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Supplementary Information for article:

Selenophene *vs.* Thiophene in Benzothiadiazole–Based Low Energy Gap Donor Acceptor Polymers for Photovoltaic Applications

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Preparation of monomers and polymers

All reactions were carried out under inert nitrogen or argon atmosphere.

4,7-Di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole

A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (1.39 g, 4.73 mmol) and tributyl (selenophen-2-yl)stannane (4.97 g, 11.83 mmol) was degassed under Ar before a dry THF (40 ml) was added. The resulting solution was degassed under Ar before a mixture of Pd_2dba_3 (173.07 mg, 0.189 mmol) and tri-o-tolylphosphine (460.21 mg, 1.512 mmol) was added. The reaction mixture was degassed and heated to 75 °C overnight. Then the reaction cooled and the solvent was removed in vacuo, then the crude product was purified *via* silica gel column chromatography, eluting with (CH_2Cl_2/hexane, 1:1). Finally the product was recrystallized from (ethanol/toluene, 9:1) to obtain pure 4,7-di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole as a red solid (1.30 g, 70 % yield). The product gave a single spot on TLC (Rf = 0.66) in CH_2Cl_2/hexane (1:1). M.p. = 131-135 °C. ^{1}H

NMR ($CDCl_3$): (δ_H/ppm) 8.22 (d, 2H, J = 5.62 Hz); 8.18 (d, 2H, J = 3.84 Hz); 7.90 (s, 2H); 7.47 (t, 2H, J = 4.74). ^{13}C NMR ($CDCl_3$): (δ_C/ppm) 152.51, 144.10, 133.51, 130.16, 128.29, 127.68, 125.17. FT-IR (ATR): (cm^{-1}) 3851.4, 3099.3, 3050.7, 3012.3, 2846.3, 2459.98, 2122.7, 1878.9, 1815.2, 1726.3, 1656.1, 1587.5, 1531.6, 1515.3, 1480.2, 1426.5, 1359.1, 1315.8, 1272.1, 1237, 1222.4, 1201.4, 1086, 1061, 1044.5, 908.1, 874.7, 849.4, 826.1, 838.4, 789.9, 712.2. Mass (EI+): (m/z) 392, 394, 396 ($M^{\bullet+}$). Anal. calcd. for $C_{14}H_8N_2SSe_2$: C, 42.65; H, 2.05; N, 7.11; S, 8.13. Found: C, 42.47; H, 1.72; N, 6.97; S, 10.22.

4,7-Bis(5-bromoselenophen-2-yl)benzo[c][1,2,5]thiadiazole ***2c***

A mixture of 4,7-di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole (0.208 g, 0.528 mmol), NBS (0.180 g, 1.011 mmol) and chloroform (10 ml) was stirred in dark for 36 hours at room temperature. A further amount of chloroform (5 ml) was added and the mixture stirred for one hour. The formed precipitate was filtered then washed with water (150 ml), ethanol (150 ml), acetone (150 ml) and diethyl ether (150 ml) to obtain 4,7-bis(5-bromoselenophen-2-yl)benzo[c][1,2,5]thiadiazole **2c** as a dark red powder (0.236 g, 81.1 % yield). M.p. = 226 - 231 °C. ^{1}H NMR ($CDCl_3$): (δ_H/ppm) 7.90 (s, 2H); 7.82 (d, 2H, J = 4.28 Hz); 7.39 (d, 2H, J = 4.28 Hz). FT-IR (ATR): (cm^{-1}) 3064.6, 2227.9, 2127.2, 1873.6, 1743.2, 1669, 1574.3, 1537.7, 1523.2, 1481.7, 1727.5, 1363.3, 1349.2, 1298.5, 1269.5, 1230, 1217.9, 1207.1, 1093.1, 1058.4, 1047.4, 930.2, 898.7, 867.1, 833.6, 785.42, 721.1, 674.9. Mass (EI+): (m/z) 549, 550, 551, **552**, 553, 554, 555 ($M^{\bullet+}$). Anal. Calcd. for $C_{14}H_6Br_2N_2SSe_2$: C, 30.46; H, 1.10; N, 5.07; Br, 28.95; S, 5.81. Found: C, 30.54; H, 0.94; N, 5.02; Br, 28.90; S, 5.85.

5,6-Bis-(octyloxy)-4,7-di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole

A mixture of 4,7-dibromo-5,6-bis-(octyloxy)-benzo[c][1,2,5]thiadiazole (1.82 g, 3.3067 mmol) and 2-trimethyltin selenophene (2.9 g, 9.8693 mmol) in toluene (8 ml) in a single-necked flask was degassed. Pd(OAc)$_2$ (20.0 mg, 8.91 × 10^{-2} mmol) and tri(o-tolyl)phosphine (54.23 mg, 0.178 mmol) were then added to the solution followed by degassing and heating the mixture to 100 ^{o}C for 72 hours. The mixture was cooled to room temperature and diethyl ether (100 ml) and water (100 ml) was added. The organic phase was separated and the water phase was washed with diethyl ether (2 ×100 ml). The combined organic phase was washed with brine (100 ml) and then water (100 ml), dried over $MgSO_4$ and the solvent evaporated to afford the crude product. The product was purified by column chromatography: the column was prepared using 0.5% triethylamine solution in petroleum and eluted with 2% triethylamine solution in petroleum ether, (R_f = *0.24*). The product was obtained as a red solid. (2.0 g, 93% yield). M.p. = 77-81 °C. ^{1}H NMR ($CDCl_3$): (δ_H/ppm) 8.88 (d, 2H, J = 4.04 Hz); 8.24 (d, 2H, J = 5.8 Hz); 7.51 (t, 2H, J = 4.94 Hz); 4.16 (t, 4H, J = 7.24 Hz); 2.02-1.91 (m, 4H); 1.51-1.28 (m, 20H); 0.92 (t, 6H, J = 3.72 Hz). Mass (EI+): (m/z) 648, 650, 652 ($M^{\bullet+}$).

4,7-Bis(5-bromoselenophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5] thiadiazole ***2d***

A mixture of 5,6-bis-(octyloxy)-4,7-di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole (0.6005 g, 0.923 mmol) and NBS (0.3367 g, 1.892 mmol) in dry chloroform (15 ml) was degassed under Ar, before stirring in the dark for 36 hours at room temperature. The solvent was then removed in vacuo and the crude product was purified *via* silica gel column chromatography, eluting with (hexane/CH_2Cl_2/triethylamine; 90/9/2) to obtain the product **2d** as a red crystals (0.425 g, 56.96 % yield). The product gave a single spot on TLC (Rf = 0.40) in CH_2Cl_2/hexane (1:10). M.p. = 193-196 °C. ^{1}H NMR ($CDCl_3$): (δ_H/ppm) 8.69 (d, 2H, J = 4.44 Hz); 7.42 (d, 2H, J = 4.4 Hz); 4.17 (t, 4H, J = 7.36 Hz); 2.03 – 1.95

(m, 4H); 1.49 – 1.32 (m, 20H); 0.92 (t, 6H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$): (δ_C/ppm) 151.04, 150.11, 140.03, 133.11, 132.80, 120.09, 118.70, 74.77, 31.81, 30.52, 29.47, 29.27, 25.86, 22.67, 14.11. FT-IR (ATR): (cm^{-1}) 2954.2, 2851.1, 2921.6, 2159.4, 2014.4, 1556.7, 1494.5, 1466.1, 1437.8, 1426.2, 1392.1, 1375.6, 1347.6, 1281.5, 1213.5, 1176.5, 1090.8, 1056.8, 1016.6, 953.7, 938.4, 920.9, 894.8, 883.6, 855.5, 830.4, 757.7, 745.5, 722.5, 675.3, 650.1, 633.2. TOF MS (ES+): (m/z) 804.94, 805.94, 806.94, 808.94, 810.94 and 812.93; Anal. Calcd for $C_{30}H_{38}Br_2N_2O_2SSe$: C, 44.57; H, 4.74; N, 3.47; Br, 19.77; S, 3.97. Found: C, 44.57; H, 4.68; N, 3.42; Br, 19.82; S, 5.86.

Poly[9-(1-octyl-nonyl)-9H-carbazole-2,7-diyl-alt-(4',7'-di-2-selenophenyl-2',1',3'-benzothiadiazole)-5,5-diyl] ***PCDSeBT***

A 100-ml one-necked flask under argon containing 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**1a**) (281 mg, 0.427 mmol) and 4,7-bis(5-bromoselenophen-2-yl)-benzo[c][1,2,5]thiadiazole (**2c**) (236 mg, 0.427 mmol) in dry toluene (15 ml) was degassed. To the mixture was added tetraethylammonium hydroxide solution (5 ml) followed by degassing. Then $Pd(OAc)_2$ (7 mg, 0.0312 mmol) and tri(*o*-tolyl)phosphine (20 mg, 0.0657 mmol) were added and the system was degassed under argon and heated to 95 °C for 24 hours. The mixture was cooled to room temperature and another portion of toluene (15 ml) was added, degassed and then bromobenzene (0.1 ml) was added, degassed and heated to 95 °C for 1 hour. Again, the mixture was cooled to room temperature and phenylboronic acid (120 mg) was added, degassed and heated to 95 °C for 3 hours. After cooling to room temperature, the mixture was dissolved in $CHCl_3$ (400 ml) and to this solution, an ammonium hydroxide solution (28% in H_2O, 50 ml) was added and then stirred overnight. The organic phase was separated and washed with distilled water, concentrated to approximately 50 ml and poured into degassed methanol/water (10:1, 400 ml). The resulting mixture was then stirred overnight and filtered through a membrane filter. The collected solid was cleaned using a Soxhlet extraction with solvents in order methanol, acetone, hexane, toluene and chloroform. The toluene and chloroform fractions were concentrated to approximately 50 ml and then poured into degassed methanol (400 ml), the resulting mixtures were left to stir overnight and the solids from the two fractions were collected by filtration through a membrane filter. Both of the fractions afforded the polymer as a dark purple powder. Toluene fraction (101.9 mg, 30.0 % yield), GPC (1,2,4-trichlorobenzene at 100 °C): M_w = 9400, M_n = 3900, PD = 2.43. Chloroform fraction (114.2 mg, 34 % yield), GPC (1,2,4-trichlorobenzene at 100 °C): M_w = 13700, M_n = 5500, PD = 2.48. (216 mg, 63.5 % yield in total including the toluene and chloroform fractions). Anal. Calcd for $C_{43}H_{47}N_3SSe_2$: C, 64.90; H, 5.95; N, 5.28; Br, 0. Found: C, 62.18; H, 6.52; N, 4.29, Br, 0. ^1H NMR ($C_2D_2Cl_4$): (δ_H / ppm) 8.31 (bm, 2H); 8.25 (bm, 2H); 8.14 (bm, 2H); 7.97 (bm, 2H); 7.73 (bm, 2H); 7.63 (bm, 2H); 4.74 (br, 1H); 2.46 (bm, 2H), 2.15 (bm, 2H); 1.52 – 1.28 (bm, 22H); 0.95 (bm, 2H); 0.89 (t, 6H). FT-IR (ATR): (cm^{-1}) 3056.65, 2921.8, 2851.6, 2160.4, 2013.2, 1620.7, 1597.1, 1561.4, 1486.6, 1446.7, 1429.4, 1333.3, 1258.7, 1214.1, 1081.9, 1014.3, 870.4, 791.5, 766.4, 721.3, 696.7, 686.9, 661.2, 638.7, 618.2.

Poly[9,9-dioctyl-9H-fluorene-2,7-diyl-alt-(4',7'-di-2-selenophenyl-2',1',3'-benzothiadiazole)-5,5-diyl] ***PFDSeBT***

A mixture of 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (**1b**) (224 mg, 0.401 mmol) and 4,7-bis(5-bromoselenophen-2-yl)-benzo[c][1,2,5] thiadiazole (**2c**) (221.3 mg, 0.401 mmol) in THF (12 ml) was degassed. To the mixture was added a saturated solution of $NaHCO_3$ (1.2 ml, degassed) under inert atmosphere. Then $Pd(OAc)_2$ (5.3 mg, 0.0238 mmol) and tri(*o*-tolyl)phosphine (14.9 mg, 0.0489 mmol) were added and the system was degassed and heated to 90 °C for 3 hours. The mixture was cooled to room temperature and another portion of THF (12 ml) was added, degassed and then bromobenzene (0.1 ml) was added, degassed and heated to 90 °C for 1 hour. Again, the mixture was cooled to room temperature and phenylboronic acid (120 mg) was added, degassed and heated to 90 °C for 3 hours. After cooling to room temperature, the mixture was dissolved in $CHCl_3$ (300 ml) and to this solution, an ammonium hydroxide solution (28% in H_2O, 50 ml) was added and stirred overnight. Then the organic phase was separated and washed with distilled water, concentrated to approximately 50 ml and poured into degassed methanol/water (10:1, 300 ml). The resulting mixture was then stirred overnight and filtered through a membrane filter. The collected solid was cleaned and separated by Soxhlet extraction with solvents in order methanol, acetone, hexane, toluene, chloroform and chlorobenzene. The toluene, chloroform and chlorobenzene fractions were concentrated to approximately 50 ml and then poured into degassed methanol (500 ml), the resulting mixtures were stirred overnight and the solids were collected separately by filtration through membrane filters. All the fractions were dark purple powders. Toluene fraction (87.4 mg, 27.9 % yield), GPC (1,2,4-trichlorobenzene at 100 ˚C): $M_w = 4600$, $M_n = 1900$, PD = 2.40. Chloroform fraction (99.9 mg, 31.89 % yield), GPC (1,2,4-trichlorobenzene at 100 ˚C): $M_w = 17100$, $M_n = 6900$, PD = 2.49. Chlorobenzene fraction (40.3 mg, 12.86 % yield), GPC (1,2,4-trichlorobenzene at 100 ˚C): $M_w = 30600$, $M_n = 13200$, PD = 2.31; (227.6 mg, 72.65 % yield in total including the toluene, chloroform and chlorobenzene fractions). Anal. Calcd for $C_{43}H_{46}N_2SSe_2$:

C, 66.14; H, 5.94; N, 3.59; Br, 0. Found: C, 48.86; H, 7.22; N, 1.69, Br, 0. ^{1}H NMR ($C_2D_2Cl_4$ at 100 °C): (δ_H / ppm) 8.27 (bm, 2H); 7.97 (bm, 2H); 7.80-7.52 (br, 6H); 7.44-7.21 (bm, 2H); 2.14 (bm, 4H); 1.52 (bm, 2H); 1.36-1.23 (bm, 20H); 0.97 (bm, 2H); 0.90 (t, 6H). FT-IR (ATR): (cm^{-1}) 3052.3, 2922.5, 2850.9, 2172.9, 1605.2, 1575.8, 1541.9, 1486.2, 1449.5, 1415.2, 1360.6, 1258.7, 1205, 1086.2, 1014.6, 907.9, 871.4, 795.2, 754.1, 684.9, 661.1, 618.9, 639.1, 554.6.

Poly[9,9-dioctyl-9H-fluorene-2,7-diyl-alt-(4,7-di-2thiophen-2-yl)-2',1',3'-benzothiadiazole-5,5-diyl] ***PFDTBT***

9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (**1b**) (152.4 mg, 0.273 mmol) and 4,7-bis(5-bromothiophen-2-yl)-benzo[c][1,2,5]thiadiazole (**2e**) (125 mg, 0.273 mmol) were introduced to a two-necked flask under argon. To the mixture was added toluene (5 ml) and the mixture was degassed. Then 20 wt% tetraethyl ammonium hydroxide (1.3 ml, 1.76mmol), previously degassed was added. To this mixture was added $Pd(OAc)_2$ (1.5 mg, 6.6 × 10^{-3} mmol), tri(*o*-tolyl)phosphine (4 mg, 0.0132 mmol) under an inert argon atmosphere and it was heated to 95 °C overnight. The mixture was cooled to room temperature and bromobenzene (0.1 ml, 0.147 g; 0.936 mmol) was added. It was then degassed and heated to 90 °C for 1 h. The mixture was cooled to room temperature and phenylboronic acid (0.120 g; 0.984 mmol) was added. The mixture was degassed and heated to 90 °C for 3 h. After cooling to room temperature, $CHCl_3$ (200 ml) was added to solubilize the polymer. An ammonium hydroxide solution (28% in H_2O, 50 ml) was then added and the mixture was stirred overnight. The organic phase was separated and washed with distilled water (2 × 100 ml). It was then concentrated to about 50 ml in volume and poured into a degassed methanol/water mixture (10:1, v;v, 300 ml). The resulting mixture was then stirred overnight and filtered through a membrane filter. The collected solid was cleaned using a Soxhlet extraction under an inert atmosphere with methanol, acetone, hexane, toluene and chloroform. The toluene and chloroform fractions were concentrated to about 50 ml and then poured into methanol (200 ml). The resulting mixtures were stirred overnight and the solids collected by filtration to afford the two polymer fractions as purple powders. Toluene fraction (37 mg, 19 % yield), GPC (1,2,4-trichlorobenzene at 100 ˚C): M_n = 5300, M_w = 7300, PD = 1.38. Chloroform fraction (71 mg, 37 % yield), GPC (1,2,4-trichlorobenzene at 100 ˚C): M_n = 15100, M_w = 23800, PD = 1.57. Anal. Calcd. for $C_{43}H_{46}N_2S_3$: C, 75.17; H, 6.75; N, 4.08. Found: C, 73.50; H, 6.06; N, 4.44. ^{1}H NMR ($C_2D_2Cl_4$ at 100 °C): (δ_H / ppm) 8.2 (bs, Ar-H), 8.01 (bs, Ar-H), 7.8 (m, Ar-H), 7.6 (bs, Ar-H), 2.12 (bm, CH_2), 1.52 (bm, CH_2), 1.24–1.28 (bm, CH_2), 0.91 ppm (bm, CH_3).

Poly[9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl-alt-(5,6-bis(octyloxy)-4,7-di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole-5,5-diyl] ***PCDSeBT-8***

A mixture of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**1a**) (105.7 mg, 0.161 mmol) and 4,7-bis(5-bromoselenophen-2-yl)-5,6-bis-(octyloxy)-benzo[c][1,2,5]thiadiazole (**2d**) (130 mg, 0.161 mmol) in THF (4 ml) was degassed. To the mixture was added a saturated solution of $NaHCO_3$ (1 ml, degassed) under inert conditions, then $Pd(OAc)_2$ (2.5 mg, 0.0111 mmol) and tri(*o*-tolyl)phosphine (7 mg, 0.0229 mmol) were added and the system was degassed under argon and heated to 90 °C. A precipitate formed after 2 hours at 90 °C. The mixture was cooled to room temperature and another portion of THF (5 ml) was added, the mixture was then degassed and heated to 90 °C for a further 2 hours, followed by cooling down, adding another portion of THF (4 ml) and then bromobenzene (0.1 ml) and heating to 90 °C for 1 hour. Again, the mixture was cooled to room temperature and phenylboronic acid (50 mg) was added, the mixture degassed and heated to 90 °C for 3 hours. After cooling to room temperature, the mixture was dissolved in $CHCl_3$ (200 ml) and to this solution was added an ammonium hydroxide solution (28% in H_2O, 50 ml) then the mixture was stirred overnight. The organic phase was separated and washed with distilled water, concentrated to approximately 40 ml and poured into degassed methanol/water (10:1, 300 ml). The resulting mixture was then stirred overnight and filtered through a membrane filter. The collected solid was cleaned and fractionated using Soxhlet extraction with solvents in order methanol, acetone, hexane and toluene. The toluene fraction was concentrated to approximately 50 ml and then poured into methanol (300 ml). The resulting mixture was stirred overnight and the solid was collected by filtration through a membrane filter to afford the polymer as a dark red powder (101.0 mg, 60.0 % yield). GPC (1,2,4-trichlorobenzene at 100 ˚C): M_n = 26000, M_w = 62900, PD = 2.41. Anal. Calcd. for $C_{59}H_{79}N_3O_2SSe_2$: C, 67.34; H, 7.57; N, 3.99; Br, 0. Found: C, 53.97; H, 8.08; N, 2.42; no detectable Br. ^{1}H NMR ($C_2D_2Cl_4$): (δ_H / ppm) 8.92 (bm, 2H); 8.19 (bm, 2H); 7.87 (bm, 2H); 7.79 (bm, 2H); 7.65 (bm, 2H); 4.75 (bm, 1H); 4.37 (bm, 4H); 2.49 (bm, 2H); 2.15 (bm, 4H); 1.63 (bm, 4H); 1.50-1.36 (bm, 24H); 1.36-1.11 (bm, 18H); 0.99 (t, 6H); 0.90 (t, 6H). FT-IR (ATR): (cm^{-1}) 2922.4, 2852.6, 2185.5, 1598, 1560.3, 1445.3, 1411.8, 1375.8, 1336.61, 1282.1, 1259.5, 1218.9, 1171.8, 1073.8, 1016.1, 891.7, 852.5, 794.4, 722.1, 682.4, 487.2.

Poly[9,9-dioctyl-9H-fluorene-2,7-diyl-alt-(5,6-bis(octyloxy)-4,7-di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole-5,5-diyl] ***PFDSeBT-8***

A mixture of 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (**1b**) (103.6 mg, 0.186 mmol) and 4,7-bis(5-bromoselenophen-2-yl)-5,6-bis-

(octyloxy)-benzo[c][1,2,5]thiadiazole (**2d**) (150 mg, 0.186 mmol) in dry THF (5.5 ml) was degassed. To the mixture was added a saturated solution of $NaHCO_3$ (1.2 ml, degassed). Then $Pd(OAc)_2$ (2.9 mg, 0.0129 mmol) and tri(*o*-tolyl)phosphine (8.1 mg, 0.0266 mmol) were added, the system was degassed and heated to 90 °C. A precipitate formed after 3 hours at this temperature. The mixture was then cooled to room temperature and another portion of THF (5 ml) was added, degassed and then heated to 90 °C overnight. The mixture was cooled to room temperature and another portion of THF (5 ml) was added, degassed and then bromobenzene (0.1 ml) was added, degassed and heated to 90 °C for 1 hour. Again, the mixture was cooled to room temperature and phenylboronic acid (60 mg) was added, degassed and heated to 90 °C for 3 hours. After cooling to room temperature, the mixture was dissolved in $CHCl_3$ (200 ml) and to this solution was added an ammonium hydroxide solution (28% in H_2O, 50 ml) and the mixture was stirred overnight. Then the organic phase was separated and washed with distilled water, concentrated to approximately 40 ml and poured into degassed methanol/water (10:1, 300 ml). The resulting mixture was then stirred overnight and filtered through a membrane filter. The collected solid was cleaned using a Soxhlet extraction with solvents in order methanol, acetone, hexane and toluene (250 ml). The toluene fraction was concentrated to approximately 50 ml and then poured into degassed methanol (300 ml). The resulting mixture was stirred overnight and the solid collected by filtration through a membrane filter. The fraction provided the polymer as a dark red powder (142.8 mg, 74.0 % yield). GPC (1,2,4-trichlorobenzene at 100 °C): $M_n = 54200$, $M_w = 126000$, PD = 2.33. Anal. calcd for $C_{59}H_{78}N_2O_2SSe_2$: C, 68.32; H, 7.58; N, 2.70; Br, 0. Found: C, 50.83; H, 7.49; N, 1.41; no detectable Br. ^1H NMR ($C_2D_2Cl_4$): (δ_H / ppm) 8.91 (bm, 2H);

7.89-7.59 (bm, 8H); 4.36 (bm, 4H); 2.15 (bm, 8H); 1.63 (bm, 4H); 1.54-1.37 (bm, 20H); 1.36-1.19 (bm, 20H); 1.00 (t, 6H); 0.90 (t, 6H). FT-IR (ATR): (cm^{-1}) 2961, 2924.9, 2853.9, 1459.6, 1413.3, 1376.9, 1258.6, 1076.7, 1011.2, 863.5, 702.8, 790.8, 702.8.

Poly[9,9-dioctyl-9H-fluorene-2,7-diyl-alt-(5,6-bis-(octyloxy)-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)-5,5-diyl] ***PFDTBT-8***

To a mixture of 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (**1b**) (425.6 mg, 0.7622 mmol) and 4,7-bis-(5-bromothiophen-2-yl)-5,6-bis-(octyloxy)-benzo[c][1,2,5]thiadiazole (**2f**) (544.5 mg, 0.7622 mmol) in THF (12 ml) was added a saturated solution of $NaHCO_3$ (2.5 ml, degassed) under inert atmosphere. $Pd(OAc)_2$ (7.3 mg), tri(*o*-tolyl)phosphine (19.8 mg) were then added and the mixture was degassed and heated to 90 °C. A precipitate formed in the first hour of the reaction. The mixture was cooled to room temperature and another portion of THF (12 ml) was added, degassed and then heated to 90 °C for 24 hours. The mixture was cooled to room temperature and THF (12 ml) and bromobenzene (0.1 ml) were added. The mixture was degassed and heated 90 °C for 1 hour. Again, the mixture was cooled to room temperature and phenylboronic acid (120 mg) was added, degassed and heated to 90 °C for 3 hours. After cooling to room temperature, the mixture was dissolved in $CHCl_3$ (200 ml) and to this solution, an ammonium hydroxide solution (28% in H_2O, 50 ml) was added and stirred overnight. The organic phase was separated and washed with distilled water, concentrated to about 50 ml and poured into methanol/water (10:1, 300 ml). The resulting mixture was then stirred overnight and filtered through a membrane filter. The collected solid was cleaned using Soxhlet extraction with solvents in order methanol, acetone, hexane, toluene and chloroform. Each of the toluene and chloroform fractions were concentrated to about 50 ml and then poured separately into degassed methanol (200 ml). The resulting mixtures were stirred overnight and the solids were collected by filtration. The toluene fraction was obtained as a red fibrous solid (558 mg). The chloroform fraction was a dark red fibrous solid (101 mg). Toluene fraction (558 mg, 77.7 % yield), GPC (1,2,4-trichlorobenzene at 100 ˚C): M_n = 33200, M_w = 348900, PD = 10.5. Chloroform fraction (71 mg, 14 % yield), GPC (1,2,4-trichlorobenzene at 100 ˚C): M_n = 78400, M_w = 468671, PD = 5.98. ^{1}H NMR ($CDCl_3$): δ = 8.61 (br, 2H), 7.76 (d, 6H), 7.58 (br, 2H), 4.26 (br, 4H), 2.09 (br, 8H), 1.58 (br, 4H), 1.36 (br, 16H), 1.16 (br, 24H), 0.88 (t, 6H), 0.78 (t, 6H); ^{13}C NMR ($CDCl_3$): δ = 151.82, 151.00, 146.39, 140.46, 133.49, 132.00, 124.92, 122.97, 120.17, 120.05, 117.55, 74.54, 55.3640.56, 31.88, 31.79, 30.60, 30.11, 29.69, 29.37, 29.26, 26.15, 23.87, 22.70, 22.59, 14.12, 14.05. Anal. Calcd. for $C_{59}H_{78}N_2O_2S_3$, C 75.11, H 8.33, N 2.97; Found C 74.76, H 8.37, N 2.69.

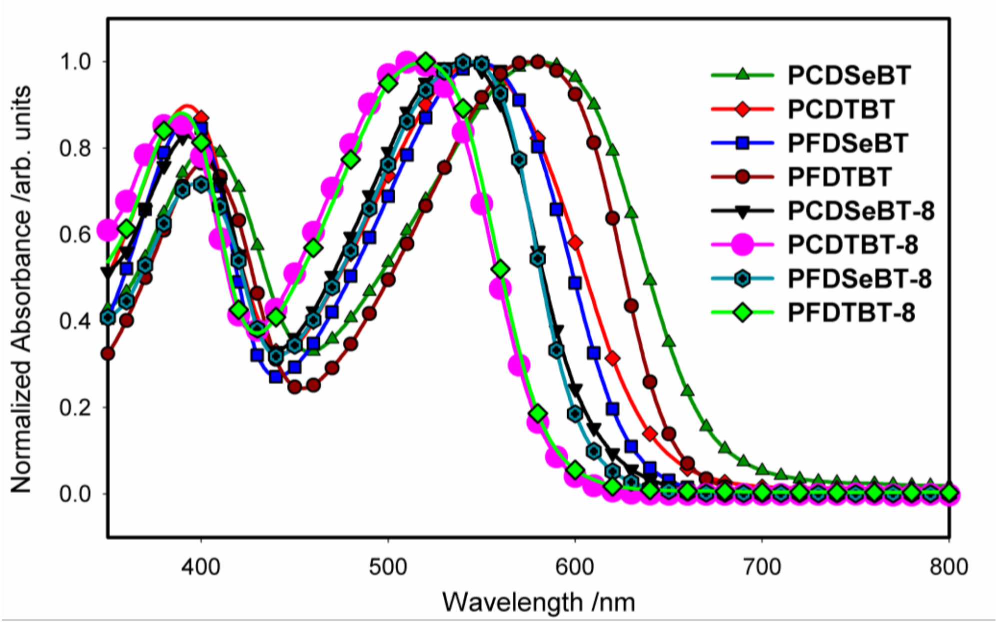

Figure S1. UV-Vis spectra of polymers in chloroform solutions.