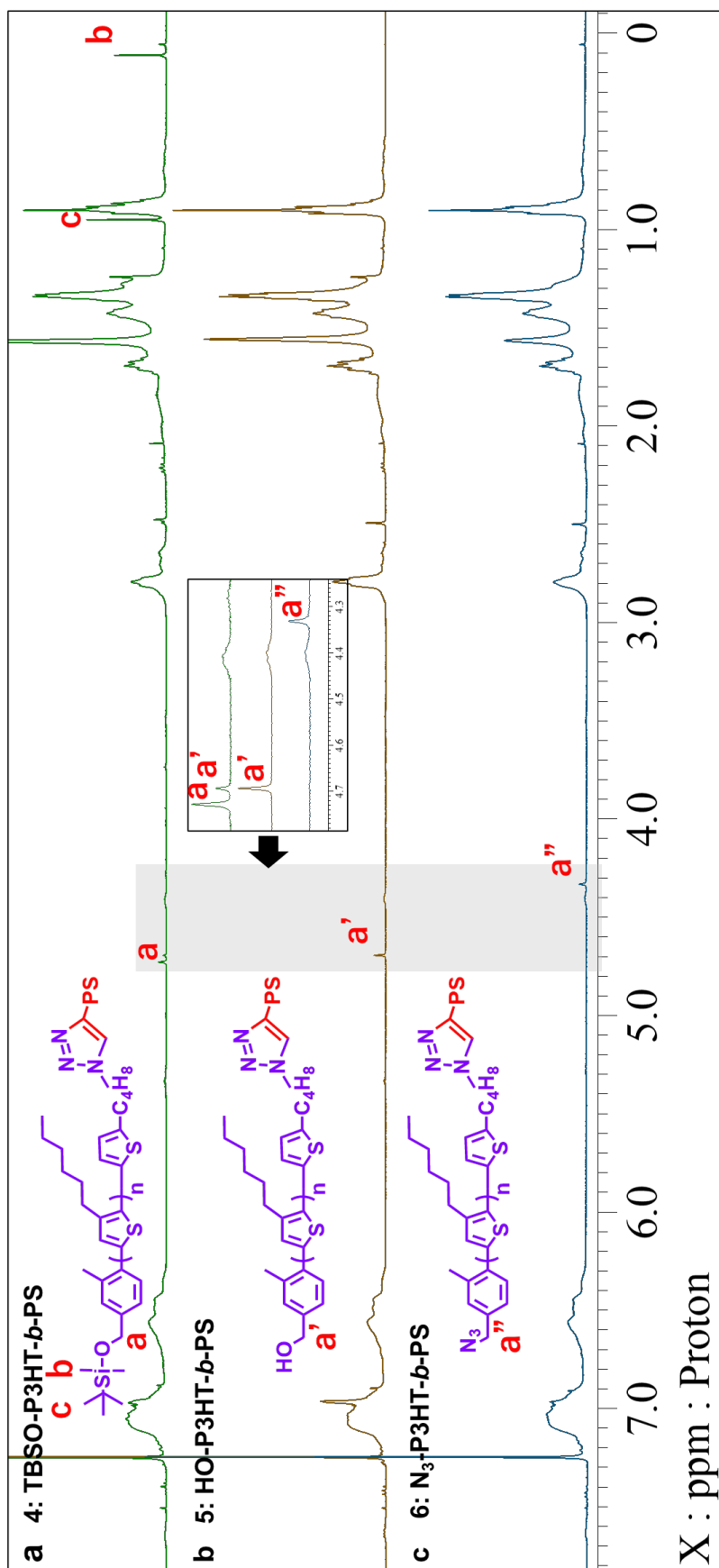


Figure S7. ¹H NMR spectra of (a) **4**, (b) **5** and (c) **6**.

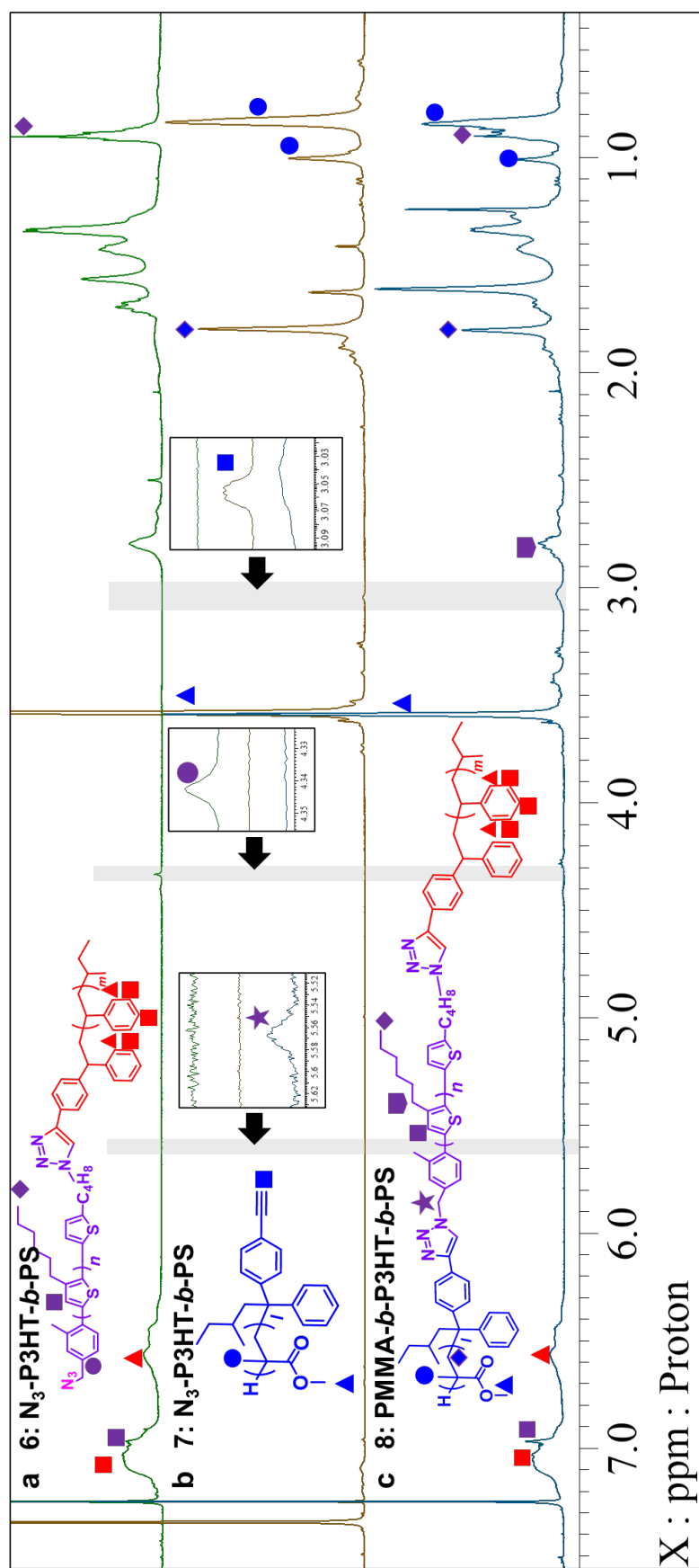


Figure S8. ¹H NMR spectra of (a) **6**, (b) **7** and (c) **8**.

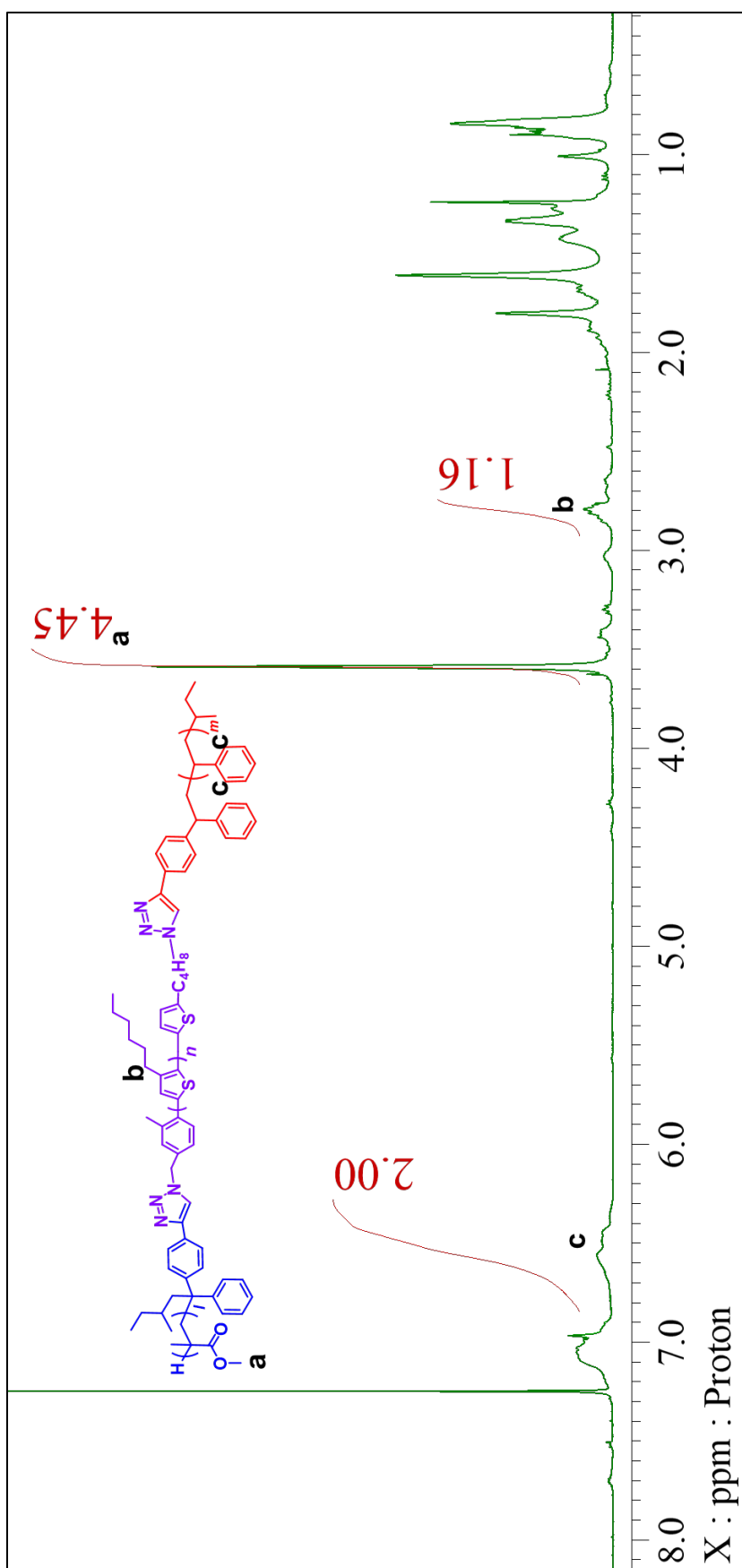


Figure S9. ¹H NMR spectra of **8** with integral values for the signals **a**, **b**, and **c**.

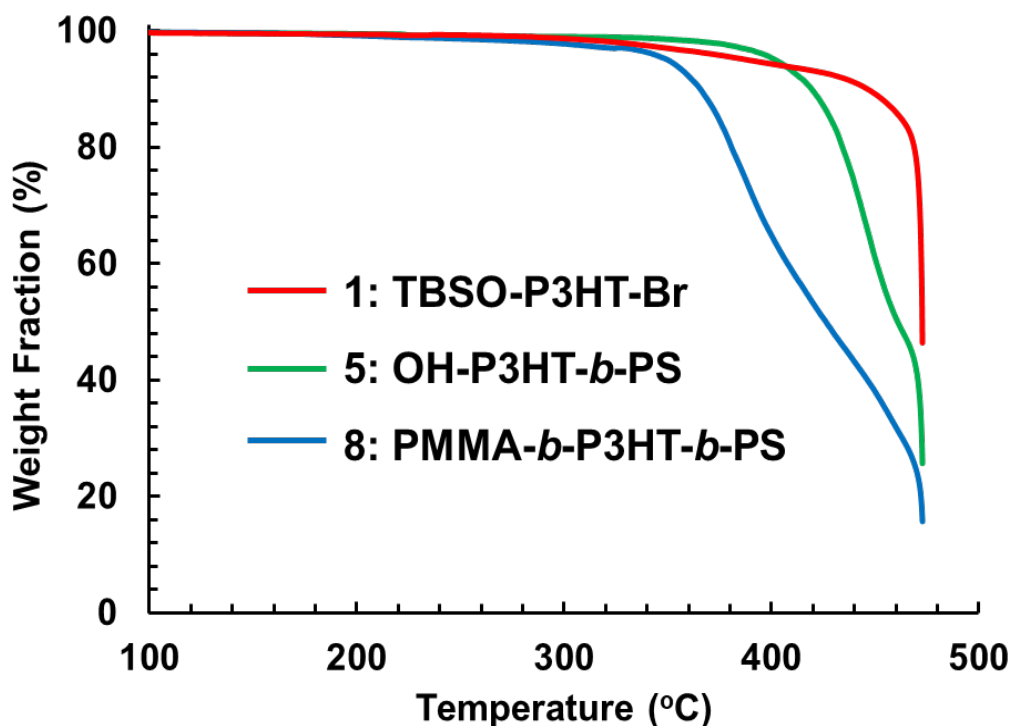


Figure S10. TG thermograms of 1, 5 and 8.

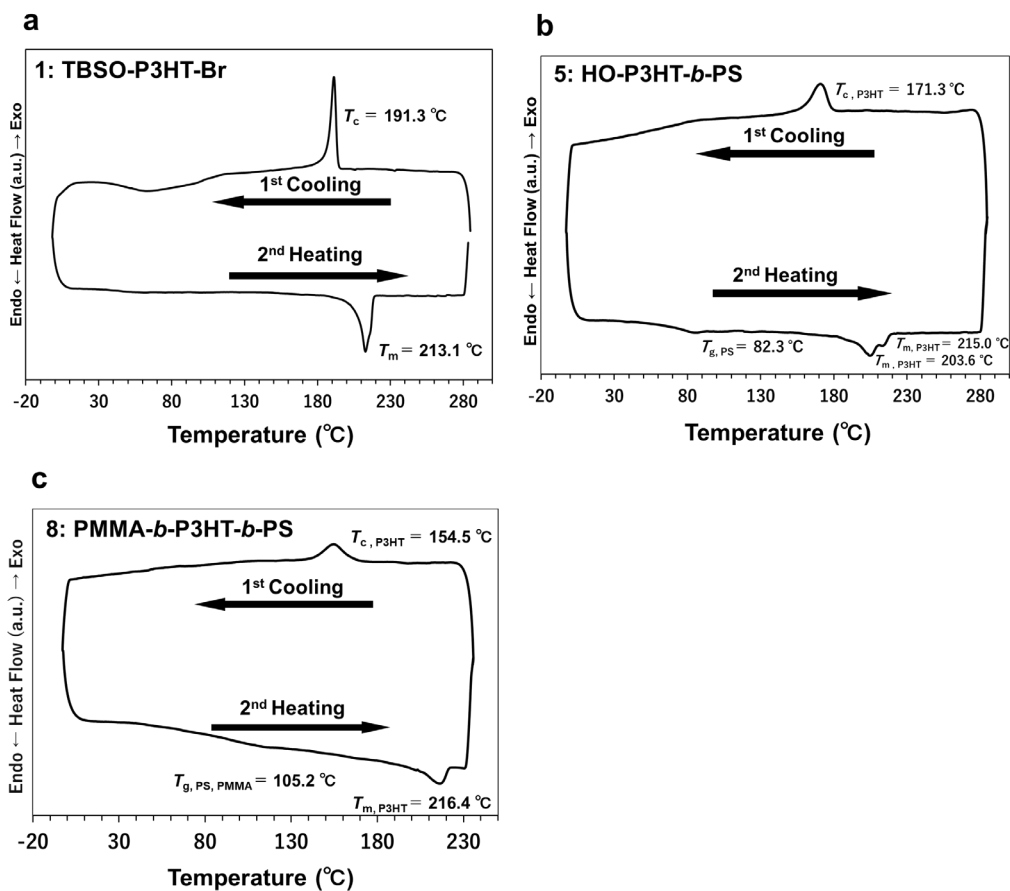


Figure S11. DSC thermograms of (a) 1, (b) 5 and (c) 8.

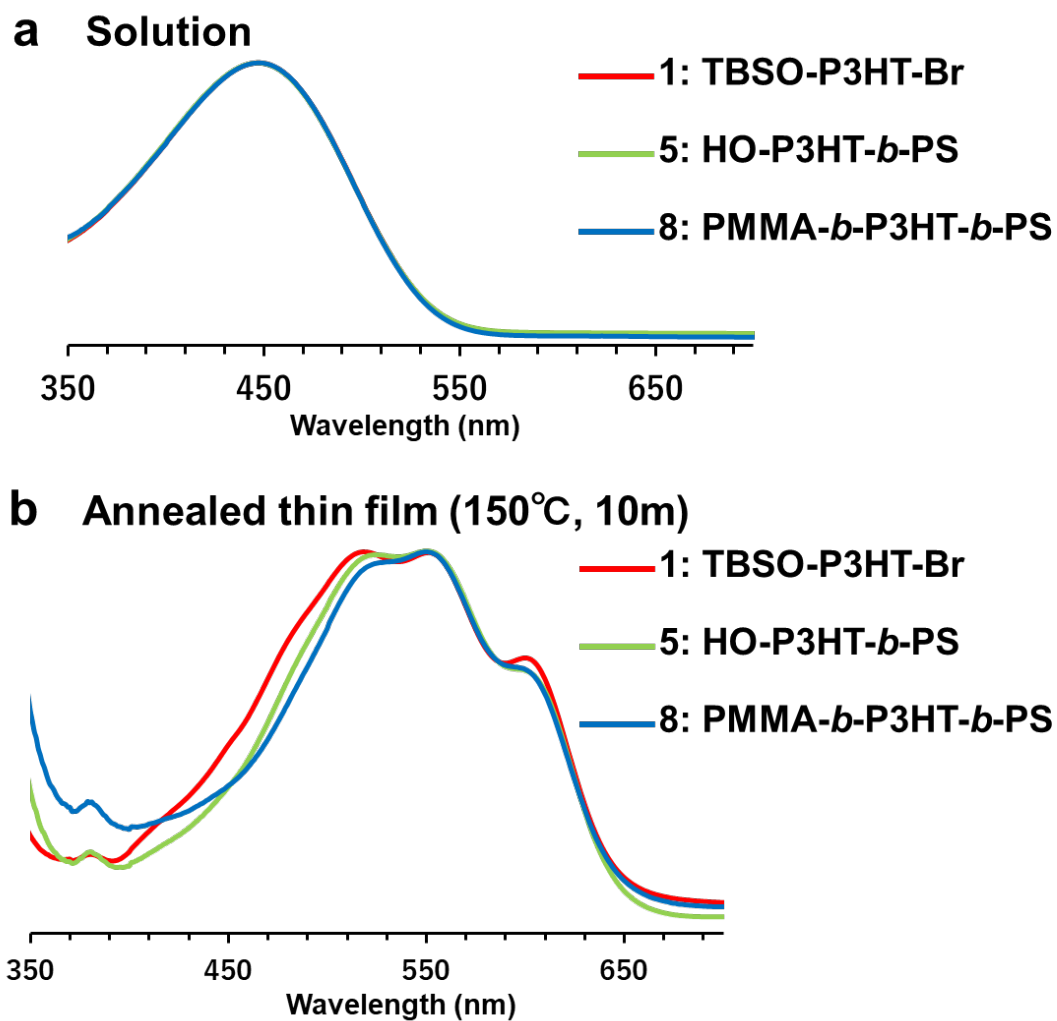


Figure S12. UV-Vis spectra of **1**, **5**, and **8** (a) in chloroform solutions and (b) in thin films states.

References:

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