Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Synthesis and Characterization of Low Bandgap π-Conjugated Copolymers Incorporating 4,7-Bis(3,3'/4,4'-Hexylthiophene-2-yl)Benzo[*c*][2,1,3] Thiadiazole Units for Photovoltaic Application

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Experimental section

Quantum mechanical calculations. For the quantum mechanics calculations on the four representative copolymers of **P1**, **P3**, **P5**, and **P7**, we used the same procedure as applied successfully to predict the PCE of BT-based donor copolymers in our previous study.[1] We took the initial geometries of the component units (EDOT, BT, TP, and T) from the X-ray crystallographic structures,[2-4] and then, by connecting them to each other and attaching ethyl side chains to the position 3 or 4 of the T unit, we built various simple models representing **P1**, **P3**, **P5**, and **P7**. Then, their ground-state geometries were optimized at the B3LYP/6-311G(d,p) level of the density functional theory (DFT).[5-9] The normal mode analysis at each final geometry confirmed that all optimized geometries were minimum-energy structures. The *Jaguar v6.5* quantum chemistry software[10,11] was used for all these calculations. At each final geometry, the vertical singlet-singlet electronic transition energies were also calculated using the same level [B3LYP/6-311G(d,p)] of time-dependent DFT (TDDFT) method[12-15] The *Gaussian03* program[16] was employed for these calculations. All the calculations were carried out in the gas phase, because the solvation in the organic solvents used in this work has only minor effects on the calculated electronic structures and spectra.

Materials, measurements and characterizations. Unless otherwise noted, all manipulations and reactions involving air-sensitive reagents were performed under a dry oxygen-free nitrogen atmosphere. All reagents and solvents were obtained from commercial sources and dried using standard procedures before use. All reactions were monitored by TLC for completion. Flash column chromatography was performed with Merck silica gel 60 (particle size 230-400 mesh ASTM). Neutralized silica gel was prepared by adding triethylamine to the silica gel in the same eluent used for column chromatography. Analytical thin layer chromatography (TLC) was conducted with Merck 0.25 mm 60F silica gel precoated aluminum plates and UV-254 fluorescent indicators. The low temperature reactions were essentially performed in a low temperature bath (PSL1810-SHANGHA EYELA). A syringe pump KD Scientific (KDS-100) was used for delivering accurate and precise amounts of reagents during the dropwise addition processes. ^{1}H and ^{13}C NMR spectra were measured on a Varian spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) in $CDCl_3$ at 25 ^{o}C with TMS as the internal standard and chemical shifts were recorded in ppm units. The coupling constants (*J*) are given in Hz. The UV-vis absorption spectra were obtained using a Varian Cary UV-Vis-NIR-5000 spectrophotometer on the pure polymer samples obtained after Soxhlet extraction. The thermal degradation temperature was measured using thermogravimetric analysis (TGA-TA instrument Q-50) under nitrogen atmosphere. DSC was performed on a TA instrument (DSC-TA instrument Q-20) under nitrogen atmosphere at a heating rate of 10 °C/min. CV measurements were performed on B-class solar simulator: Potentiostate/Galvanostate (SP-150 OMA company); the supporting electrolyte was tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in acetonitrile (0.1 M) at a scan rate of 50 mV s^{-1}. A three-electrode cell was used; A Pt wire and silver/silver chloride [Ag in 0.1 M KCl] were used as the counter and reference electrodes, respectively. The polymer films for electrochemical measurements were spin coated from a polymer-chlorobenzene solution on ITO glass slides, ca. 10 mg/mL. The GPC analysis was carried with a Shimadzu (LC-20A Prominence Series) instrument; Chloroform was used as a carrier solvent (flow rate: 1 mL/min, at 30 °C) and calibration curves were made with standard polystyrene samples. Microwave assisted polymerizations were performed in a focused microwave synthesis system^{CEM} (Discover S-Class System). Surface morphology and phase separation of the active layer were measured using atomic force microscope (AFM; XE-100, Park systems) in tapping mode.

Solar cell device fabrication. For device fabrication, the ITO coated glass was cleaned in ultrasonic bath with DI water, acetone and isopropyl alcohol for 15 min. Sonication in isopropyl alcohol decrease surface energy of the substrate and increase its wetting properties and then cleaned with UV-ozone for 15 min. UV-ozone cleaning further changes the surface energy by increasing density of oxygen bonds on the surface. Highly conducting poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron P, AL4083) was spin coated at 5000 rpm for 40s and backed at 120 °C for 10 min. The active layer contained a blend of copolymers as electron donor and $PC_{60}BM$ as electron acceptor, which was prepared from a 1:1 by weight solution (12 mg/mL) in chlorobenzene, then spin-coating the blend from solution at 2000 rpm. Its thickness was measured using surface profiler (NanoMap 500LS). Al (100 nm) cathode was thermally evaporated through shadow mask via thermal evaporation in vacuum ($<5 \times 10^{-7}$ torr) in thickness of approximately. Thermal annealing was carried out by directly placing the device on a hotplate, in a glove-box for 10 min under N_2 ambient. Current-voltage (I-V) characteristics were recorded using Keithley 2420 Source meter under illumination of an AM 1.5 G (AM = air mass) solar simulator with an intensity 100 mW/cm^2 (Oriel®, Sol3A™). All devices were fabricated and tested in oxygen and moisture free nitrogen ambient inside the glove-box.

Synthesis. *2,5-bis(tributylstannyl)-3,4-ethylenedioxythiophene (**8**).*[17a] EDOT (**7**, 1.42 g, 10 mmol) was dissolved in dry THF (40 mL) and cooled to 0 °C. After stirring for 15 min, LDA

(15 mL, 2 M in THF/heptane/ethyl benzene) was added dropwise within 15 min and after complete addition the reaction mixture was warmed to room temperature and stirred for an additional 1 h. The reaction mixture was cooled again to 0 ^{o}C followed by adding tributylstannyl chloride (8.1 mL, 30 mmol) and stirred for additional 1 h at 0 ^{o}C followed by adding water and ethyl acetate. The organic phase was separated, washed thoroughly with water and finally dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue thus obtained was purified by flash chromatography with hexane as an eluent on pretreated silica gel with triethylamine to give 6.61 g of **8** as a colorless oil (yield, 92%). ^{1}H NMR (400 MHz; $CDCl_3$), δ (ppm): 4.03-4.02 (d, 4H, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$, J = 4 Hz); 1.60-1.40 (m, 12 , 2 X Sn-($\mathrm{C}H_2$-)$_3$); 1.26-1.20 (m, 12H, 2 X Sn-($\mathrm{CH_2C}H_2$-)$_3$); 1.00 (m, 12H, 2 X Sn-($\mathrm{CH_2CH_2C}H_2$-)$_3$); 0.83-0.79 (m, 18H, 2 X ($\mathrm{C}H_3$)$_3$). ^{13}C NMR (100 MHz; $CDCl_3$), δ (ppm): 148.29; 115.81; 64.62; 29.01; 27.48; 13.69; 10.48. Anal. Calcd. for $C_{30}H_{58}O_2SSn_2$: C, 50.03; H, 8.12; S, 4.45; Sn, 32.96. Found: C, 50.18; H, 8.08; S, 4.39.

5,5'-bis(3,4-ethylenedioxythiophene) (**9**).[17b] Into a three-necked round bottomed flask containing a solution of EDOT (**7**, 4.26 g, 30 mmol) in 150 mL of dry THF cooled to –80 °C, *n*-BuLi (12 mL, 2.5 M in hexane) was added dropwise within a period of 30 min. The reaction mixture was stirred for 45 min and then 4.03 g (30 mmol) of $CuCl_2$ was added in one portion at the same temperature. The reaction temperature was raised up to –40 °C and stirred further for additional 2 h and then poured into water followed by filtration. The green precipitate was washed thoroughly with pentane and the organic layer was separated and washed thoroughly with water followed by drying over anhydrous Na_2SO_4. The solvent was evaporated at reduced pressure and the crude solid was dissolved in $CHCl_3$ and passed through a dry flash silica column chromatography using $CHCl_3$ as an eluent to afford 6.43 g of the desired product **9** (yield, 76%). ^{1}H NMR (400 MHz; $CDCl_3$), δ (ppm): 6.26 (s, 2H, 2 X $\mathrm{C}H\mathrm{S}$); 4.32-4.31 (d, 4H, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$, J = 4 Hz); 4.24-4.23 (d, 4H, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$, J = 4 Hz). ^{13}C NMR (100 MHz; $CDCl_3$), δ (ppm): 141.22; 137.02; 109.89; 97.52; 64.98; 64.59. Anal. Calcd. for $C_{12}H_{10}O_4S_2$: C, 51.05; H, 3.57; S, 22.71. Found: C, 51.00; H, 3.64; S, 22.80.

Reaction of 5,5'-bis(3,4-ethylenedioxythiophene (**9**) *with tributyltin chloride.*The products were prepared by modification of the reported methods:[17c,d] To a solution containing of bis-EDOT (**9**, 2.4 g, 8.50 mmol) in dry THF (100 mL) and cooled at –80 ^{o}C, *n*-BuLi (8.5 mL, 21.25 mmol, 2.5 M in hexane) was added dropwise within a period of 30 min. The reaction mixture was stirred for 1 h at –80 ^{o}C followed by stirring at –60 ^{o}C for 3 h. After cooling again to –80 ^{o}C, tributyltin chloride (6 mL, 21.25 mmol) was added dropwise within 15 min to the reaction mixture. After being stirred at –80 ^{o}C for 30 min, the reaction mixture was allowed to return to room temperature and stirred further for 2 h, followed by quenching with aqueous NH_4Cl. The reaction mixture was extracted with ethyl acetate followed by washing the organic layer with water and dried over anhydrous Na_2SO_4. The solvent was evaporated and the crude mixture of products was purified by flash column chromatography on silica gel pretreated with triethylamine to afford 1.69 g of **10** as a yellow solid (yield, 23%) and 4.58 g of **11** as a light yellow solid (yield, 75%).

5-Tributylstannyl-2,2'-bis(3,4-ethylenedioxythiophene) (**10**). ^{1}H NMR (400 MHz; $CDCl_3$), δ (ppm): 6.22 (s, 1H, CHS); 4.29-4.16 (m, 8H, 2 X OCH_2CH_2O); 1.60-1.45 (m, 6H, 3 X $CH_3(CH_2)_2$CH_2); 1.34-1.30 (m, 6H, 3 X CH_3CH_2CH_2); 1.13-1.11 (m, 6H, 3 X CH_3CH_2); 0.91-0.87 (t, 9H, 3 X CH_3, J = 16 Hz). ^{13}C NMR (100 MHz; $CDCl_3$), δ (ppm): 147.06; 141.13; 137.68; 136.69; 115.52; 110.43; 106.80; 96.90; 64.88; 64.48; 28.96; 27.04; 13.58; 10.48. Anal. Calcd. for $C_{24}H_{36}O_4S_2Sn$: C, 50.45; H, 6.35; S, 11.22; Sn, 20.78. Found: C, 50.40; H, 6.39; S, 11.19.

5,5'-Tributylstannyl-2,2'-bis(3,4-ethylenedioxythiophene) (**11**). ^{1}H NMR (400 MHz; $CDCl_3$),[17c] δ (ppm): 4.29-4.28 (d, 4H, OCH_2CH_2O, J = 4 Hz); 4.18-4.17 (d, 4H, OCH_2CH_2O, J = 4 Hz); 1.60-1.50 (m, 12H, 6 X CH_3 CH_2CH_2CH_2-); 1.33-1.31 (m, 12H, 6 X CH_3CH_2CH_2-)$_3$); 1.12-1.02 (m, 12H, 6 X CH_3CH_2-); 0.90-0.86 (t, 18H, 6 X CH_3, J = 16 Hz). ^{13}C NMR (100 MHz; $CDCl_3$), δ (ppm): 147.06; 141.13; 137.68; 136.69; 115.52; 110.43; 106.80; 96.90; 64.88; 64.48; 29.96; 27.04; 13.58; 10.48. Anal. Calcd. for $C_{36}H_{62}O_4S_2Sn_2$: C, 50.25; H, 7.26; S, 7.45; Sn, 27.59. Found: C, 50.35; H, 7.33; S 7.37.

General Procedure for the Microwave-assisted Stille Cross-Coupling Polymerization. Into a highly dried screw capped glass tube, an equimolar ratios from the desired dibromo and di-tributylstannyl derivatives (0.5 mmol) were dissolved in dry DMF and the mixture was degassed with N_2 for at least 30 min followed by adding $Pd(PPh)_4$ (5 mol% relative to Br). The capped glass tube was then placed into the microwave reactor and irradiated under the following conditions: 5 min at 100 ^{o}C, 5 min at 120 ^{o}C, and for 25 min at 150 ^{o}C. End-capping process was performed into two steps; firstly, end-capping with phenylboronic acid pinacol ester followed by bromobenzene. The end-capping conditions are as follow: 2 min at 100 ^{o}C, 2 min at 120 ^{o}C and finally for 5 min at 150 ^{o}C. After the final end-capping process, the microwave screw capped glass tube was then allowed to return to room temperature and the crude polymer was poured into methanol. The crude polymer was collected via filtration and washed successively with methanol. The residual solid was loaded into an extraction thimble and washed successively with methanol (24 h) followed by acetone (24 h), followed by drying under vacuum and subject to analyze by GPC and ^{1}H NMR analyses.

Note: all copolymers were prepared by the aforementioned microwave conditions except only for **P3** and **P7** which prepared under the following microwave conditions: 5 min at 80 ^{o}C, 5 min at 100 ^{o}C, and for 15 min at 130 ^{o}C, followed by the same end-capping method.

Synthesis of **P1** *via Thermal C-H Arylation Method*. A 25 mL round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. Into this flask, an equimolar ratios from each of **1** (0.16 g, 0.25 mmol) and EDOT (**7**, 0.04 g, 0.25 mmol) were dissolved in dry DMF (20 mL) and purged with nitrogen for 20 min. Potassium acetate (0.15 g, 1.56 mmol, 6.0 equiv), *n*-Bu_4NBr (0.16 g, 0.5 mmol, 2.0 equiv), and $Pd(OAc)_2$ (0.01 g, 0.05 mmol, 0.2 equiv) were then added under a stream of nitrogen, and the reaction mixture was purged for an additional 20 min. The reaction mixture was then heated under reflux at 100 ^{o}C and stirred for 72 h. End-capping was performed into one step with phenylboronic acid pinacol ester. The end-capping conditions are as follow: 2 min at 100 ^{o}C, 2 min at 120 ^{o}C and finally for 5 min at 150 ^{o}C, followed by returning to room temperature and then poured into methanol. The crude product was collected via filtration and washed successively with methanol. The residual solid was loaded into an extraction thimble and washed successively with methanol (48 h) followed by acetone (48 h). The resulting polymer (**P1**) was then dried under vacuum, and subject to analyze by GPC and ^{1}H NMR analyses (M_n = 3393 and PDI = 3.82).

General Procedure for the Microwave-Assisted C-H Arylation Polymerization (*Synthesis of* **P1**, **P2**, **P4-P6** *and* **P8**). Into highly dried in a screw capped glass tube, an equimolar ratios from each of the desired dibromo- and EDOT **7** or bis-EDOT **9** or 2,3-dimethylthieno[3,4-*b*]pyrazine (**5b**) (0.5 mmol) was dissolved in dry DMF and purged with nitrogen for 20 min. Potassium acetate (6.0 equiv), tetrabutylammonium bromide (*n*-Bu_4NBr; 2.0 equiv), and $Pd(OAc)_2$ (0.2 equiv) were then added under a stream of nitrogen. The capped tube was then placed into the microwave reactor and irradiated under the following conditions: 5 min at 100 ^{o}C, 5 min at 120 ^{o}C, and for 30 min at 150 ^{o}C. End-capping was performed into one step with phenylboronic acid pinacol ester. The end-capping conditions are as follow: 2 min at 100 ^{o}C, 2 min at 120 ^{o}C and finally for 5 min at 150 ^{o}C. The microwave screw capped glass tube was then allowed to return to room temperature and the reaction mixture was poured into methanol. The crude polymer was collected via filtration and washed successively with methanol. The residual solid was loaded into an extraction thimble and washed successively with methanol (24 h) and acetone (24 h) followed by drying under vacuum and then subject to analyze by GPC and ^{1}H NMR analyses. The chemical yields, average molecular weights (M_n)

as well as molecular weight distributions (PDI; $M_\mathrm{w}/M_\mathrm{n}$) of all copolymers are summarized in Table 1.

Poly[(3,4-ethylenedioxythiophene-5,7-diyl)-alt-(4,7-bis(3-hexylthiophen-2-yl)benzo[c][2,1,3] thiadiazole)-5,5-diyl] (**P1**). ^{1}H NMR (400 MHz; $\mathrm{CDCl_3}$), δ (ppm): 7.67-7.62 (s, br, 2H, $\mathrm{C}\mathit{H}\mathrm{C}\mathit{H}$ (Ph)); 7.21 (s, 2H, 2 X $\mathrm{C}\mathit{H}$=C-S); 4.42 (br s, 4H, $\mathrm{OC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{O}$); 2.69 (br s, 4H, 2 X $\mathrm{ArC}\mathit{H}_2\mathrm{CH_2}$-); 1.67 (br s, 4H, 2 X $\mathrm{ArCH_2C}\mathit{H}_2$-); 1.29-1.24 (br m, 12H, 2 X $\mathrm{CH_3(C}\mathit{H}_2)_3$); 0.85-0.80 (br t, 6H, 2 X $\mathrm{C}\mathit{H}_3$). Anal. Calcd. for $(\mathrm{C_{32}H_{34}N_2O_2S_4})_n$: C, 63.33; H, 5.65; N, 4.62; S, 21.13. Found: C, 63.55; H, 5.59; N, 4.70; S, 21.21.

Poly[(bis(3,4-ethylenedioxythiophene-5',7-diyl)-alt-(4,7-bis(3-hexylthiophen-2-yl)benzo[c] [2,1,3]thiadiazole)-5,5-diyl] (**P2**). ^{1}H NMR (400 MHz; $\mathrm{CDCl_3}$), δ (ppm): 7.65 (s, br, 2H, $\mathrm{C}\mathit{H}\mathrm{C}\mathit{H}$ (Ph)); 7.24 (s, 2H, 2 X $\mathrm{C}\mathit{H}$=C-S); 4.44 (s, br, 8H, 2 X $\mathrm{OC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{O}$); 2.68 (br s, 4H, 2 X $\mathrm{ArC}\mathit{H}_2\mathrm{CH_2}$); 1.67 (br s, 4H, 2 X $\mathrm{ArCH_2C}\mathit{H}_2$-); 1.27-1.24 (br m, 12H, 2 X $\mathrm{CH_3(C}\mathit{H}_2)_3$); 0.85-0.82 (br t, 6H, 2 X $\mathrm{C}\mathit{H}_3$). Anal. Calcd. for $(\mathrm{C_{38}H_{38}N_2O_4S_5})_n$: C, 61.09; H, 5.13; N, 3.75; O, 8.57; S, 21.46. Found: C, 61.00; H, 5.22; N, 3.70; S, 21.56.

Poly[(thieno[3,4-b]pyrazine-5,7-diyl)-alt-(4,7-bis(3-hexylthiophen-2-yl)benzo[c][2,1,3] thiadiazole)-5,5-diyl] (**P3**). ^{1}H NMR (400 MHz; $\mathrm{CDCl_3}$), δ (ppm): 8.54-8.53 (s, 2H, N=$\mathrm{C}\mathit{H}_2$-$\mathrm{C}\mathit{H}_2$=N); 7.76 (br s, 2H, $\mathrm{C}\mathit{H}\mathrm{C}\mathit{H}$ (Ph)); 7.68 (s, 2H, 2 X $\mathrm{C}\mathit{H}$=C-S); 2.77-2.73 (br t, 4H, 2 X Ar-$\mathrm{C}\mathit{H}_2\mathrm{CH_2}$), 1.73-1.71 (br m, 4H, 2 X Ar-$\mathrm{CH_2C}\mathit{H}_2$-); 1.33-1.26 (br m, 12H, 2 X $\mathrm{CH_3(C}\mathit{H}_2)_3$); 0.92-0.83 (br m, 6H, 2 X $\mathrm{C}\mathit{H}_3$). Anal. Calcd. for $(\mathrm{C_{32}H_{32}N_4S_4})_n$: C, 63.96; H, 5.37; N, 9.32; S, 21.35. Found: C, 64.11; H, 5.48; N, 9.38; S, 5.40.

Poly[(2,3-dimethylthieno[3,4-b]pyrazine-5,7-diyl)-alt-(4,7-bis(3-hexylthiophen-2-yl)benzo[c] [2,1,3]thiadiazole)-5,5-diyl] (**P4**). ^{1}H NMR (400 MHz; $\mathrm{CDCl_3}$), δ (ppm): 7.76-7.75 (br s, 2H, $\mathrm{C}\mathit{H}\mathrm{C}\mathit{H}$ (Ph)); 7.65 (s, 2H, 2 X $\mathrm{C}\mathit{H}$=C-S); 2.72-2.62 (br m, 10H, 2 X Ar-$\mathrm{C}\mathit{H}_2\mathrm{CH_2}$- + 2 X N=C-$\mathrm{C}\mathit{H}_3$); 1.72-1.64 (br m, 4H, 2X Ar-$\mathrm{CH_2C}\mathit{H}_2$-); 1.31-1.25 (br m, 12H, 2 X $\mathrm{CH_3(C}\mathit{H}_2)_3$); 0.85-0.84 (br t, 6H, 2 X $\mathrm{C}\mathit{H}_3$). Anal. Calcd. for $(\mathrm{C_{34}H_{36}N_4S_4})_n$: C, 64.93; H, 5.77; N, 8.91; S, 20.39. Found: C, 64.80; H, 5.81; N, 8.79; S, 20.24.

Poly[(3,4-ethylenedioxythiophene-5,7-diyl)-alt-(4,7-bis(4-hexylthiophen-2-yl)benzo[c][2,1,3] thiadiazole)-5,5-diyl] (**P5**). ^{1}H NMR (400 MHz; $\mathrm{CDCl_3}$), δ (ppm): 8.03 (br m, 2H, $\mathrm{C}\mathit{H}\mathrm{C}\mathit{H}$ (Ph)); 7.85-7.83 (br s, 2H, 2 X $\mathrm{C}\mathit{H}$=C-Ph); 4.43 (s, 4H, $\mathrm{OC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{O}$); 2.89-2.68 (br m, 4H, 2 X $\mathrm{ArC}\mathit{H}_2\mathrm{CH_2}$-); 1.77-1.70 (br m, 4H, 2 X Ar-$\mathrm{CH_2C}\mathit{H}_2$-); 1.46-1.25 (br m, 12H, 2 X $\mathrm{CH_3(C}\mathit{H}_2)_3$); 0.91-0.86 (br t, 6H, 2 X $\mathrm{C}\mathit{H}_3$). Anal. Calcd. for $(\mathrm{C_{32}H_{34}N_2O_2S_4})_n$: C, 63.33; H, 5.65; N, 4.62; O, 5.27; S, 21.13. Found: C, 63.25; H, 5.75; N, 4.60; S, 21.08.

Poly[bis(3,4-ethylenedioxythiophene-5',7-diyl)-alt-(4,7-bis(4-hexylthiophen-2-yl)benzo[c] [2,1,3]thiadiazole)-5,5-diyl] (**P6**). ^{1}H NMR (400 MHz; $\mathrm{CDCl_3}$), δ (ppm): 8.06 (br s, 2H, C*H*C*H* (Ph)); 7.81 (br s, 2H, 2 X C*H*=C-Ph); 4.39-4.25 (br s, 8H, 2 X OCH_2CH_2O); 2.85 (br s, 4H, $ArCH_2CH_2$-); 1.77-1.70 (br s, 4H, 2 X $ArCH_2CH_2$-); 1.42-1.25 (br m, 12H, 2 X $CH_3(CH_2)_3$); 0.89-0.84 (br s, 6H, 2 X CH_3). Anal. Calcd. for $(C_{38}H_{38}N_2O_4S_5)_n$: C, 61.09; H, 5.13; N, 3.75; S, 21.46. Found: C, 61.25; H, 5.05; N, 3.84; S, 21.40.

Poly[(thieno[3,4-b]pyrazine-5,7-diyl)-alt-(4,7-bis(4-hexylthiophen-2-yl)benzo[c][2,1,3] thiadiazole)-5,5-diy] (**P7**). ^{1}H NMR (400 MHz; $CDCl_3$), *δ* (ppm): 8.63 (br s, 2H, $N=CH_2CH_2=N$); 7.98 (br s, 2H, C*H*C*H* (Ph)); 7.83 (br s, 2H, 2 X C*H*=C-Ph); 2.67 (br s, 4H, 2 X $ArCH_2CH_2$-); 1.82-1.68 (m, br, 4H, 2 X Ar-CH_2CH_2-); 1.47-1.25 (br m, 12H, 2 X $CH_3(CH_2)_3$); 1.05-0.89 (br s, 6H, 2 X CH_3). Anal. Calcd. for $(C_{32}H_{32}N_4S_4)_n$: C, 63.96; H, 5.37; N, 9.32; S, 21.35. Found: C, 63.88; H, 5.47; N, 9.30; S, 21.24.

Poly[(2,3-dimethylthieno[3,4-b]pyrazine-5,7-diyl)-alt-(4,7-bis(4-hexylthiophen-2-yl)benzo[c] [2,1,3]thiadiazole)-5,5-diyl] (**P8**). ^{1}H NMR (400 MHz; $CDCl_3$), *δ* (ppm): 7.98-7.83 (br m, 2H, C*H*C*H* (Ph)); 7.72 (br s, 2H, 2 X C*H*=C-Ph); 2.69-2.56 (br m, 10H, 2 X $ArCH_2CH_2$- + 2X N=C-CH_3); 1.71-1.68 (br s, 4H, 2 X Ar-CH_2CH_2-); 1.32-1.25 (br s, 12H, 2 X $CH_3(CH_2)_3$); 0.89-0.79 (br s, 6H, 2 X CH_3). Anal. Calcd. for $(C_{34}H_{36}N_4S_4)_n$: C, 64.93; H, 5.77; N, 8.91; S, 20.39. Found: C, 64.55; H, 5.52; N, 8.85; S, 20.19.

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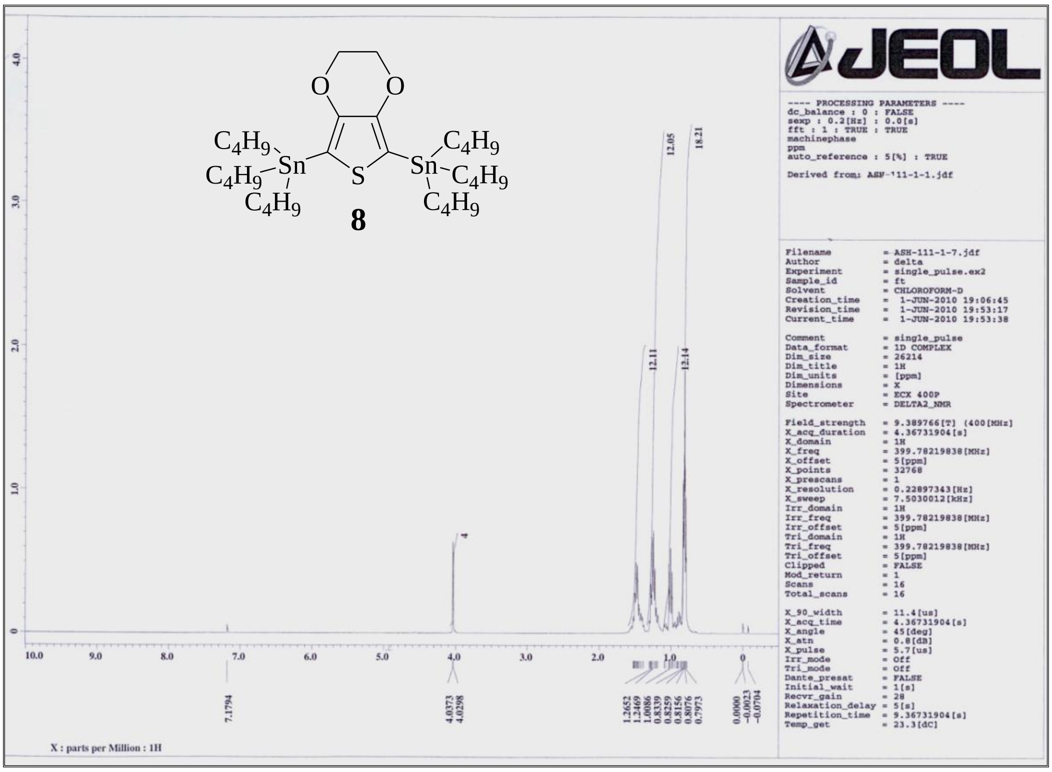
- ^{1}H and ^{13}C-NMR spectra of compounds 8-11

Figure S1. ^{1}H NMR (400 MHz) spectrum of compound **8** in $CDCl_3$



```
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fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: ASH-'11-1-1.jdf

Filename            = ASH-111-1-7.jdf
Author              = delta
Experiment          = single_pulse.ex2
Sample_id           = ft
Solvent             = CHLOROFORM-D
Creation_time       =  1-JUN-2010 19:06:45
Revision_time       =  1-JUN-2010 19:53:17
Current_time        =  1-JUN-2010 19:53:38

Comment             = single_pulse
Data_format         = 1D COMPLEX
Dim_size            = 26214
Dim_title           = 1H
Dim_units           = [ppm]
Dimensions          = X
Site                = ECX 400P
Spectrometer        = DELTA2_NMR

Field_strength      = 9.389766[T] (400[MHz]
X_acq_duration      = 4.36731904[s]
X_domain            = 1H
X_freq              = 399.78219838[MHz]
X_offset            = 5[ppm]
X_points            = 32768
X_prescans          = 1
X_resolution        = 0.22897343[Hz]
X_sweep             = 7.5030012[kHz]
Irr_domain          = 1H
Irr_freq            = 399.78219838[MHz]
Irr_offset          = 5[ppm]
Tri_domain          = 1H
Tri_freq            = 399.78219838[MHz]
Tri_offset          = 5[ppm]
Clipped             = FALSE
Mod_return          = 1
Scans               = 16
Total_scans         = 16

X_90_width          = 11.4[us]
X_acq_time          = 4.36731904[s]
X_angle             = 45[deg]
X_atn               = 0.8[dB]
X_pulse             = 5.7[us]
Irr_mode            = Off
Tri_mode            = Off
Dante_presat        = FALSE
Initial_wait        = 1[s]
Recvr_gain          = 28
Relaxation_delay    = 5[s]
Repetition_time     = 9.36731904[s]
Temp_get            = 23.3[dC]
```
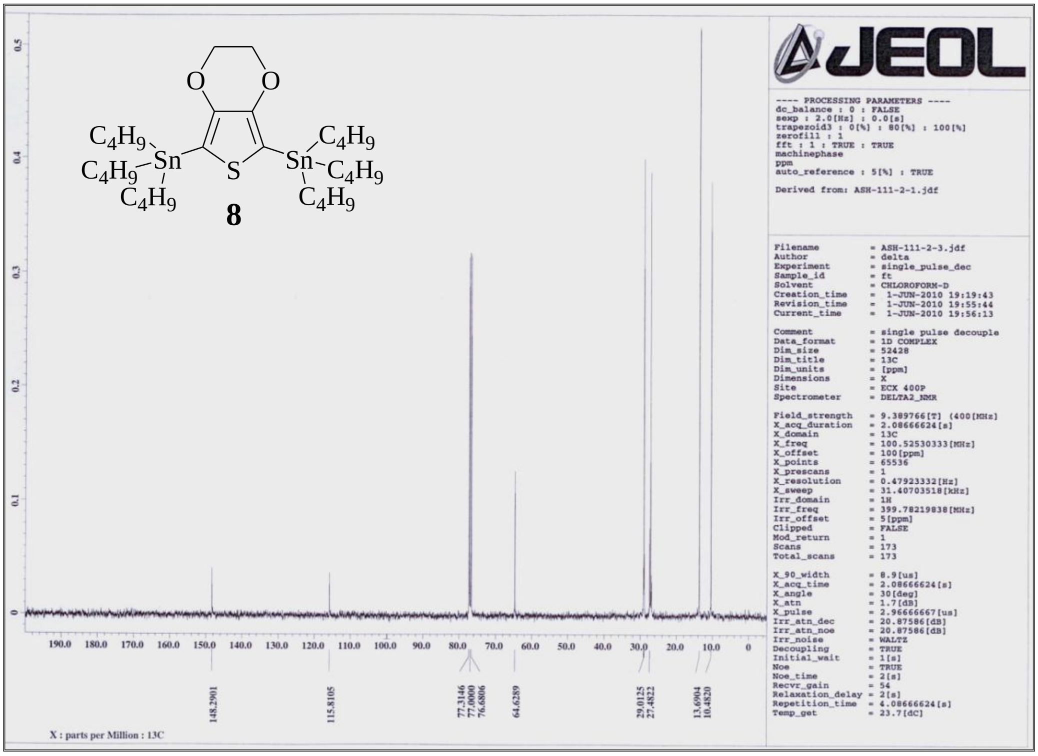
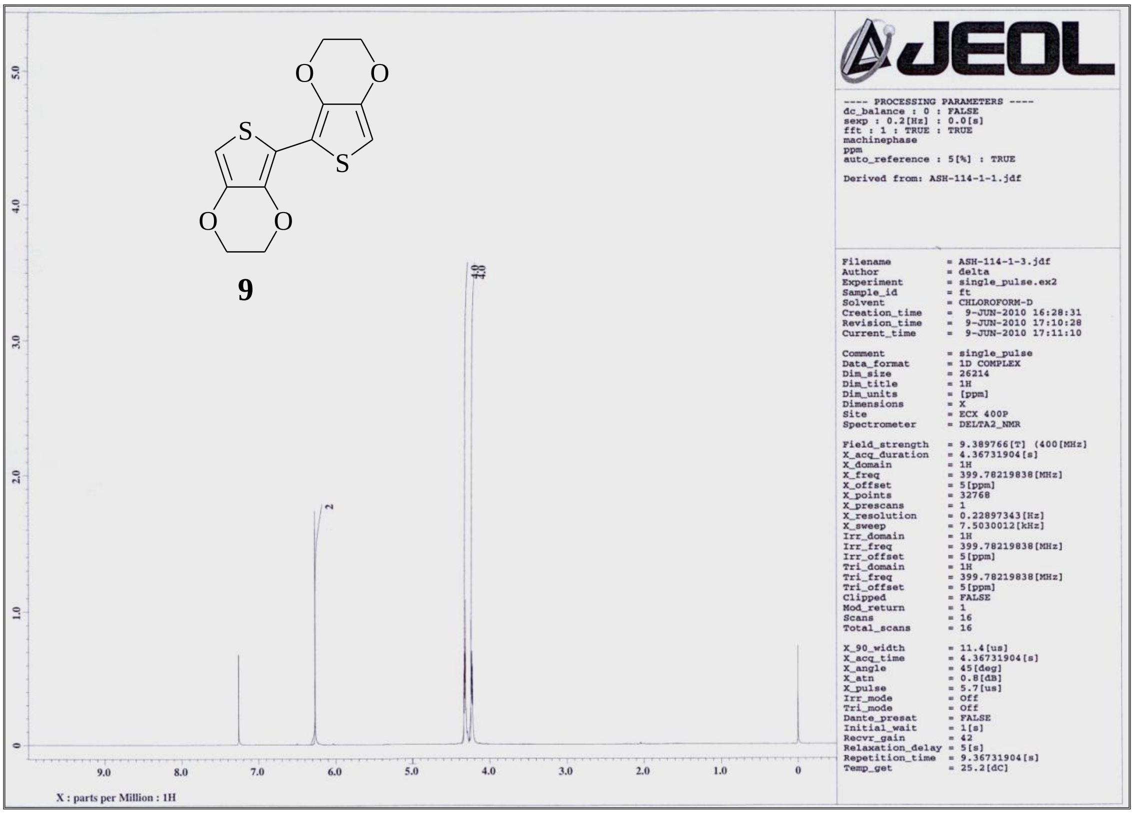

Figure S2. ^{13}C-{^{1}H}(100 MHz) NMR spectrum of compound **8** in $CDCl_3$



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: ASH-111-2-1.jdf

Filename            = ASH-111-2-3.jdf
Author              = delta
Experiment          = single_pulse_dec
Sample_id           = ft
Solvent             = CHLOROFORM-D
Creation_time       =  1-JUN-2010 19:19:43
Revision_time       =  1-JUN-2010 19:55:44
Current_time        =  1-JUN-2010 19:56:13

Comment             = single pulse decouple
Data_format         = 1D COMPLEX
Dim_size            = 52428
Dim_title           = 13C
Dim_units           = [ppm]
Dimensions          = X
Site                = ECX 400P
Spectrometer        = DELTA2_NMR

Field_strength      = 9.389766[T] (400[MHz]
X_acq_duration      = 2.08666624[s]
X_domain            = 13C
X_freq              = 100.52530333[MHz]
X_offset            = 100[ppm]
X_points            = 65536
X_prescans          = 1
X_resolution        = 0.47923332[Hz]
X_sweep             = 31.40703518[kHz]
Irr_domain          = 1H
Irr_freq            = 399.78219838[MHz]
Irr_offset          = 5[ppm]
Clipped             = FALSE
Mod_return          = 1
Scans               = 173
Total_scans         = 173

X_90_width          = 8.9[us]
X_acq_time          = 2.08666624[s]
X_angle             = 30[deg]
X_atn               = 1.7[dB]
X_pulse             = 2.96666667[us]
Irr_atn_dec         = 20.87586[dB]
Irr_atn_noe         = 20.87586[dB]
Irr_noise           = WALTZ
Decoupling          = TRUE
Initial_wait        = 1[s]
Noe                 = TRUE
Noe_time            = 2[s]
Recvr_gain          = 54
Relaxation_delay    = 2[s]
Repetition_time     = 4.08666624[s]
Temp_get            = 23.7[dC]
```

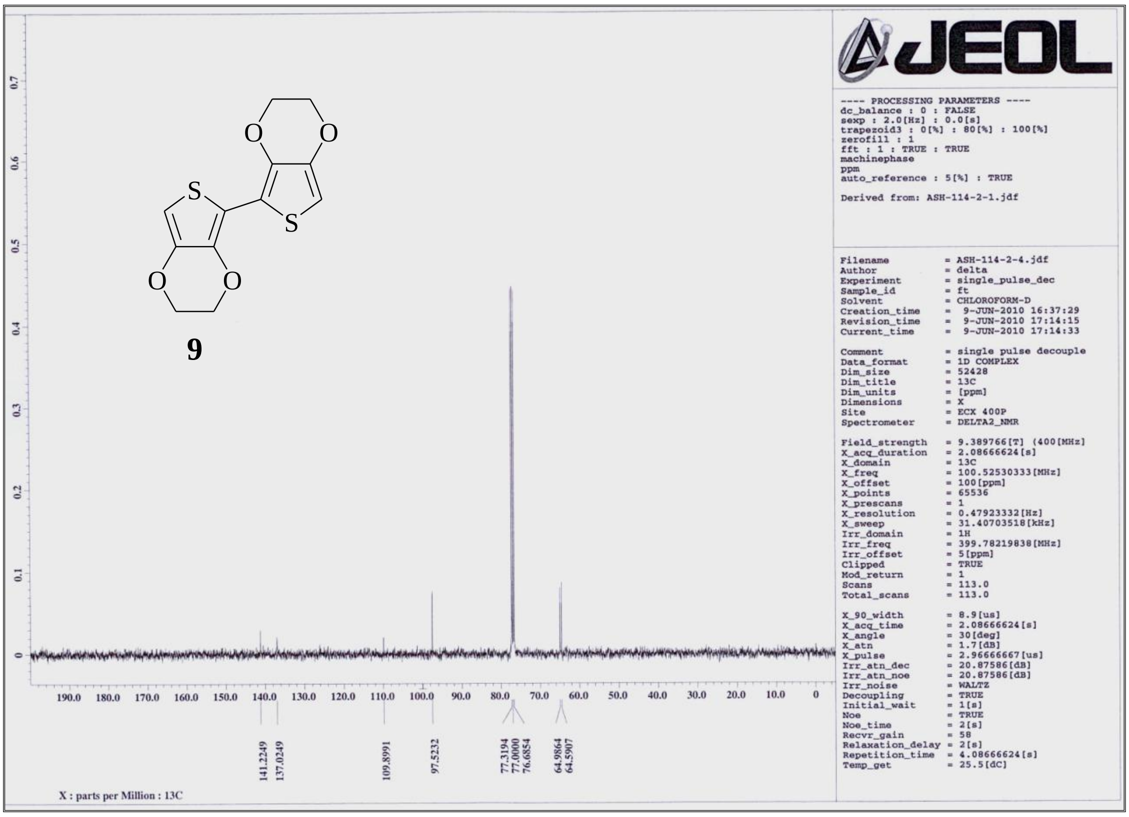
Figure S3. ^{1}H NMR (400 MHz) spectrum of compound **9** in $CDCl_3$



9

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: ASH-114-1-1.jdf

Filename           = ASH-114-1-3.jdf
Author             = delta
Experiment         = single_pulse.ex2
Sample_id          = ft
Solvent            = CHLOROFORM-D
Creation_time      =  9-JUN-2010 16:28:31
Revision_time      =  9-JUN-2010 17:10:28
Current_time       =  9-JUN-2010 17:11:10

Comment            = single_pulse
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 1H
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 400P
Spectrometer       = DELTA2_NMR

Field_strength     = 9.389766[T] (400[MHz]
X_acq_duration     = 4.36731904[s]
X_domain           = 1H
X_freq             = 399.78219838[MHz]
X_offset           = 5[ppm]
X_points           = 32768
X_prescans         = 1
X_resolution       = 0.22897343[Hz]
X_sweep            = 7.5030012[kHz]
Irr_domain         = 1H
Irr_freq           = 399.78219838[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 1H
Tri_freq           = 399.78219838[MHz]
Tri_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 16
Total_scans        = 16

X_90_width         = 11.4[us]
X_acq_time         = 4.36731904[s]
X_angle            = 45[deg]
X_atn              = 0.8[dB]
X_pulse            = 5.7[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
Recvr_gain         = 42
Relaxation_delay   = 5[s]
Repetition_time    = 9.36731904[s]
Temp_get           = 25.2[dC]
```

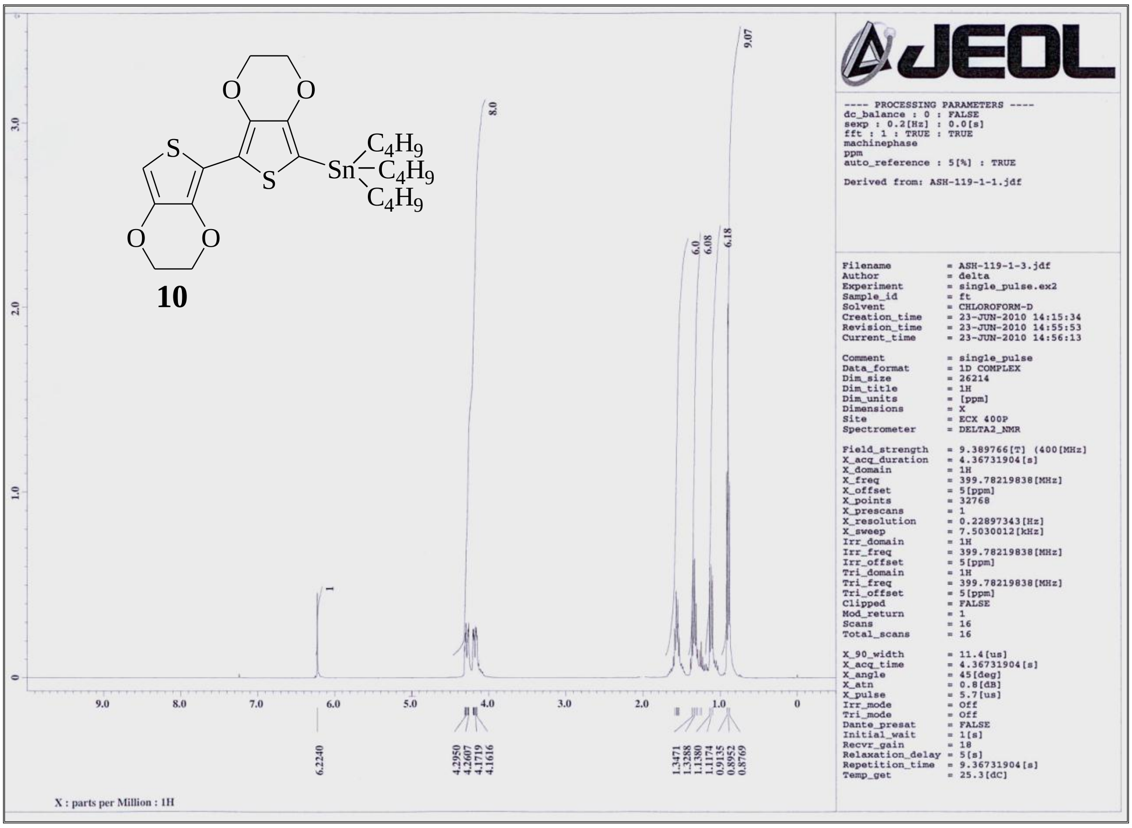
Figure S4. ^{13}C-{^{1}H}(100 MHz) NMR spectrum of compound 9 in $CDCl_3$



9

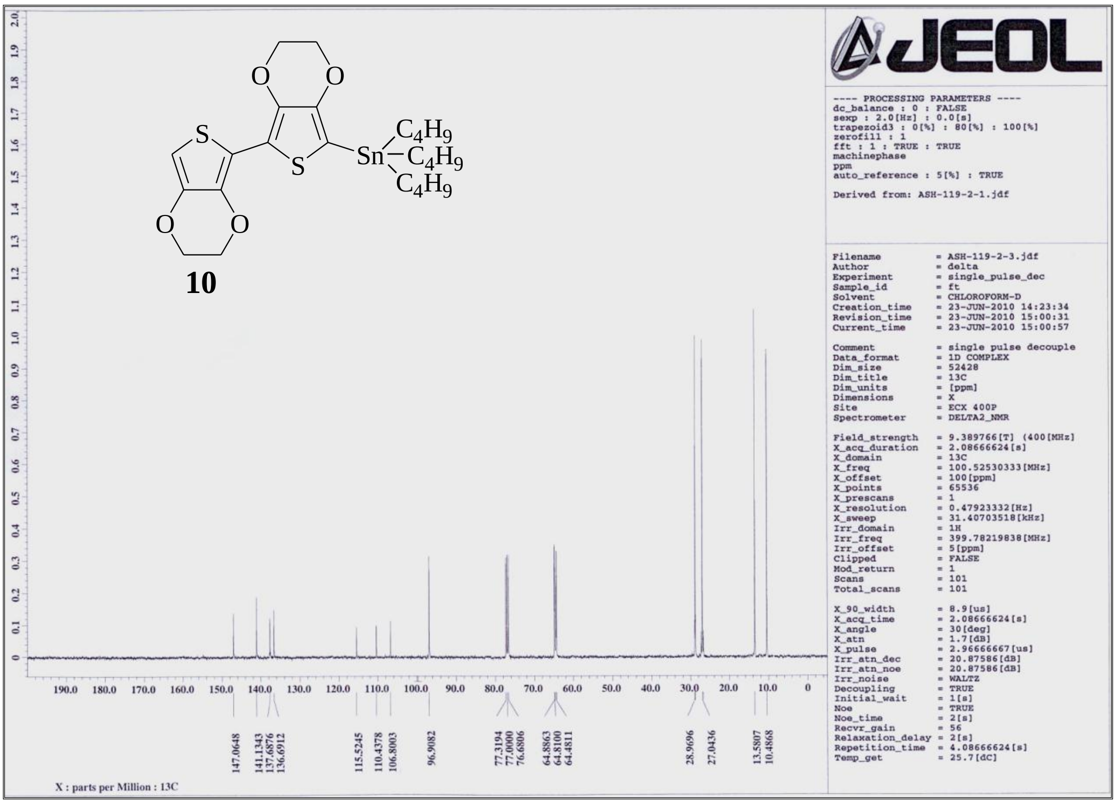
```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: ASH-114-2-1.jdf

Filename           = ASH-114-2-4.jdf
Author             = delta
Experiment         = single_pulse_dec
Sample_id          = ft
Solvent            = CHLOROFORM-D
Creation_time      =  9-JUN-2010 16:37:29
Revision_time      =  9-JUN-2010 17:14:15
Current_time       =  9-JUN-2010 17:14:33

Comment            = single pulse decouple
Data_format        = 1D COMPLEX
Dim_size           = 52428
Dim_title          = 13C
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 400P
Spectrometer       = DELTA2_NMR

Field_strength     = 9.389766[T] (400[MHz]
X_acq_duration     = 2.08666624[s]
X_domain           = 13C
X_freq             = 100.52530333[MHz]
X_offset           = 100[ppm]
X_points           = 65536
X_prescans         = 1
X_resolution       = 0.47923332[Hz]
X_sweep            = 31.40703518[kHz]
Irr_domain         = 1H
Irr_freq           = 399.78219838[MHz]
Irr_offset         = 5[ppm]
Clipped            = TRUE
Mod_return         = 1
Scans              = 113.0
Total_scans        = 113.0

X_90_width         = 8.9[us]
X_acq_time         = 2.08666624[s]
X_angle            = 30[deg]
X_atn              = 1.7[dB]
X_pulse            = 2.96666667[us]
Irr_atn_dec        = 20.87586[dB]
Irr_atn_noe        = 20.87586[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Recvr_gain         = 58
Relaxation_delay   = 2[s]
Repetition_time    = 4.08666624[s]
Temp_get           = 25.5[dC]
```

Figure S5. ^{1}H NMR (400 MHz) spectrum of compound **10** in $CDCl_3$



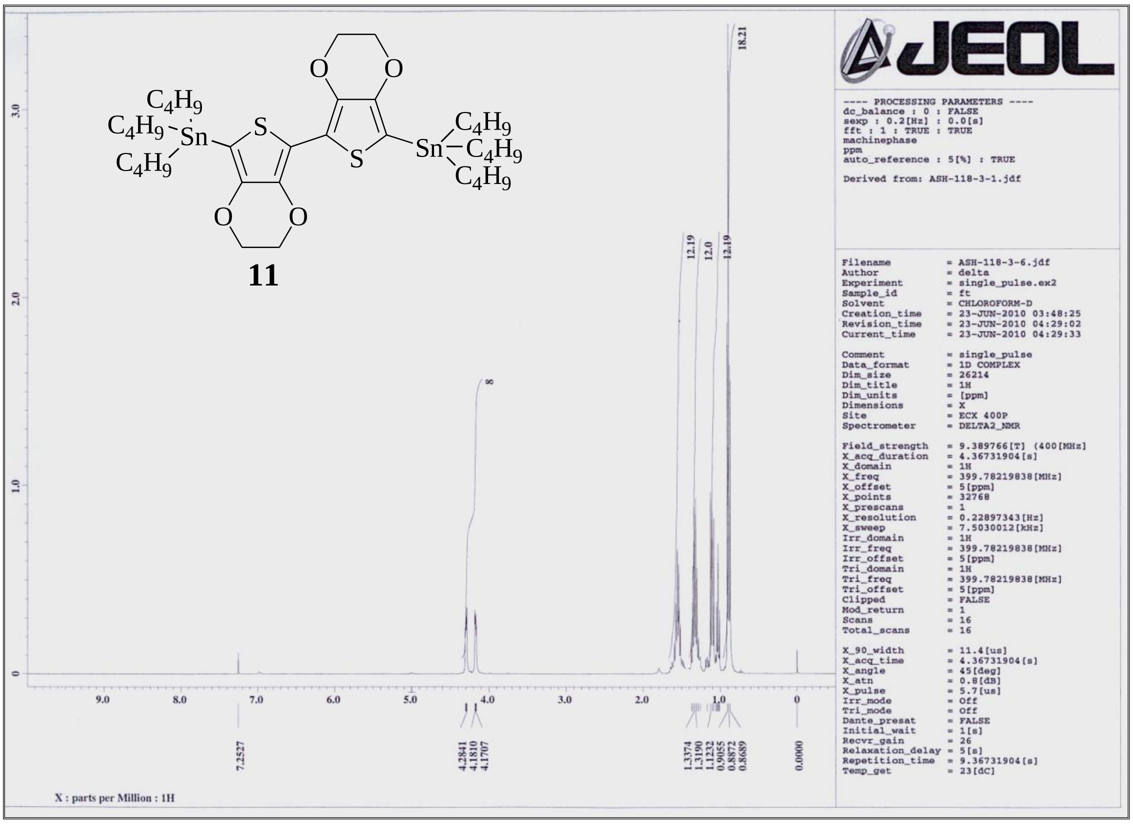
```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: ASH-119-1-1.jdf

Filename          = ASH-119-1-3.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = ft
Solvent           = CHLOROFORM-D
Creation_time     = 23-JUN-2010 14:15:34
Revision_time     = 23-JUN-2010 14:55:53
Current_time      = 23-JUN-2010 14:56:13

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 4.36731904[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22897343[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 11.4[us]
X_acq_time        = 4.36731904[s]
X_angle           = 45[deg]
X_atn             = 0.8[dB]
X_pulse           = 5.7[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 18
Relaxation_delay  = 5[s]
Repetition_time   = 9.36731904[s]
Temp_get          = 25.3[dC]
```

Figure S6. ^{13}C-{^{1}H}(100 MHz) NMR spectrum of compound **10** in $CDCl_3$



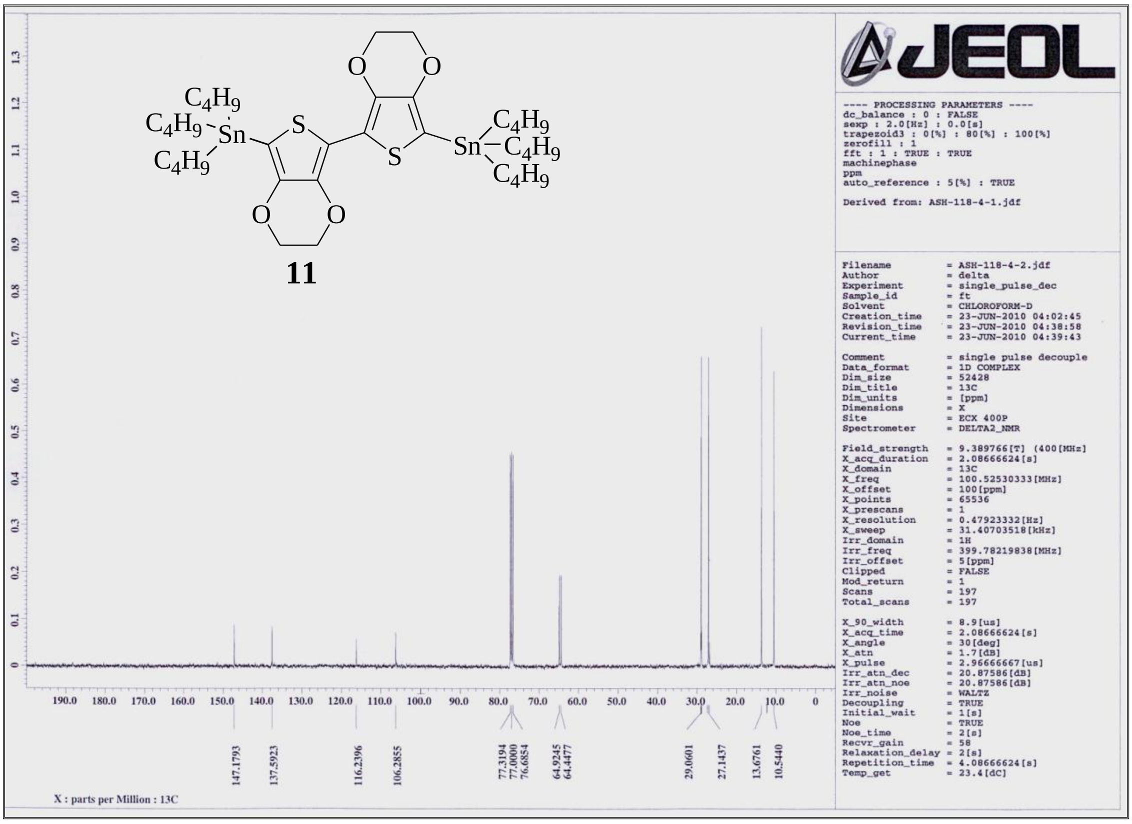
```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: ASH-119-2-1.jdf

Filename          = ASH-119-2-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = ft
Solvent           = CHLOROFORM-D
Creation_time     = 23-JUN-2010 14:23:34
Revision_time     = 23-JUN-2010 15:00:31
Current_time      = 23-JUN-2010 15:00:57

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 2.08666624[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 1
X_resolution      = 0.47923332[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 101
Total_scans       = 101

X_90_width        = 8.9[us]
X_acq_time        = 2.08666624[s]
X_angle           = 30[deg]
X_atn             = 1.7[dB]
X_pulse           = 2.96666667[us]
Irr_atn_dec       = 20.87586[dB]
Irr_atn_noe       = 20.87586[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 56
Relaxation_delay  = 2[s]
Repetition_time   = 4.08666624[s]
Temp_get          = 25.7[dC]
```

Figure S7. ^{1}H NMR (400 MHz) spectrum of compound **11** in $CDCl_3$



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: ASH-118-3-1.jdf

Filename          = ASH-118-3-6.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = ft
Solvent           = CHLOROFORM-D
Creation_time     = 23-JUN-2010 03:48:25
Revision_time     = 23-JUN-2010 04:29:02
Current_time      = 23-JUN-2010 04:29:33

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 4.36731904[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22897343[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 11.4[us]
X_acq_time        = 4.36731904[s]
X_angle           = 45[deg]
X_atn             = 0.8[dB]
X_pulse           = 5.7[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 26
Relaxation_delay  = 5[s]
Repetition_time   = 9.36731904[s]
Temp_get          = 23[dC]
```

Figure S8. ^{13}C-{^{1}H}(100 MHz) NMR spectrum of compound **11** in $CDCl_3$

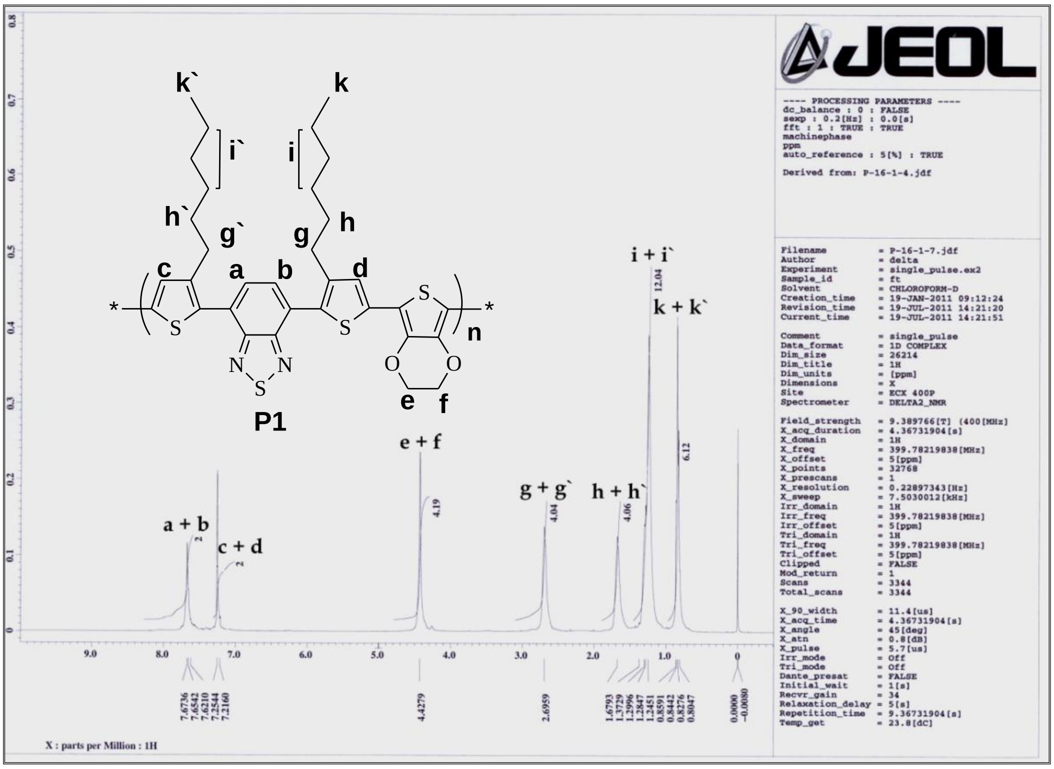


```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: ASH-118-4-1.jdf

Filename          = ASH-118-4-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = ft
Solvent           = CHLOROFORM-D
Creation_time     = 23-JUN-2010 04:02:45
Revision_time     = 23-JUN-2010 04:38:58
Current_time      = 23-JUN-2010 04:39:43

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 2.08666624[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 1
X_resolution      = 0.47923332[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 197
Total_scans       = 197

X_90_width        = 8.9[us]
X_acq_time        = 2.08666624[s]
X_angle           = 30[deg]
X_atn             = 1.7[dB]
X_pulse           = 2.96666667[us]
Irr_atn_dec       = 20.87586[dB]
Irr_atn_noe       = 20.87586[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 4.08666624[s]
Temp_get          = 23.4[dC]
```

^{1}H -

- ^{1}H NMR spectra of copolymers P1-P8

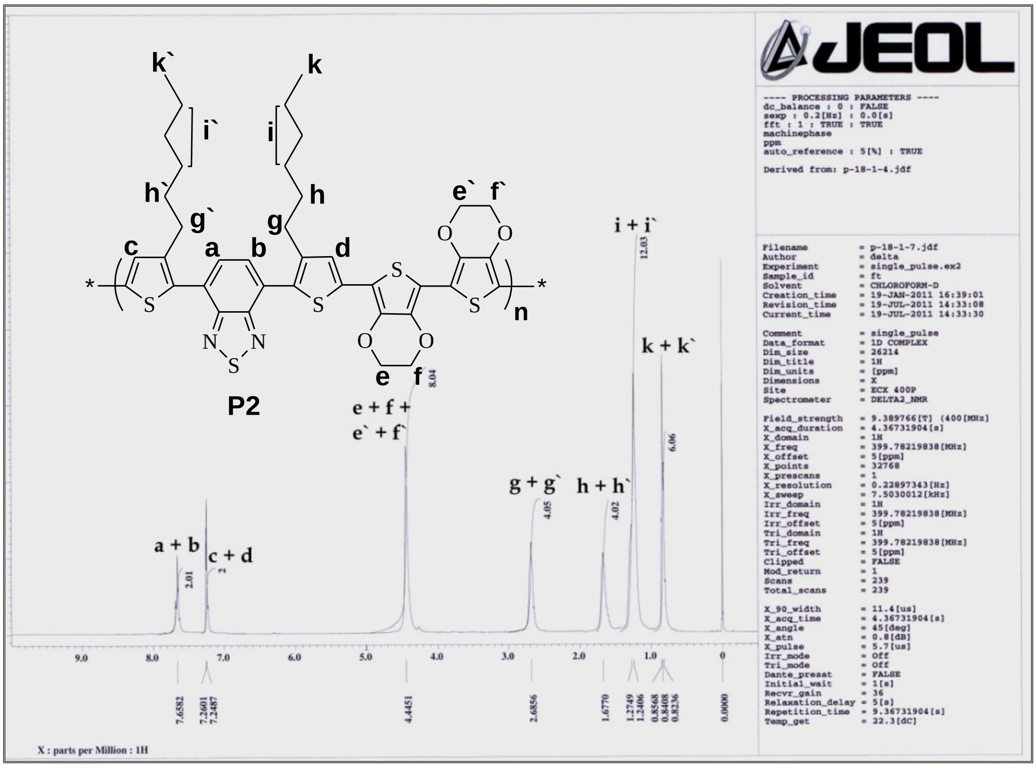
Figure S9. ^{1}H NMR (400 MHz) spectrum of copolymer **P1** in $CDCl_3$



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: P-16-1-4.jdf
```

```
Filename           = P-16-1-7.jdf
Author             = delta
Experiment         = single_pulse.ex2
Sample_id          = ft
Solvent            = CHLOROFORM-D
Creation_time      = 19-JAN-2011 09:12:24
Revision_time      = 19-JUL-2011 14:21:20
Current_time       = 19-JUL-2011 14:21:51

Comment            = single_pulse
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 1H
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 400P
Spectrometer       = DELTA2_NMR

Field_strength     = 9.389766[T] (400[MHz]
X_acq_duration     = 4.36731904[s]
X_domain           = 1H
X_freq             = 399.78219838[MHz]
X_offset           = 5[ppm]
X_points           = 32768
X_prescans         = 1
X_resolution       = 0.22897343[Hz]
X_sweep            = 7.5030012[kHz]
Irr_domain         = 1H
Irr_freq           = 399.78219838[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 1H
Tri_freq           = 399.78219838[MHz]
Tri_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 3344
Total_scans        = 3344

X_90_width         = 11.4[us]
X_acq_time         = 4.36731904[s]
X_angle            = 45[deg]
X_atn              = 0.8[dB]
X_pulse            = 5.7[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
Recvr_gain         = 34
Relaxation_delay = 5[s]
Repetition_time    = 9.36731904[s]
Temp_get           = 23.8[dC]
```

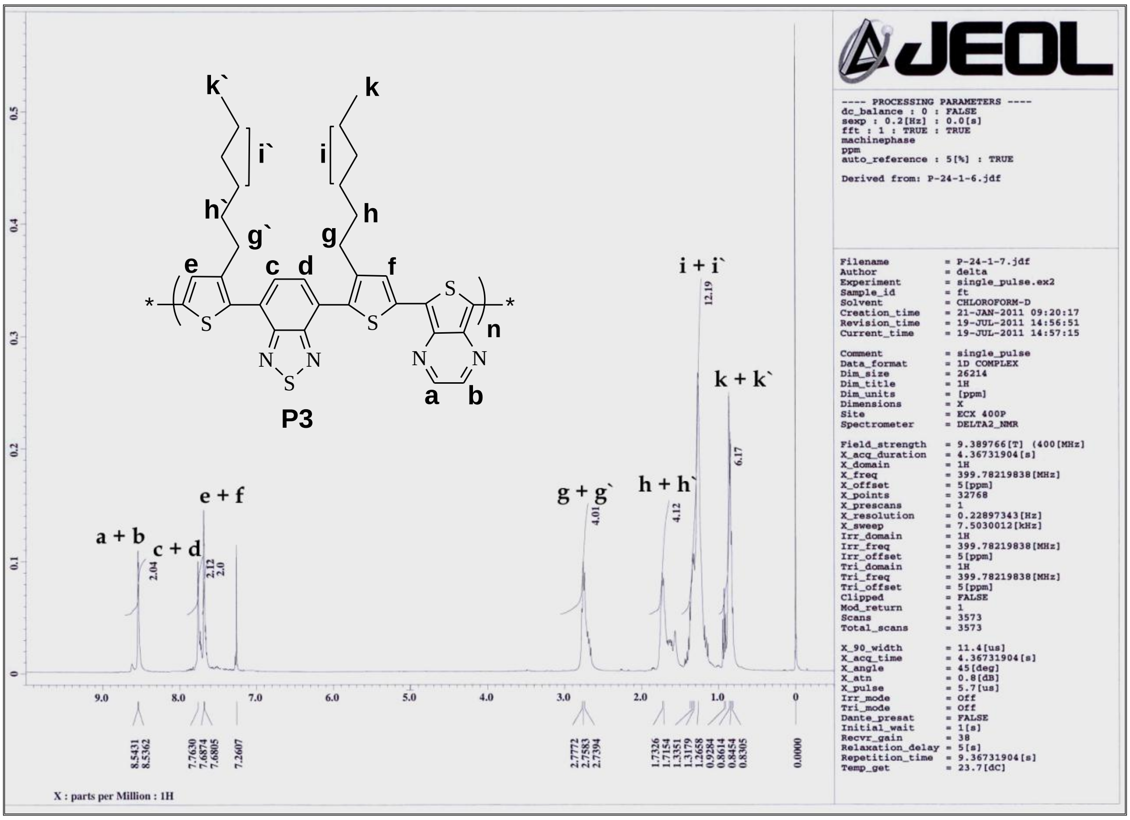
Figure S10. ^{1}H NMR (400 MHz) spectrum of copolymer **P2** in $CDCl_3$



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: p-18-1-4.jdf
```

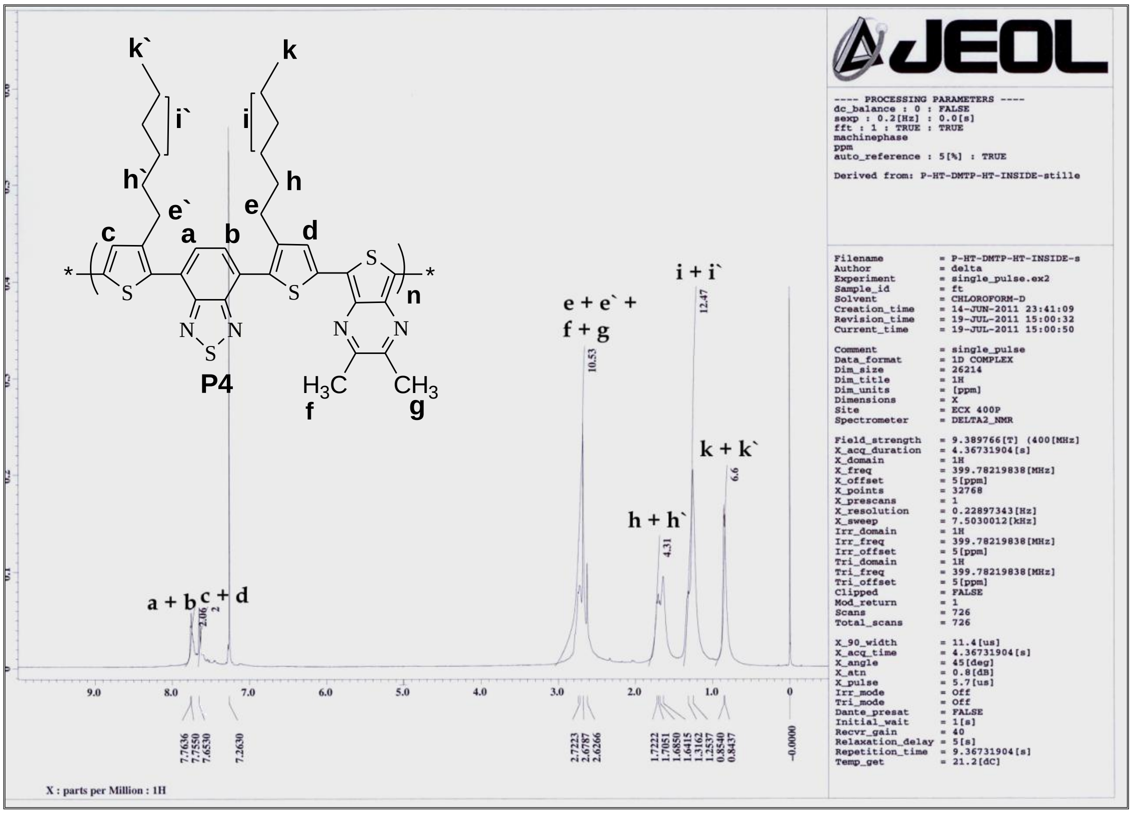
```
Filename           = p-18-1-7.jdf
Author             = delta
Experiment         = single_pulse.ex2
Sample_id          = ft
Solvent            = CHLOROFORM-D
Creation_time      = 19-JAN-2011 16:39:01
Revision_time      = 19-JUL-2011 14:33:08
Current_time       = 19-JUL-2011 14:33:30

Comment            = single_pulse
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 1H
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 400P
Spectrometer       = DELTA2_NMR

Field_strength     = 9.389766[T] (400[MHz]
X_acq_duration     = 4.36731904[s]
X_domain           = 1H
X_freq             = 399.78219838[MHz]
X_offset           = 5[ppm]
X_points           = 32768
X_prescans         = 1
X_resolution       = 0.22897343[Hz]
X_sweep            = 7.5030012[kHz]
Irr_domain         = 1H
Irr_freq           = 399.78219838[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 1H
Tri_freq           = 399.78219838[MHz]
Tri_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 239
Total_scans        = 239

X_90_width         = 11.4[us]
X_acq_time         = 4.36731904[s]
X_angle            = 45[deg]
X_atn              = 0.8[dB]
X_pulse            = 5.7[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
Recvr_gain         = 36
Relaxation_delay = 5[s]
Repetition_time    = 9.36731904[s]
Temp_get           = 22.3[dC]
```

Figure S11. ^{1}H NMR (400 MHz) spectrum of copolymer **P3** in CDCl$_3$



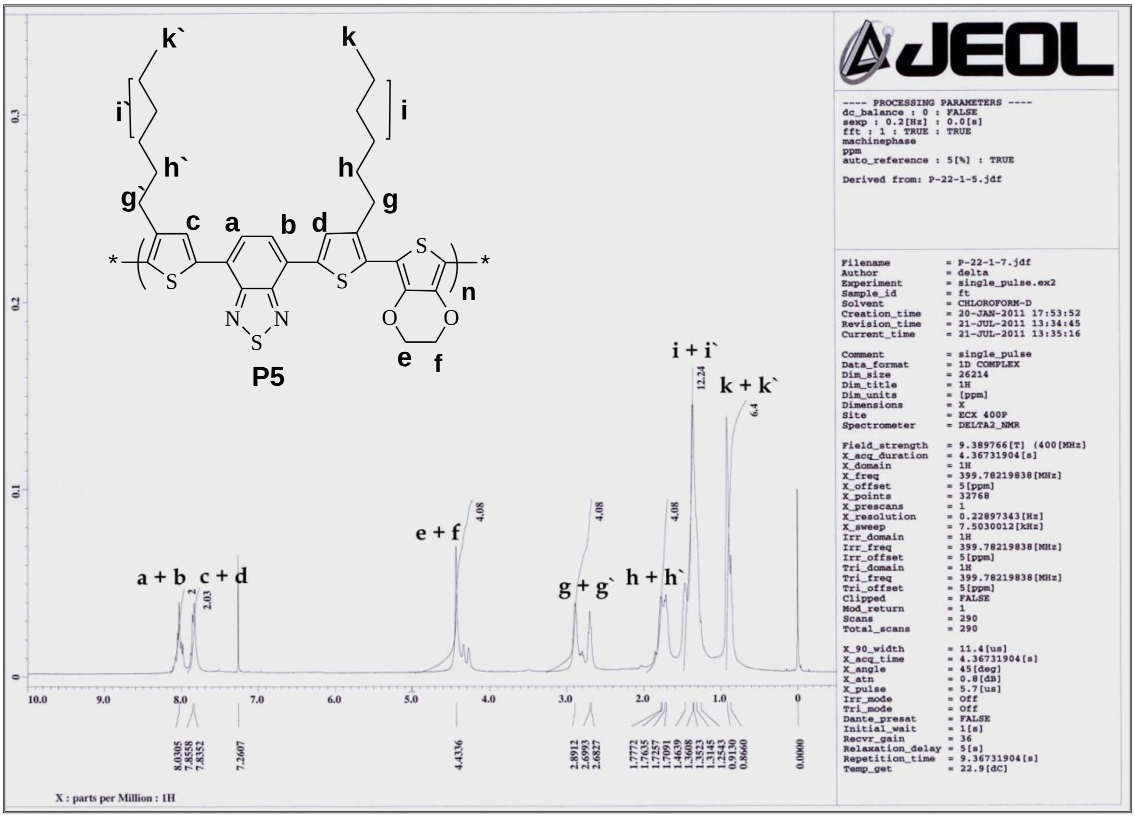
```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: P-24-1-6.jdf

Filename            = P-24-1-7.jdf
Author              = delta
Experiment          = single_pulse.ex2
Sample_id           = ft
Solvent             = CHLOROFORM-D
Creation_time       = 21-JAN-2011 09:20:17
Revision_time       = 19-JUL-2011 14:56:51
Current_time        = 19-JUL-2011 14:57:15

Comment             = single_pulse
Data_format         = 1D COMPLEX
Dim_size            = 26214
Dim_title           = 1H
Dim_units           = [ppm]
Dimensions          = X
Site                = ECX 400P
Spectrometer        = DELTA2_NMR

Field_strength      = 9.389766[T] (400[MHz]
X_acq_duration      = 4.36731904[s]
X_domain            = 1H
X_freq              = 399.78219838[MHz]
X_offset            = 5[ppm]
X_points            = 32768
X_prescans          = 1
X_resolution        = 0.22897343[Hz]
X_sweep             = 7.5030012[kHz]
Irr_domain          = 1H
Irr_freq            = 399.78219838[MHz]
Irr_offset          = 5[ppm]
Tri_domain          = 1H
Tri_freq            = 399.78219838[MHz]
Tri_offset          = 5[ppm]
Clipped             = FALSE
Mod_return          = 1
Scans               = 3573
Total_scans         = 3573

X_90_width          = 11.4[us]
X_acq_time          = 4.36731904[s]
X_angle             = 45[deg]
X_atn               = 0.8[dB]
X_pulse             = 5.7[us]
Irr_mode            = Off
Tri_mode            = Off
Dante_presat        = FALSE
Initial_wait        = 1[s]
Recvr_gain          = 38
Relaxation_delay    = 5[s]
Repetition_time     = 9.36731904[s]
Temp_get            = 23.7[dC]
```

Figure S12. ^{1}H NMR (400 MHz) spectrum of copolymer **P4** in CDCl$_3$



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: P-HT-DMTP-HT-INSIDE-stille

Filename            = P-HT-DMTP-HT-INSIDE-s
Author              = delta
Experiment          = single_pulse.ex2
Sample_id           = ft
Solvent             = CHLOROFORM-D
Creation_time       = 14-JUN-2011 23:41:09
Revision_time       = 19-JUL-2011 15:00:32
Current_time        = 19-JUL-2011 15:00:50

Comment             = single_pulse
Data_format         = 1D COMPLEX
Dim_size            = 26214
Dim_title           = 1H
Dim_units           = [ppm]
Dimensions          = X
Site                = ECX 400P
Spectrometer        = DELTA2_NMR

Field_strength      = 9.389766[T] (400[MHz]
X_acq_duration      = 4.36731904[s]
X_domain            = 1H
X_freq              = 399.78219838[MHz]
X_offset            = 5[ppm]
X_points            = 32768
X_prescans          = 1
X_resolution        = 0.22897343[Hz]
X_sweep             = 7.5030012[kHz]
Irr_domain          = 1H
Irr_freq            = 399.78219838[MHz]
Irr_offset          = 5[ppm]
Tri_domain          = 1H
Tri_freq            = 399.78219838[MHz]
Tri_offset          = 5[ppm]
Clipped             = FALSE
Mod_return          = 1
Scans               = 726
Total_scans         = 726

X_90_width          = 11.4[us]
X_acq_time          = 4.36731904[s]
X_angle             = 45[deg]
X_atn               = 0.8[dB]
X_pulse             = 5.7[us]
Irr_mode            = Off
Tri_mode            = Off
Dante_presat        = FALSE
Initial_wait        = 1[s]
Recvr_gain          = 40
Relaxation_delay    = 5[s]
Repetition_time     = 9.36731904[s]
Temp_get            = 21.2[dC]
```

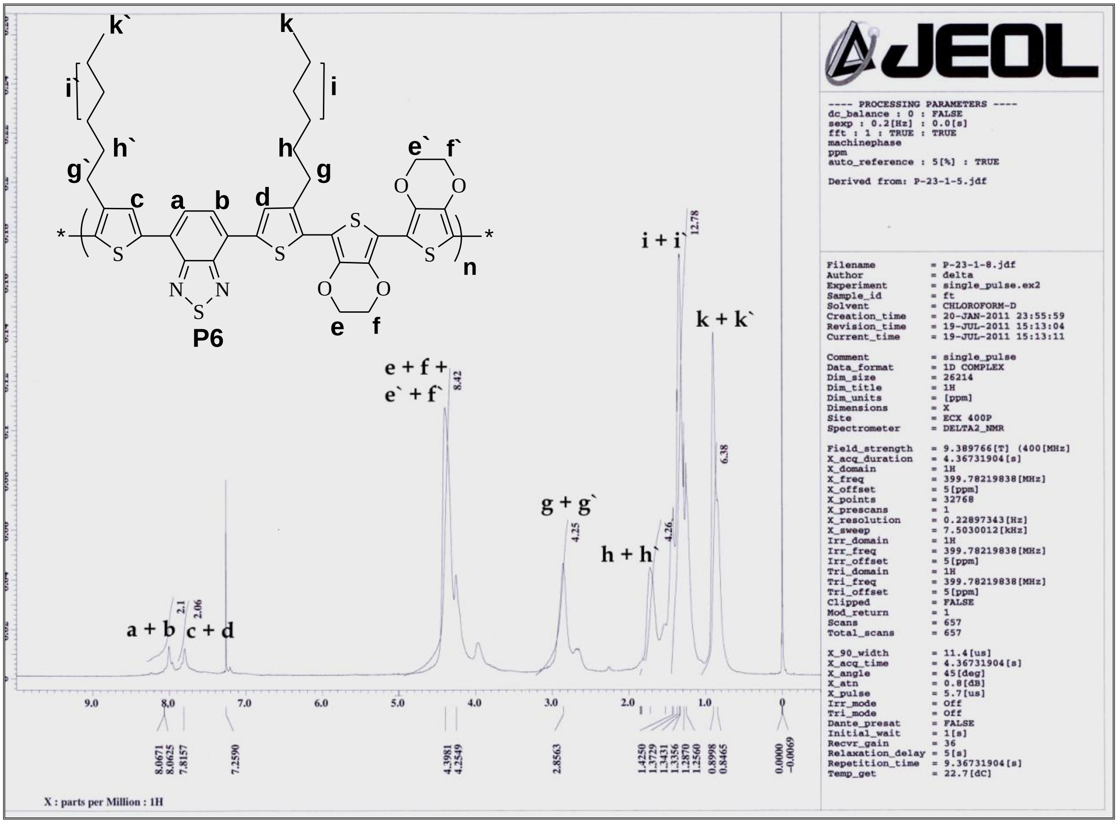
Figure S13. ^{1}H NMR (400 MHz) spectrum of copolymer **P5** in $CDCl_3$



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: P-22-1-5.jdf
```

```
Filename           = P-22-1-7.jdf
Author             = delta
Experiment         = single_pulse.ex2
Sample_id          = ft
Solvent            = CHLOROFORM-D
Creation_time      = 20-JAN-2011 17:53:52
Revision_time      = 21-JUL-2011 13:34:45
Current_time       = 21-JUL-2011 13:35:16

Comment            = single_pulse
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 1H
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 400P
Spectrometer       = DELTA2_NMR

Field_strength     = 9.389766[T] (400[MHz]
X_acq_duration     = 4.36731904[s]
X_domain           = 1H
X_freq             = 399.78219838[MHz]
X_offset           = 5[ppm]
X_points           = 32768
X_prescans         = 1
X_resolution       = 0.22897343[Hz]
X_sweep            = 7.5030012[kHz]
Irr_domain         = 1H
Irr_freq           = 399.78219838[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 1H
Tri_freq           = 399.78219838[MHz]
Tri_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 290
Total_scans        = 290

X_90_width         = 11.4[us]
X_acq_time         = 4.36731904[s]
X_angle            = 45[deg]
X_atn              = 0.8[dB]
X_pulse            = 5.7[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
Recvr_gain         = 36
Relaxation_delay = 5[s]
Repetition_time    = 9.36731904[s]
Temp_get           = 22.9[dC]
```

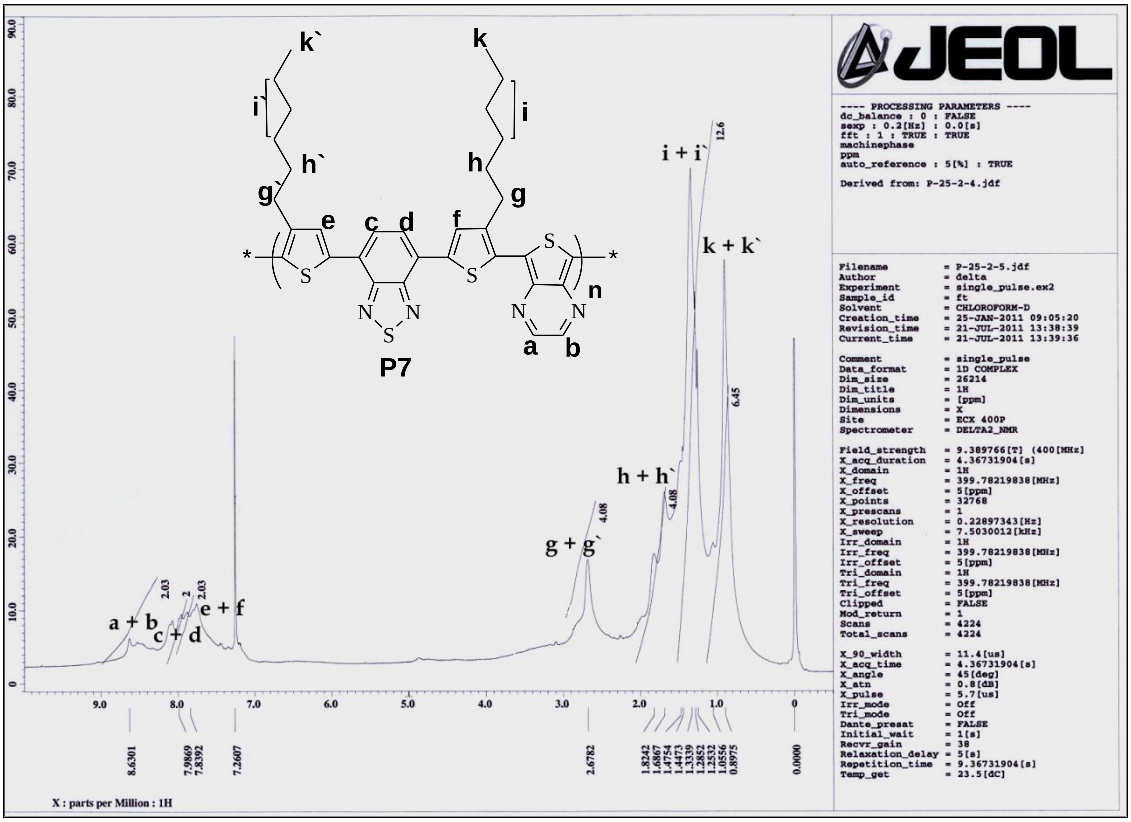
Figure S14. ^{1}H NMR (400 MHz) spectrum of copolymer **P6** in $CDCl_3$



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: P-23-1-5.jdf
```

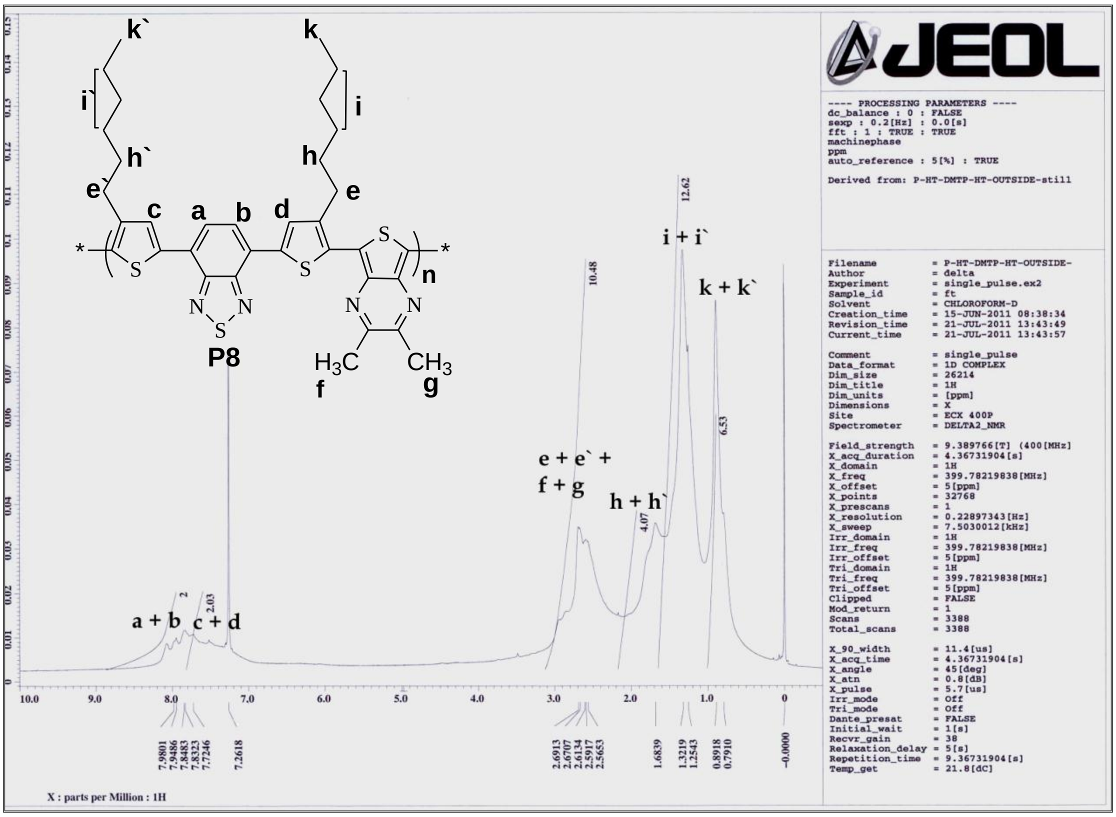
```
Filename           = P-23-1-8.jdf
Author             = delta
Experiment         = single_pulse.ex2
Sample_id          = ft
Solvent            = CHLOROFORM-D
Creation_time      = 20-JAN-2011 23:55:59
Revision_time      = 19-JUL-2011 15:13:04
Current_time       = 19-JUL-2011 15:13:11

Comment            = single_pulse
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 1H
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 400P
Spectrometer       = DELTA2_NMR

Field_strength     = 9.389766[T] (400[MHz]
X_acq_duration     = 4.36731904[s]
X_domain           = 1H
X_freq             = 399.78219838[MHz]
X_offset           = 5[ppm]
X_points           = 32768
X_prescans         = 1
X_resolution       = 0.22897343[Hz]
X_sweep            = 7.5030012[kHz]
Irr_domain         = 1H
Irr_freq           = 399.78219838[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 1H
Tri_freq           = 399.78219838[MHz]
Tri_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 657
Total_scans        = 657

X_90_width         = 11.4[us]
X_acq_time         = 4.36731904[s]
X_angle            = 45[deg]
X_atn              = 0.8[dB]
X_pulse            = 5.7[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
Recvr_gain         = 36
Relaxation_delay = 5[s]
Repetition_time    = 9.36731904[s]
Temp_get           = 22.7[dC]
```

Figure S15. ^{1}H NMR (400 MHz) spectrum of copolymer **P7** in $CDCl_3$



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: P-25-2-4.jdf

Filename           = P-25-2-5.jdf
Author             = delta
Experiment         = single_pulse.ex2
Sample_id          = ft
Solvent            = CHLOROFORM-D
Creation_time      = 25-JAN-2011 09:05:20
Revision_time      = 21-JUL-2011 13:38:39
Current_time       = 21-JUL-2011 13:39:36

Comment            = single_pulse
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 1H
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 400P
Spectrometer       = DELTA2_NMR

Field_strength     = 9.389766[T] (400[MHz]
X_acq_duration     = 4.36731904[s]
X_domain           = 1H
X_freq             = 399.78219838[MHz]
X_offset           = 5[ppm]
X_points           = 32768
X_prescans         = 1
X_resolution       = 0.22897343[Hz]
X_sweep            = 7.5030012[kHz]
Irr_domain         = 1H
Irr_freq           = 399.78219838[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 1H
Tri_freq           = 399.78219838[MHz]
Tri_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 4224
Total_scans        = 4224

X_90_width         = 11.4[us]
X_acq_time         = 4.36731904[s]
X_angle            = 45[deg]
X_atn              = 0.8[dB]
X_pulse            = 5.7[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
Recvr_gain         = 38
Relaxation_delay   = 5[s]
Repetition_time    = 9.36731904[s]
Temp_get           = 23.5[dC]
```

Figure S16. ^{1}H NMR (400 MHz) spectrum of copolymer **P8** in $CDCl_3$



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
fft : 1 : TRUE : TRUE
machinephase
ppm
auto_reference : 5[%] : TRUE

Derived from: P-HT-DMTP-HT-OUTSIDE-still

Filename           = P-HT-DMTP-HT-OUTSIDE-
Author             = delta
Experiment         = single_pulse.ex2
Sample_id          = ft
Solvent            = CHLOROFORM-D
Creation_time      = 15-JUN-2011 08:38:34
Revision_time      = 21-JUL-2011 13:43:49
Current_time       = 21-JUL-2011 13:43:57

Comment            = single_pulse
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 1H
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 400P
Spectrometer       = DELTA2_NMR

Field_strength     = 9.389766[T] (400[MHz]
X_acq_duration     = 4.36731904[s]
X_domain           = 1H
X_freq             = 399.78219838[MHz]
X_offset           = 5[ppm]
X_points           = 32768
X_prescans         = 1
X_resolution       = 0.22897343[Hz]
X_sweep            = 7.5030012[kHz]
Irr_domain         = 1H
Irr_freq           = 399.78219838[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 1H
Tri_freq           = 399.78219838[MHz]
Tri_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 3388
Total_scans        = 3388

X_90_width         = 11.4[us]
X_acq_time         = 4.36731904[s]
X_angle            = 45[deg]
X_atn              = 0.8[dB]
X_pulse            = 5.7[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
Recvr_gain         = 38
Relaxation_delay   = 5[s]
Repetition_time    = 9.36731904[s]
Temp_get           = 21.8[dC]
```

- Thermal analysis

Figure S17. TGA thermograms of copolymers **P1–P8**

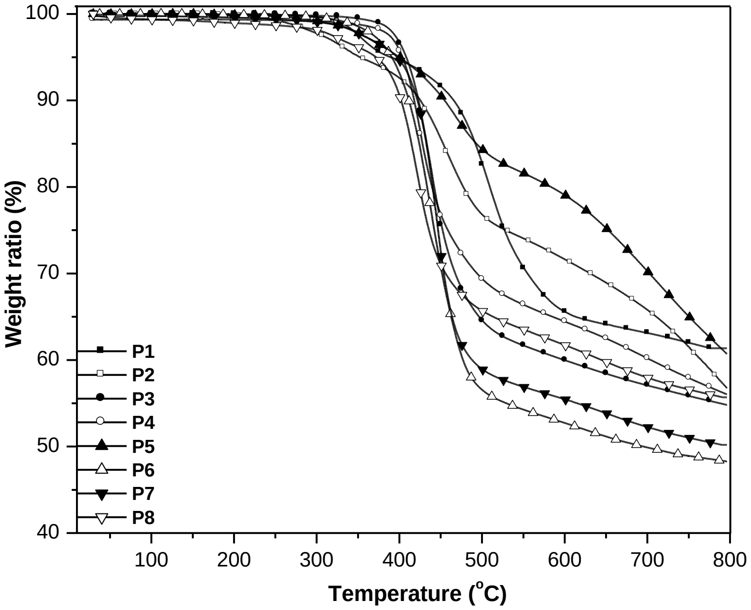
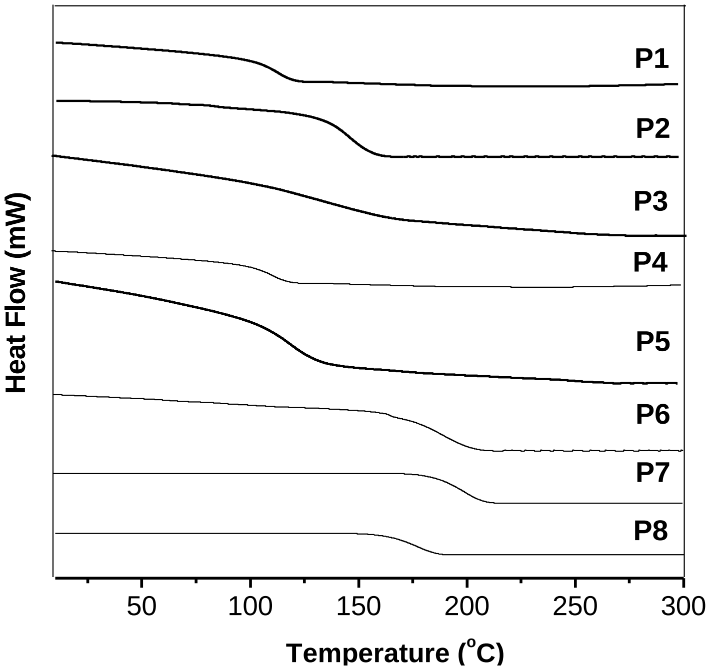


Figure S18. DSC curves of copolymers **P1–P8**



- Electrochemical analysis

Figure S19. Cyclic voltammograms of copolymers **P1−P8**