Supplementary Material

Thiophene, Benzothiadiazole Copolymers: Synthesis, Optoelectronic Properties, and Electrical Characterization for Photovoltaic Application

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Contents

Analytical data of compounds 4, 6, and 8

5,5`-Dibromo-2,2`-bithiophene, 4 (2.88 g, 89%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.96-9.95 (d, *J* = 4.00 Hz, 2 H, 2X CBr-C*H*-CH), 6.85-6.84 (d, *J* = 4.00 Hz, 2 H, 2X CBr-CH-C*H*-) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.35, 130.64, 124.12, 111.50 ppm. $C_8H_4Br_2S_2$ (626.53): Calcd. C 29.65, H 1.24, Br 49.32, S 19.79; found C 30.07, H 1.34, Br 49.55, S 19.63.

2,5-Dibromothieno[3,2-*b*]thiophene, 6 (2.74 g, 92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (s, 2 H, 2X CBr-C*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.22, 121.71, 113.57 ppm. $C_6H_2Br_2S_2$ (298.02): Calcd. C 24.18, H 0.68, Br 53.62, S 21.52; found C 24.11, H 0.72, Br 53.49, S 21.59.

5,5`-Dibromodithieno[3,2-*b*;2`,3`-*d*]thiophene, 8 (3.15 g, 89.2%) as a tan solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (s, 2 H, 2X CBr-C*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.36, 130.34, 124.12, 112.32 ppm. $C_8H_2Br_2S_3$ (354.1): Calcd. C 27.13, H 0.57, Br 45.13, S 27.17; found C 27.49, H 0.63, Br 45.01, S 27.19.

Analytical data of copolymers P1-P10

Poly[(thieno[3,2-*b*]thiophene-2,5-diyl)-*alt*-(4,7-bis(3-hexylthiophen-2-yl)benzo[c]-[2,1,3]thiadiazole)-5,5-diyl], P1: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.69-7.69 (m, 2 H, 2X CH (Ph)), 7.38 (s, 2 H, 2X CS-CH-CS), 7.23 (s, 2 H, 2X CS-CH-C-hexyl), 2.69-2.68 (br. s, 4 H, 2X C-CH_2-hexyl), 1.69-1.56 (br. m, 4 H, 2X C-CH_2-CH_2-), 1.31-1.24 (br. m, 12 H, 2X -$(CH_2)_3CH_3$), 0.84-0.83 (br. m, 12 H, 2X CH_3). $(C_{32}H_{32}N_2S_5)_n$ $(604.93)_n$: Calcd. C 63.53, H 5.33, N 4.63, S 26.50; Found C 63.62, H 5.44, N 4.52, S 26.63.

Poly[(thieno[3,2-*b*]thiophene-2,5-diyl)-*alt*-(4,7-bis(4-hexylthiophen-2-yl)benzo[c]-[2,1,3]thiadiazole)-5,5-diyl], P2: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.97 (br. m, 2H, 2X CH (Ph)), 7.82-7.79 (br. s, 2H, 2X CH-C-Ph), 7.02 (br. s, 2H, 2X CH-C-hexyl), 2.85-2.67 (br. m, 4H, 2X C-CH_2-hexyl), 1.69-1.55 (br. s, 4H, 2X C-CH_2CH_2-), 1.45-1.33 (br. m, 12 H, 2X -$(CH_2)_3CH_3$), 0.91-0.86 (br. m, 6 H, 2X CH_3). $(C_{32}H_{32}N_2S_5)_n$ $(604.93)_n$: Calcd. C 63.53, H 5.33, N 4.63, S 26.50; found C 63.40, H 5.42, N 4.51, S 26.39.

Poly[(2,2`-bithiophene-5,5`-diyl)-*alt*-(4,7-bis(3-hexylthiophen-2yl)-benzo[c][2,1,3]-thiadiazole)-5,5-diyl], P3: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.68 (br. s, 2 H, 2X CH (Ph)), 7.20 (s, 2 H, 2X CH-CS), 7.15 (s, 2 H, 2X –CHCH-CS), 7.11 (s, 2 H, 2X CH-C-hexyl), 2.68 (br. s, 4 H, 2X C-CH_2CH_2-), 1.30-1.24 (br. m, 12 H, 2X -$(CH_2)_3CH_3$), 0.84-0.83 (br. m, 6 H, 2X CH_3). $(C_{34}H_{34}N_2S_5)_n$ $(630.97)_n$: Calcd. C 64.72, H 5.43, N 4.44, S 25.41; Found C 64.89, H 5.66, N 4.22, S 25.19.

Poly[(2,2`-bithiophene-5,5`-diyl)-*alt*-(4,7-bis(4-hexylthiophen-2yl)benzo[c][2,1,3]-thiadiazole)-5,5-diyl], P4: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.79-7.96 (br. m, 2 H, 2X CH (Ph)), 7.81-7.79 (s, 2 H, 2X CH-CS), 7.14-7.12 (br. s, 2 H, 2X CH-C-hexyl), 7.03 (s, 2 H, 2X –CHCH-CS), 2.85-2.69 (br. m, 4 H, 2X CH-C-hexyl), 1.70 (br. s, 4 H, 2X C-CH_2CH_2-), 1.55-1.25 (br. m, 12 H, 2X -$(CH_2)_3CH_3$), 0.92-0.86 (br. m, 6 H, 2X CH_3). $(C_{34}H_{34}N_2S_5)_n$ $(630.97)_n$: Calcd. C 64.72, H 5.43, N 4.44, S 25.41; Found C 64.56, H 5.30, N 4.19, S 25.29.

Poly[(thieno[3,2-*b*]thiophene-3,6-diyl)-*alt*-(4,7-bis(3-hexylthiophen-2-yl)benzo[c]-[2,1,3]thiadiazole)-5,5-diyl], P5: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.73-7.71 (s, 2H, 2X CH (Ph)), 7.64 (s, 2H, 2X CHS), 7.43 (s, 2H, 2X CH-C-hexyl), 2.75-2.71 (br. m, 4H, 2X C-CH_2-hexyl), 1.71 (br. s, 4 H, 2X C-CH_2CH_2-), 1.33-1.25 (br. m, 12 H, 2X -$(CH_2)_3CH_3$), 0.85 (br. s, 6 H, 2X CH_3). $(C_{32}H_{32}N_2S_5)_n$ $(604.93)_n$: Calcd. C 63.53, H 5.33, N 4.63, S 26.50; Found C 65.41, H 5.56, N 4.50, S 26.40.

Poly[(thieno[3,2-*b*]thiophene-3,6-diyl)-*alt*-(4,7-bis(4-hexylthiophen-2-yl)benzo[c]-[2,1,3]thiadiazole)-5,5-diyl], P6: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.10-8.05 (br. s, 2H, 2X CH (Ph)), 7.86-7.84 (s, 2H, 2X CH-C-Ph), 7.48 (s, 2H, 2X CHS), 2.85-2.68 (br. m, 4H, 2X C-CH_2-hexyl), 1.71 (br. m, 4H, 2X C-CH_2CH_2-), 1.38-1.30 (br. m, 12 H, 2X C-CH_2CH_2-), 0.90-0.86 (br. m, 6 H, 2X CH_3). $(C_{32}H_{32}N_2S_5)_n$ $(604.93)_n$: Calcd. C 63.53, H 5.33, N 4.63, S 26.50; Found C 63.49, H 5.21, N 4.55, S 26.20.

Poly[(thiophene-2,5-diyl)-*alt*-(4,7-bis(3-hexylthiophen-2-yl)benzo[c][2,1,3]-thiadiazole)-5,5-diyl], P7: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.00 (br. s, 2H, 2X CH (Ph)), 7.21-7.19 (s, 2H, CS-CHCH-CS), 7.17 (s, 2H, 2X CH-C-hexyl), 2.69 (br. s, 4H, 2X

C-CH_2-hexyl), 1.69 (br. m, 4H, C-CH_2CH_2-), 1.31-1.25 (br. m, 12H, 2X -$(CH_2)_3CH_3$), 0.85 (br. s, 6H, 2X CH_3). $(C_{30}H_{32}N_2S_4)_n$ $(548.85)_n$: Calcd. C 65.65, H 5.88, N 5.10, S 23.37; Found C 65.69, H 5.91, N 5.01, S 23.40.

Poly[(thiophene-2,5-diyl)-*alt*-(4,7-bis(4-hexylthiophen-2-yl)benzo[c][2,1,3]thiadiazole)-5,5-diyl], P8: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.83-7.80 (br. m, 2H, 2X CH (Ph)), 7.79-7.77 (s, 2H, 2X CH-C-Ph), 7.23-7.20 (s, 2H, 2X CS-CHCH-CS), 2.95-2.67 (br. m, 4H, 2X C-CH_2-hexyl), 1.69-1.60 (br. s, 4H, C-CH_2CH_2-), 1.57-1.32 (br. m, 12H, 2X -$(CH_2)_3CH_3$), 0.92-0.90 (br. s, 6H, 2X CH_3). $(C_{30}H_{32}N_2S_4)_n$ $(548.85)_n$: Calcd. C 65.65, H 5.88, N 5.10, S 23.37; Found C 65.41, H 5.90, N 5.00, S 23.27.

Poly[(dithieno[3,2-*b*;2`,3`-*d*]thiophene-2,6-diyl)-*alt*-(4,7-bis(3-hexylthiophen-2-yl)-benzo[c][2,1,3]thiadiazole)-5,5-diyl], P9: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.69 (br. s, 2H, 2X CH (Ph)), 7.42 (br. s, 2H, CH-CS), 7.21 (s, 2H, 2X CH-C-hexyl), 2.69 (br. s, 4H, 2X C-CH_2-hexyl), 1.69-1.58 (br. m, 4H, C-CH_2CH_2), 1.30-1.25 (br. m, 12H, 2X -$(CH_2)_3CH_3$), 0.85 (br. s, 6H, 2X CH_3). $(C_{34}H_{32}N_2S_6)_n$ $(661.02)_n$: Calcd. C 61.78, H 4.88, N 4.24, S 29.10; Found C 61.99, H 4.71, N 4.21, S 29.01.

Poly[(dithieno[3,2-*b*;2`,3`-*d*]thiophene-2,6-diyl)-*alt*-(4,7-bis(3-hexylthiophen-2-yl)benzo[c][2,1,3]thiadiazole)-5,5-diyl], P10: ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.96-7.95 (br. m, 2H, 2X CH (Ph)), 7.79 (s, 2H, 2X CH-C-Ph), 7.37 (s, 2H, 2X CH-CS), 2.69-2.65 (br. m, 4H, 2X C-CH_2-hexyl), 1.69 (m, 4H, C-CH_2CH_2-), 1.37-1.25 (br. m, 12H, 2X -$(CH_2)_3CH_3$), 0.92-0.90 (br. s, 6H, 2X CH_3). $(C_{34}H_{32}N_2S_6)_n$ $(661.02)_n$: Calcd. C 61.78, H 4.88, N 4.24, S 29.10; Found C 61.71, H 4.99, N 4.13, S 29.05.

Figure S1. ^{1}H NMR (400 MHz) spectrum of compound **4** in $CDCl_3$

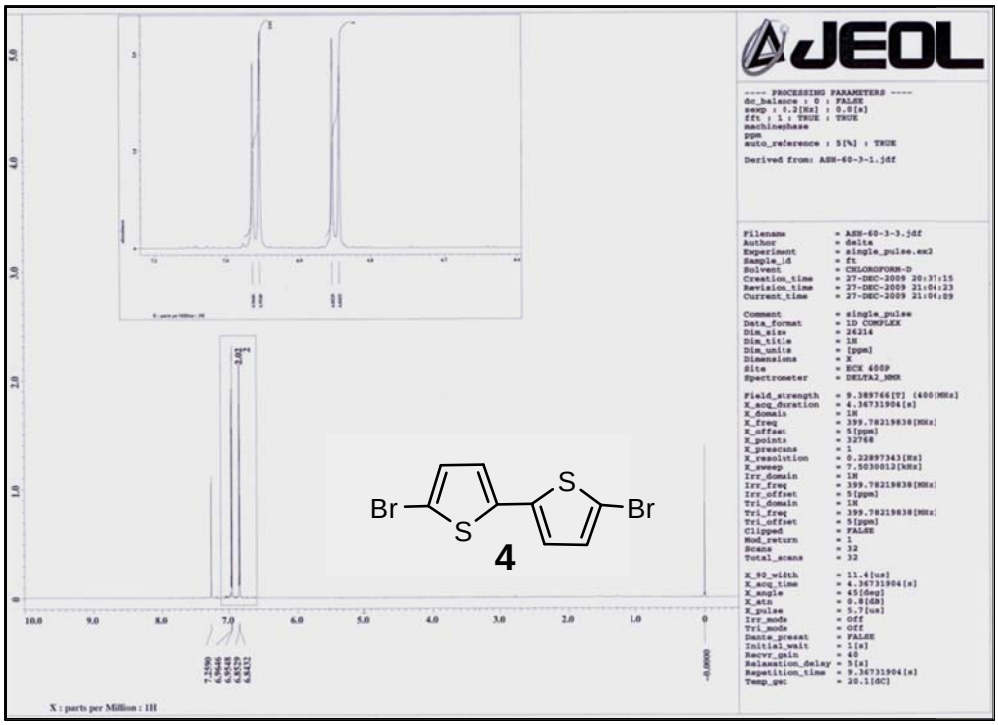


Figure S2. ^{13}C NMR (100 MHz) spectrum of compound **4** in $CDCl_3$

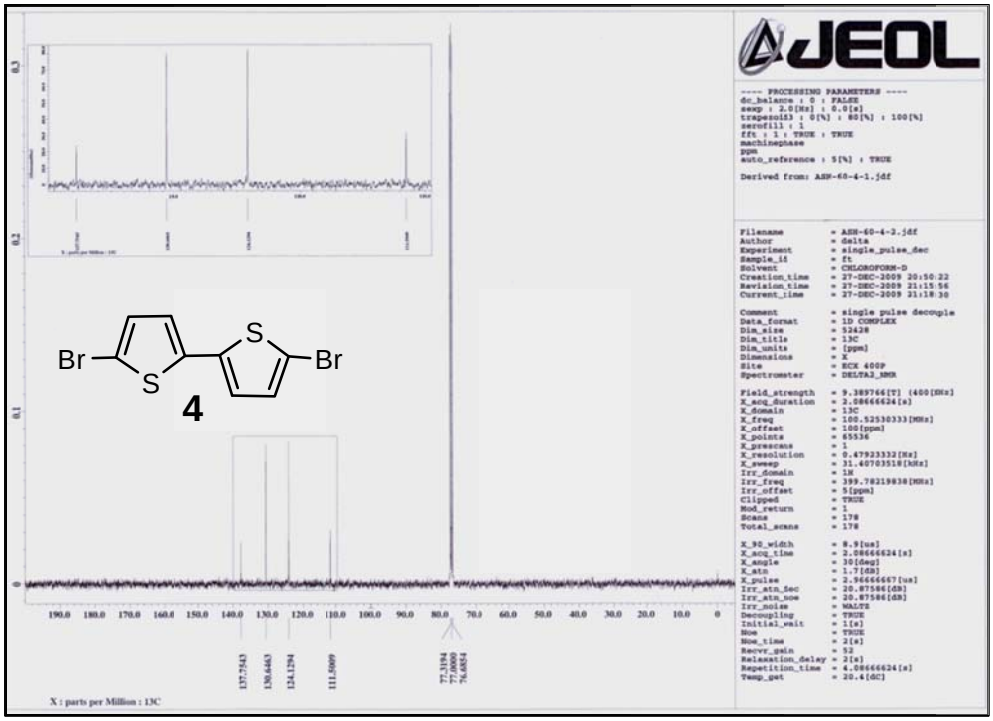


Figure S3. ^{1}H NMR (400 MHz) spectrum of compound **6** in $CDCl_3$

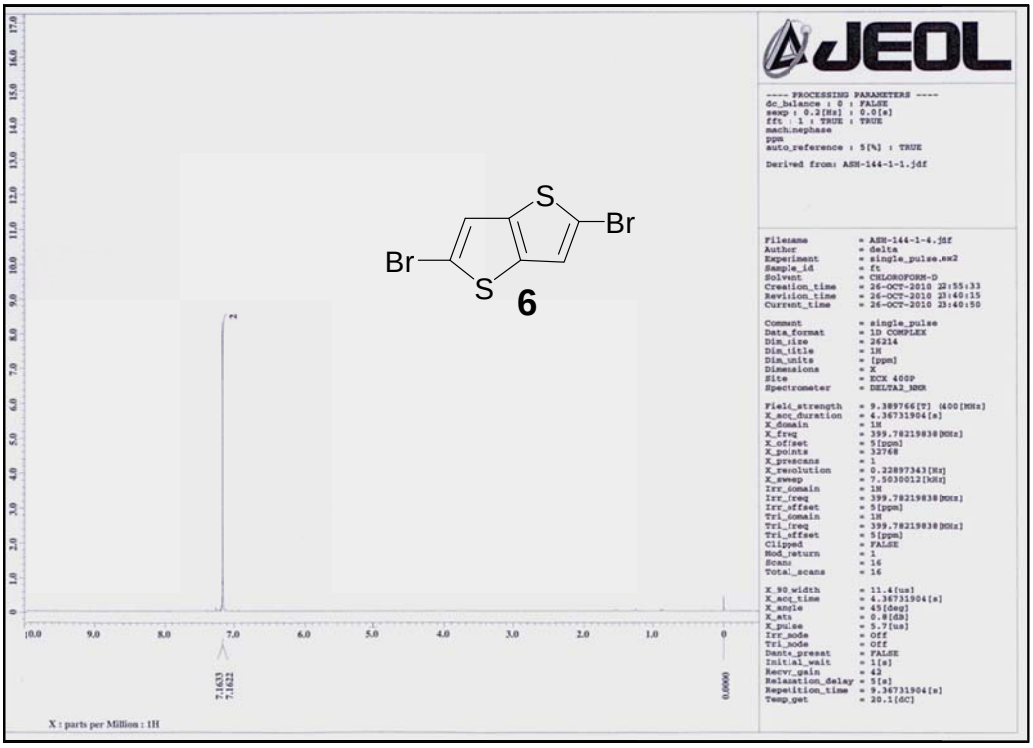


Figure S4. ^{13}C NMR (100 MHz) spectrum of compound **6** in $CDCl_3$

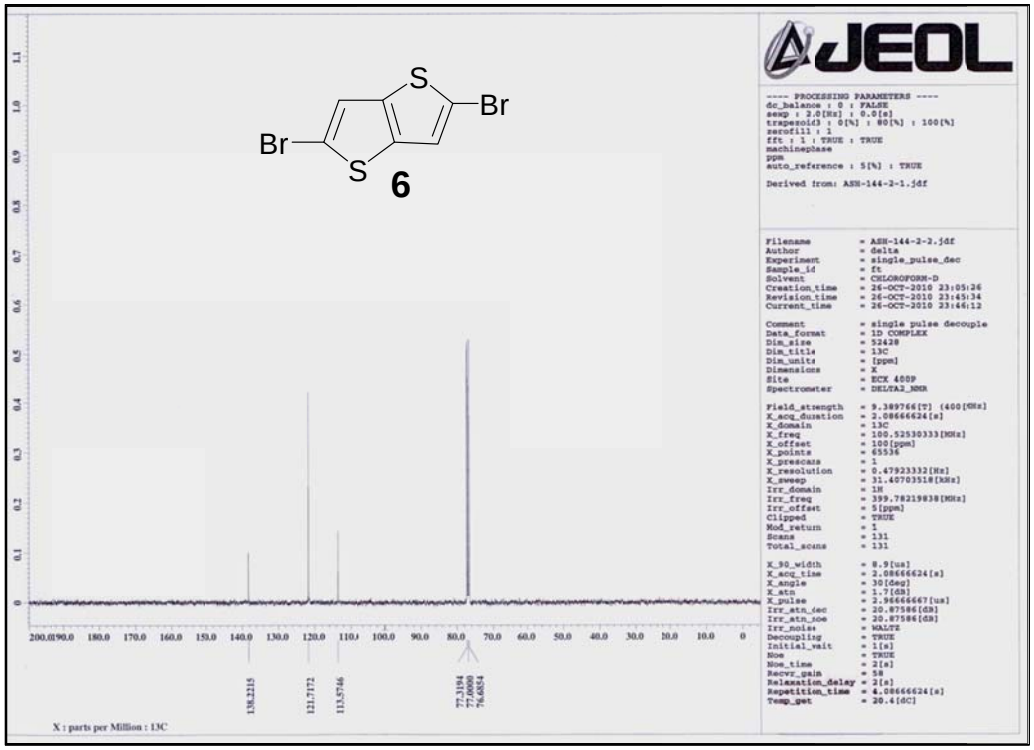


Figure S5. ^{1}H NMR (400 MHz) spectrum of compound **8** in $CDCl_3$

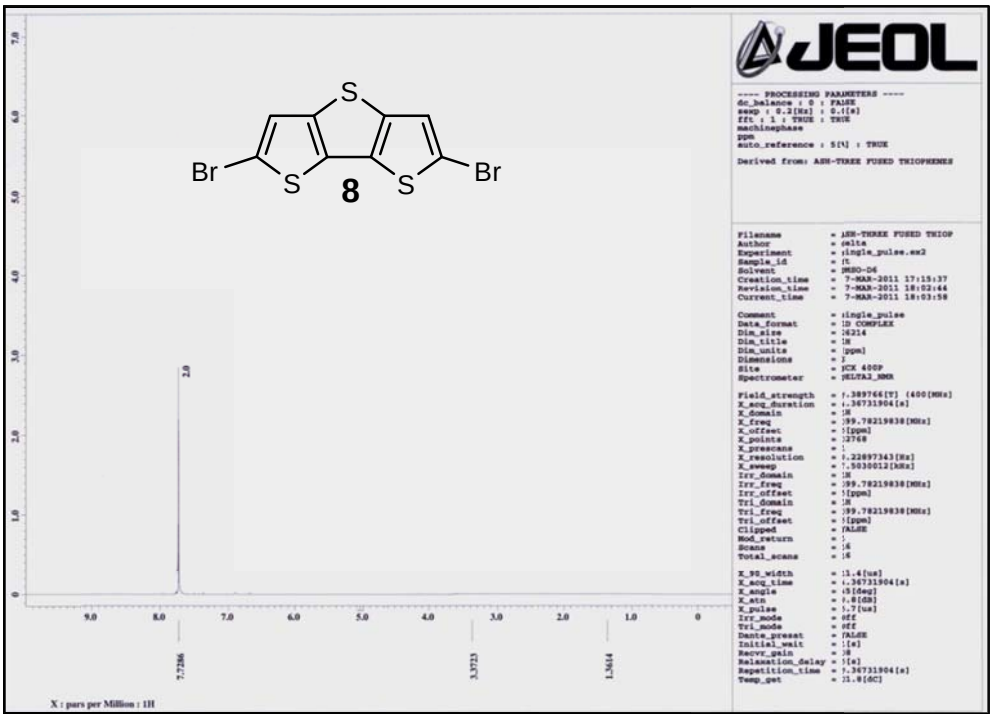


Figure S6. ^{13}C NMR (100 MHz) spectrum of compound **8** in $CDCl_3$

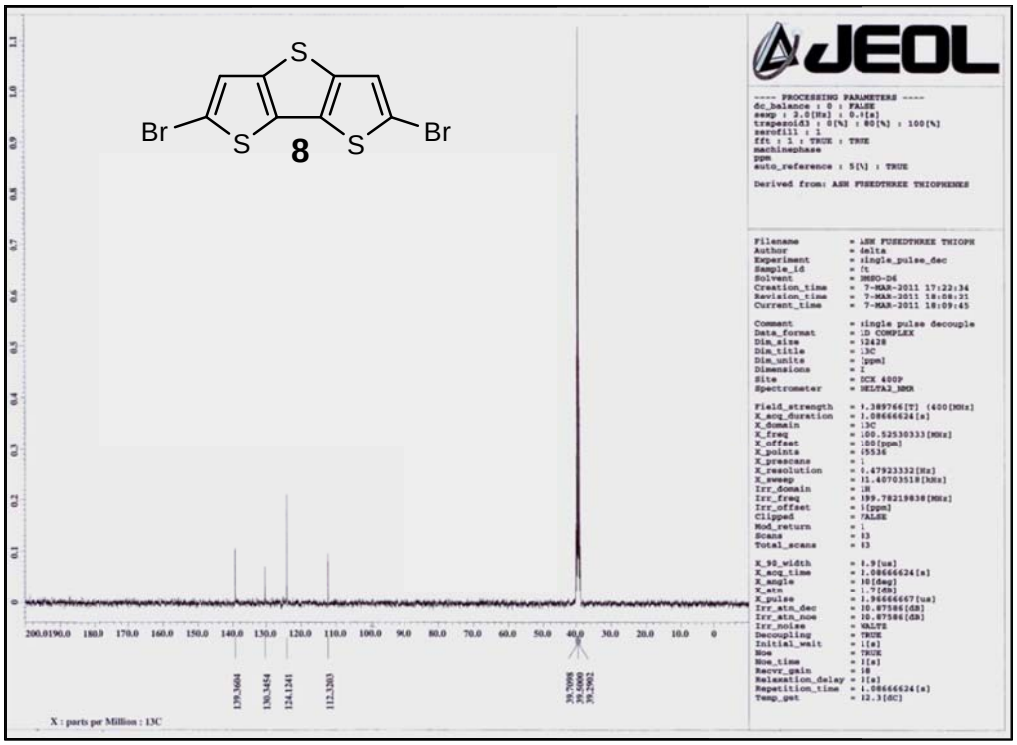


Figure S7. ^{1}H NMR (400 MHz) spectrum of copolymer **P1** in $CDCl_3$

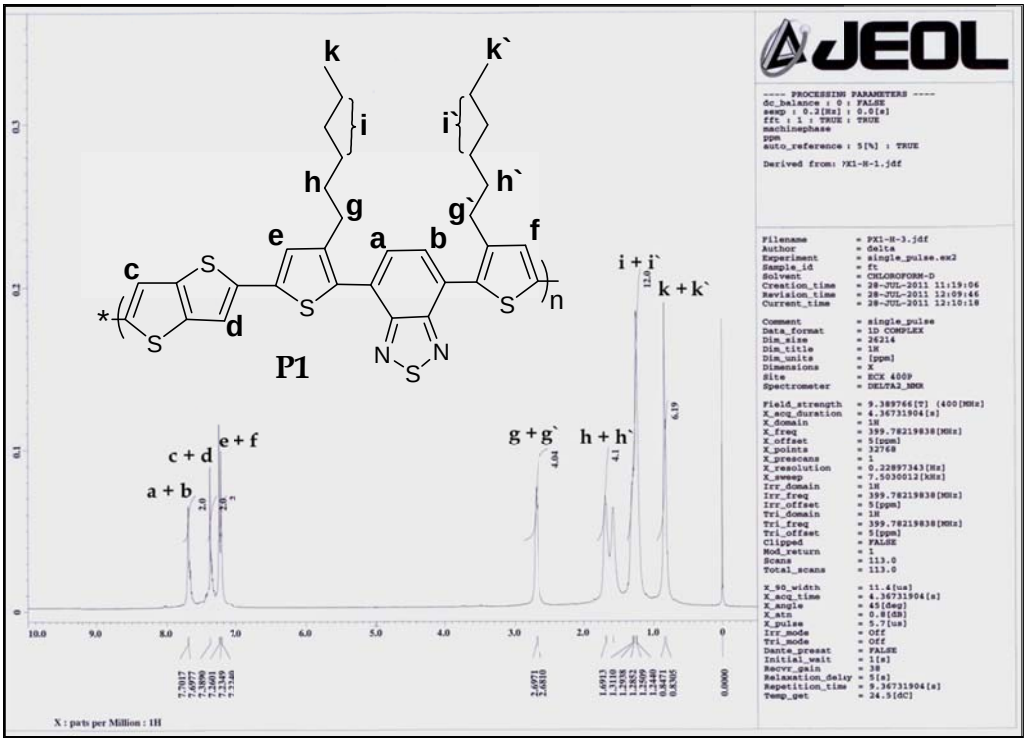


Figure S8. ^{1}H NMR (400 MHz) spectrum of copolymer **P2** in $CDCl_3$

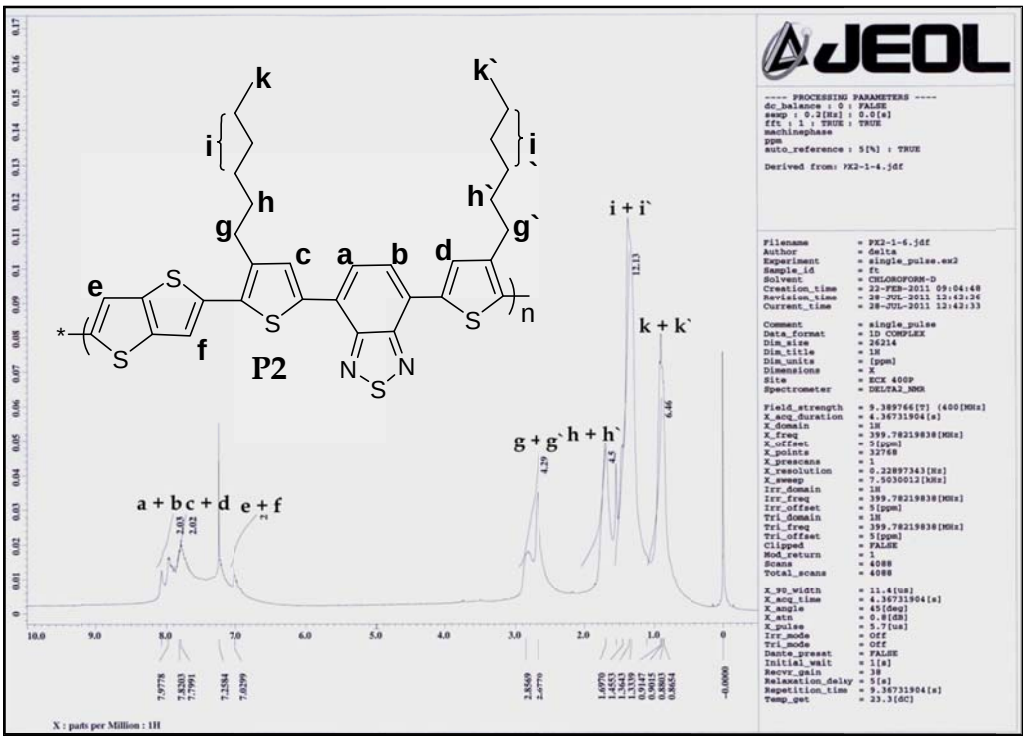


Figure S9. ^{1}H NMR (400 MHz) spectrum of copolymer **P3** in $CDCl_3$

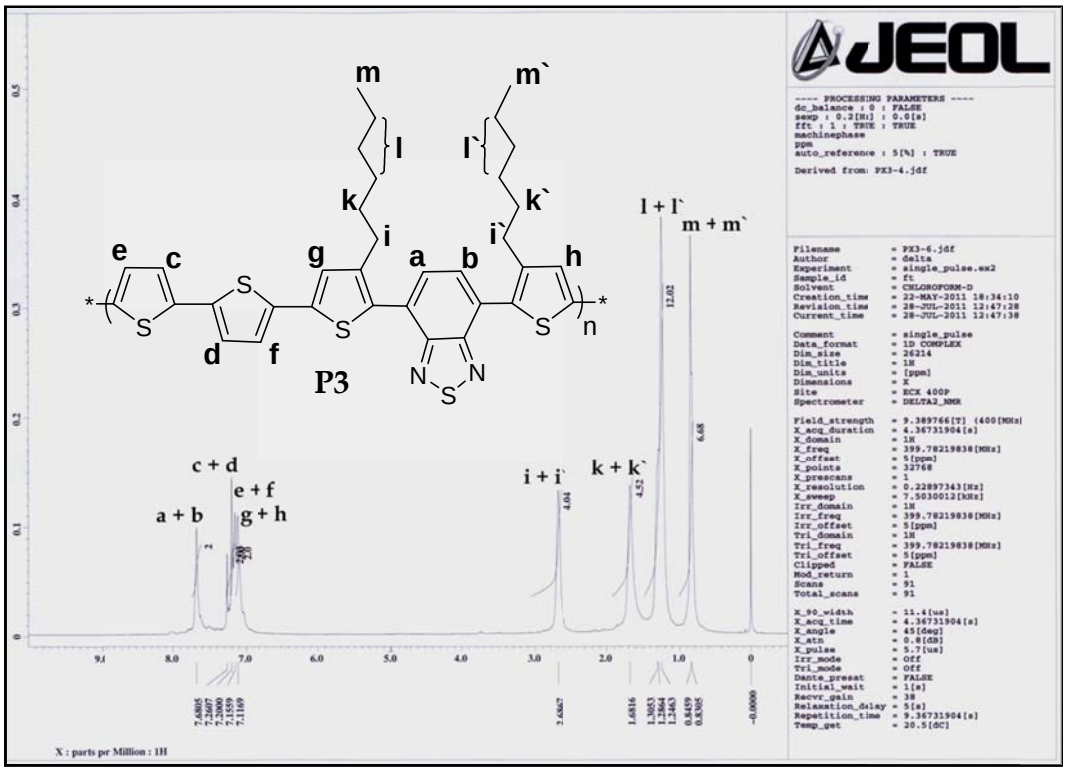


Figure S10. ^{1}H NMR (400 MHz) spectrum of copolymer **P4** in $CDCl_3$

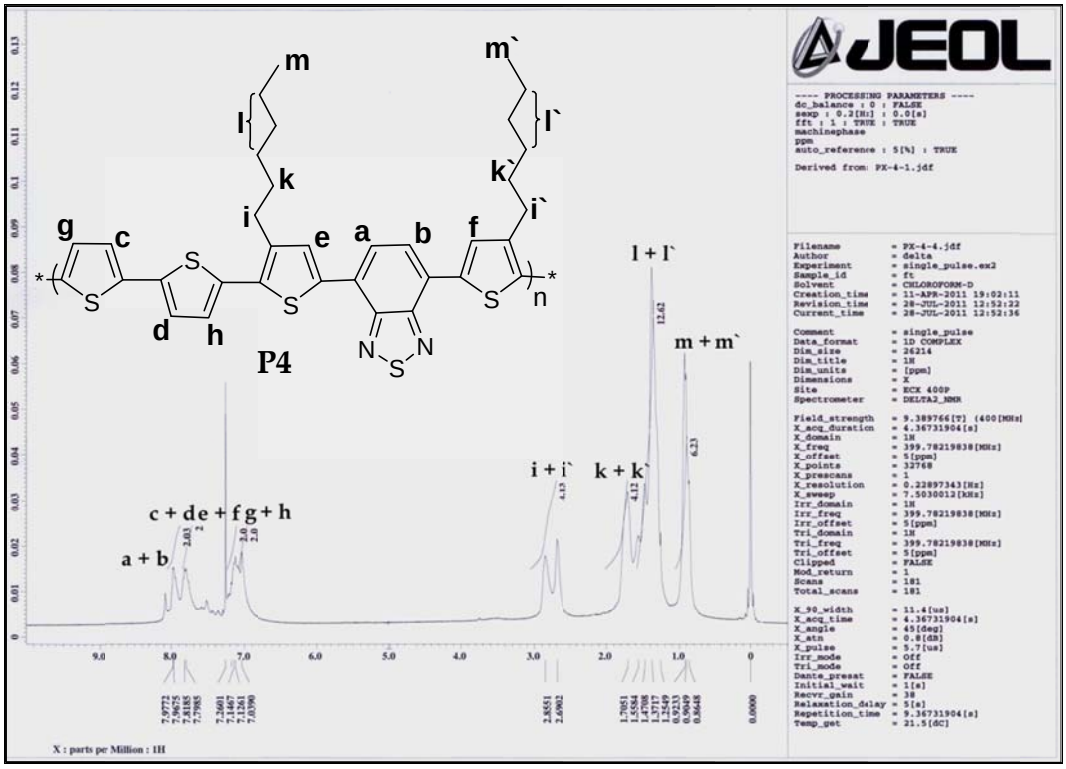


Figure S11. ^{1}H NMR (400 MHz) spectrum of copolymer **P5** in $CDCl_3$

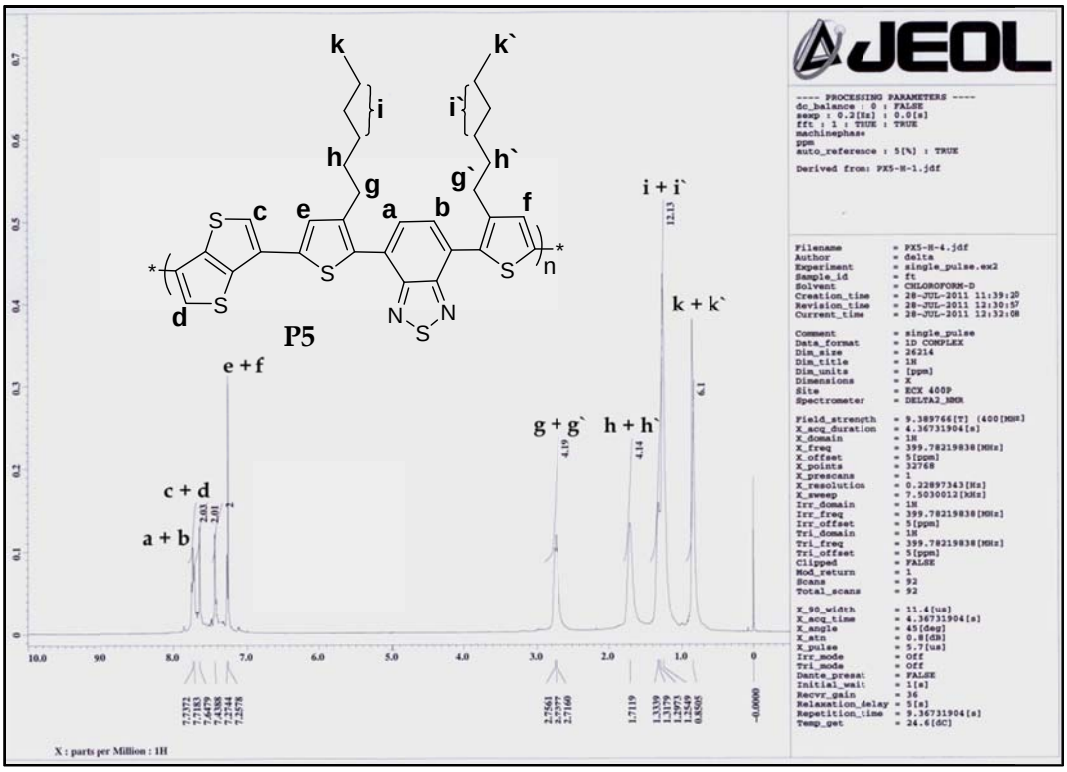


Figure S12. ^{1}H NMR (400 MHz) spectrum of copolymer **P6** in $CDCl_3$

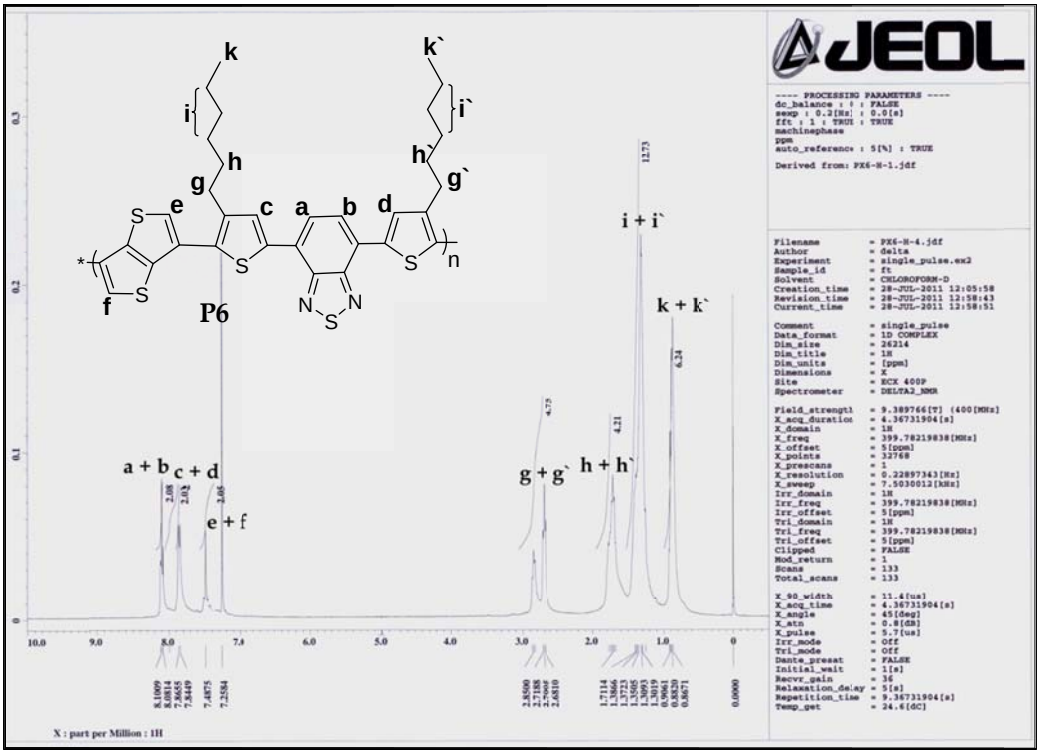


Figure S13. ^{1}H NMR (400 MHz) spectrum of copolymer **P7** in $CDCl_3$

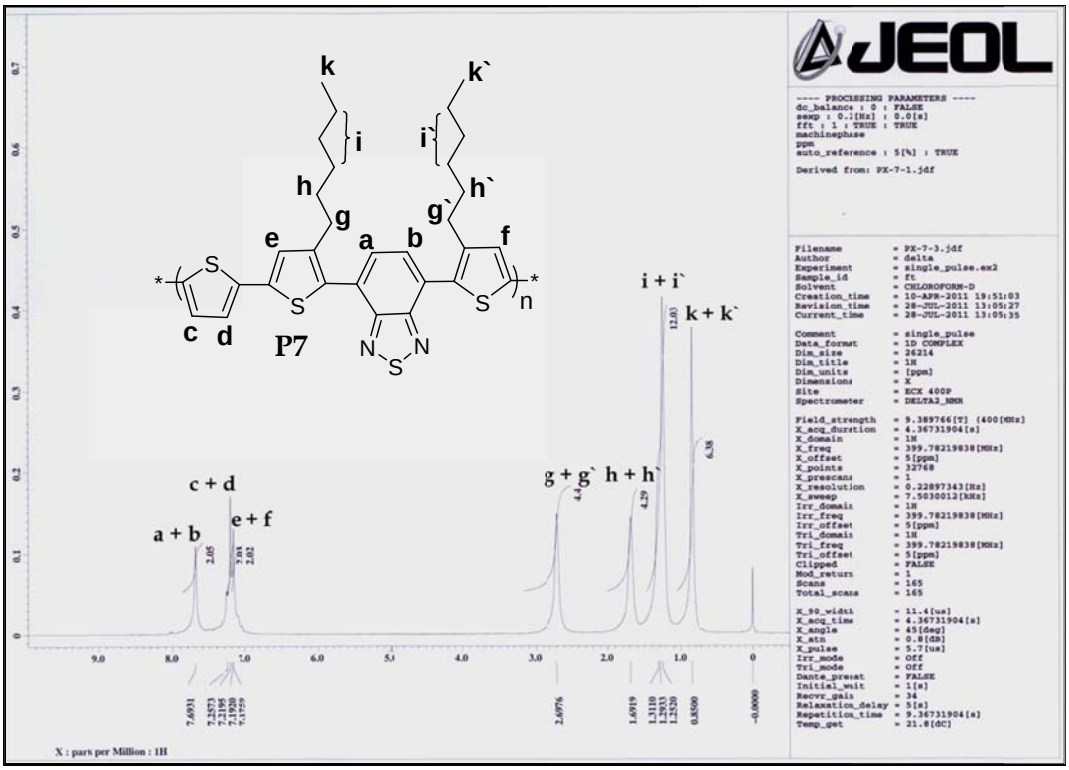


Figure S14. ^{1}H NMR (400 MHz) spectrum of copolymer **P8** in $CDCl_3$

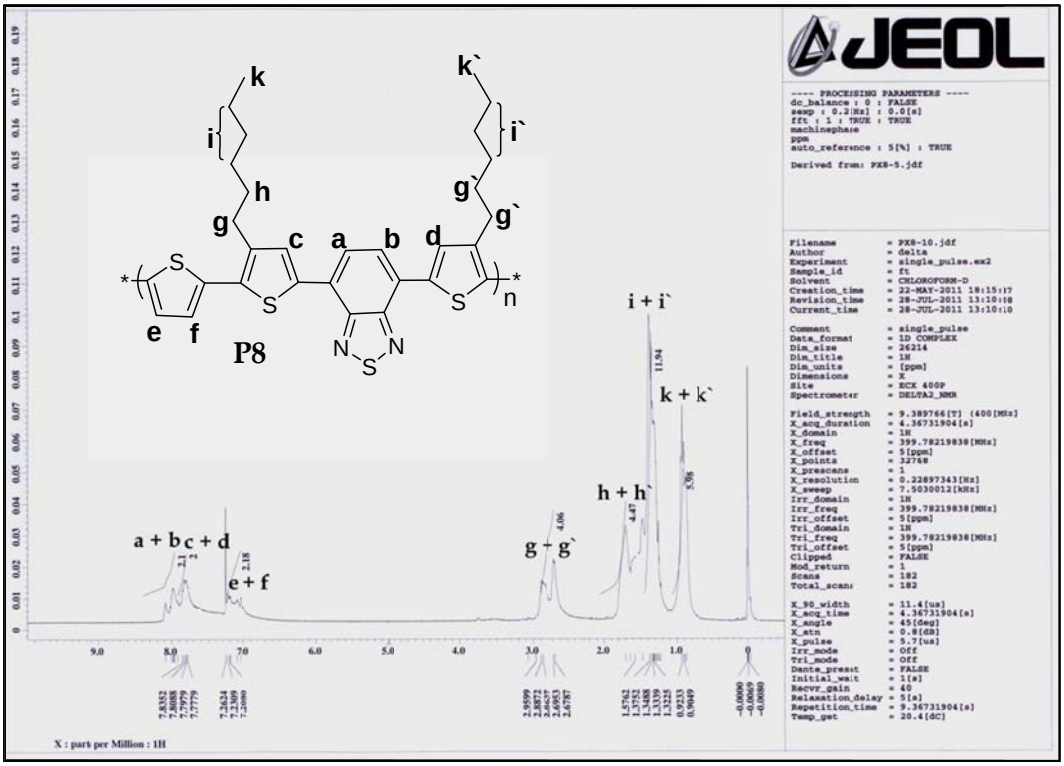


Figure S15. ^{1}H NMR (400 MHz) spectrum of copolymer **P9** in $CDCl_3$

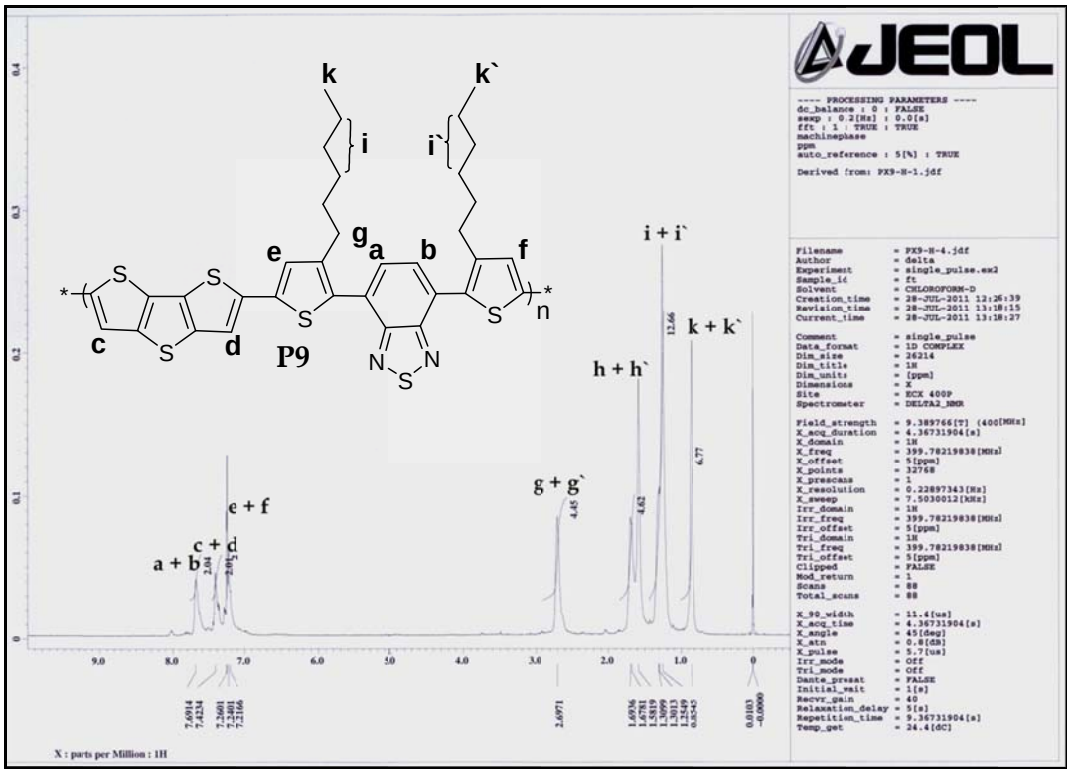
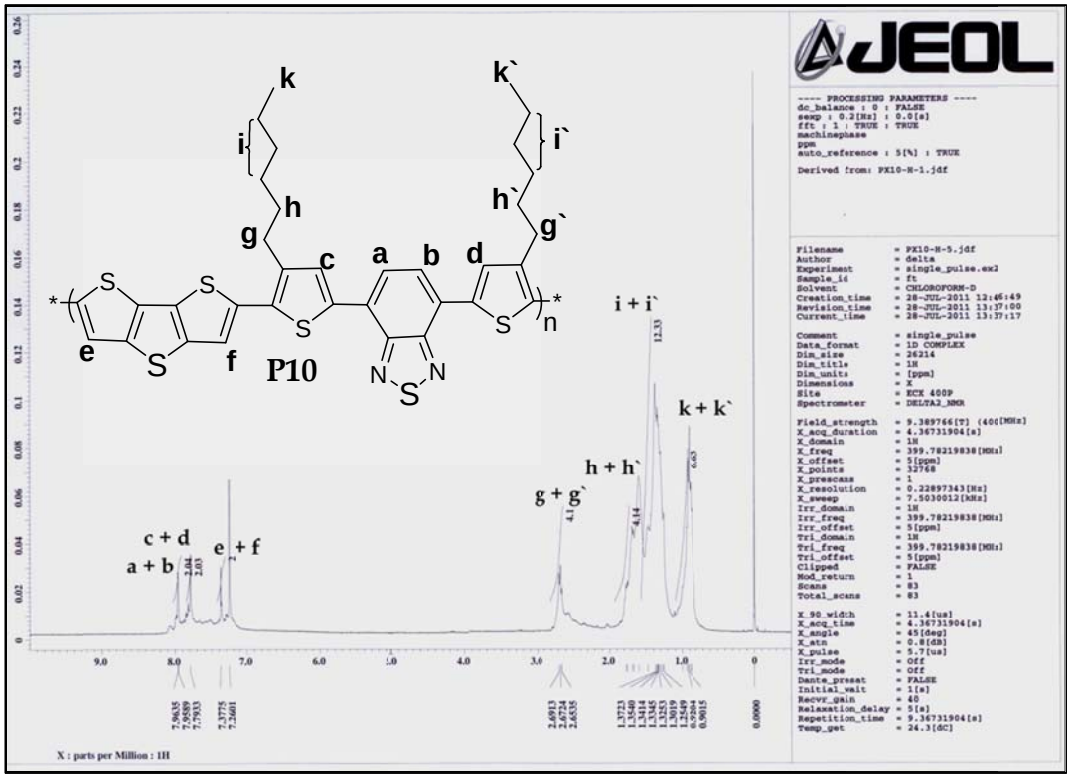


Figure S16. ^{1}H NMR (400 MHz) spectrum of copolymer **P10** in $CDCl_3$



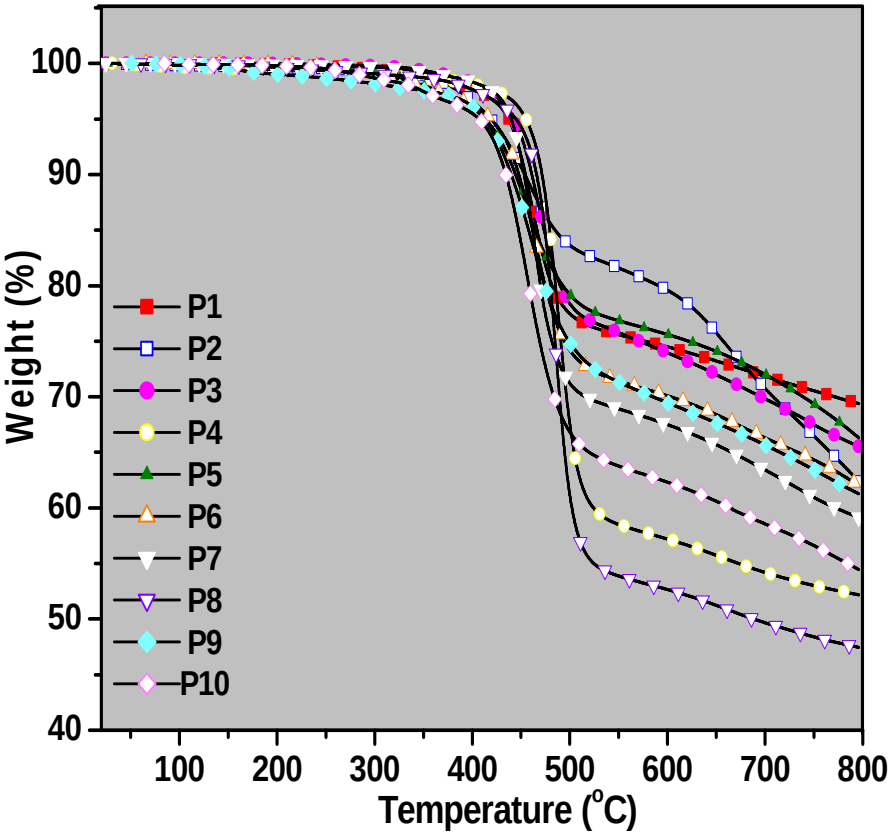


Figure S17. TGA thermograms of copolymers **P1**-**P10**.

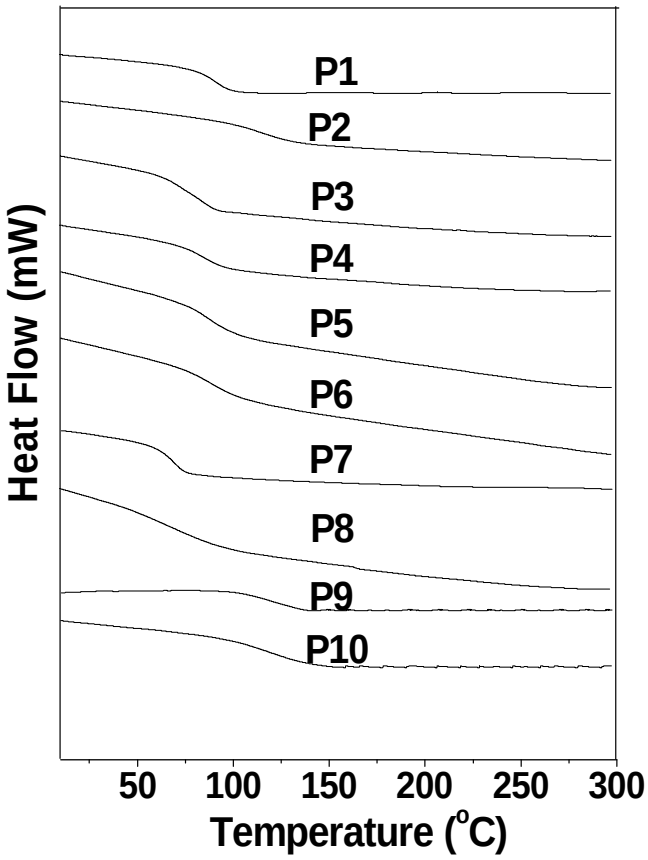


Figure S18. DSC curves of copolymers **P1-P10**.

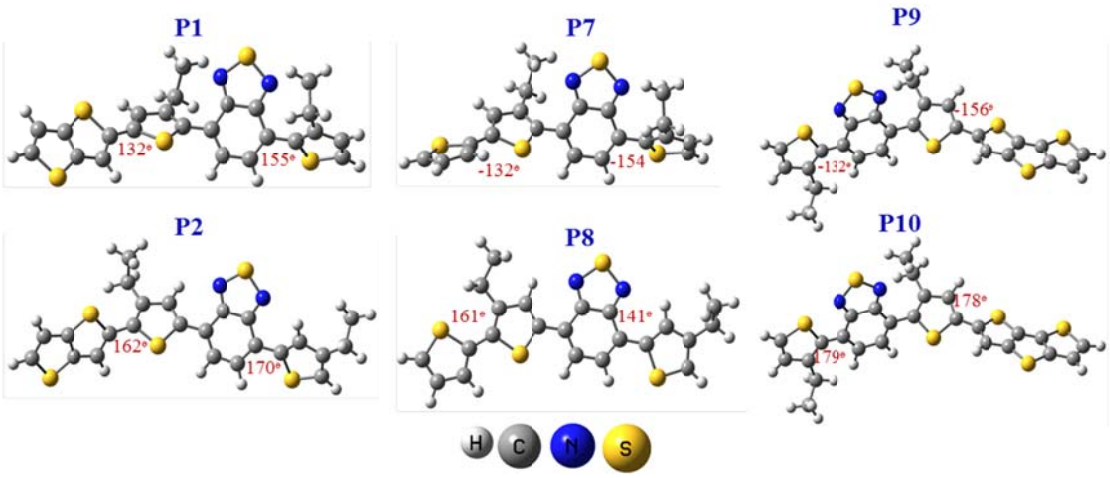


Figure S19. B3LYP/6-311++G(d,p) optimized structures of **P1, P2, P7, P8, P9** and **P10** copolymers.

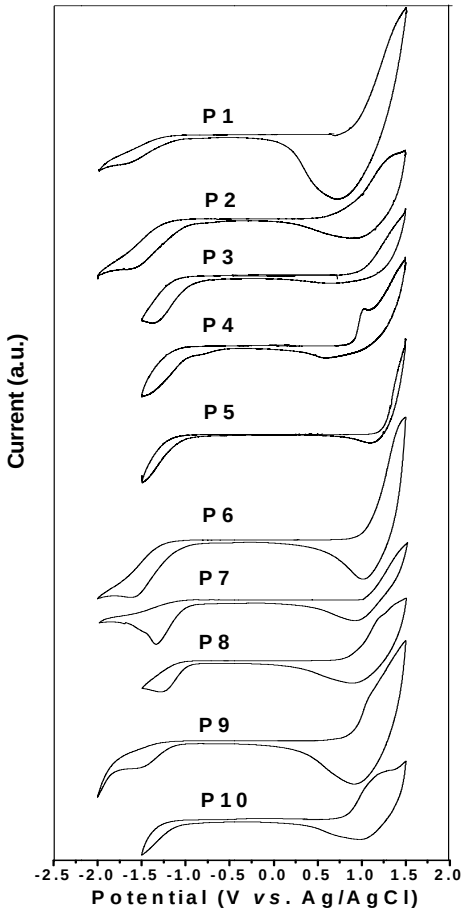


Figure S20. Cyclic voltammograms of copolymers **P1-P10**.

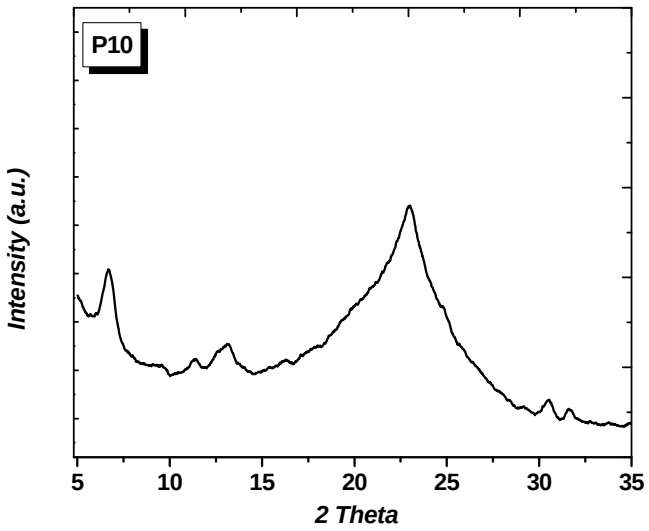


Figure S21. XRD of copolymer **P10** (poly HT–BzT–HT–*co*–DTT) thin film.