

SUPPORTING INFORMATION PARAGRAPH

Substituent Effect on the Optoelectronic Properties of Alternating Fluorene-Thiophene Copolymers

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Experimental methods, characterization data and ¹H NMR and ¹³C NMR spectra for monomers, and TGA, DSC data for all polymers are described below.

Materials. Fluorene, thiophene, 3-thiophenecarboxaldehyde, 3-cyanothiophene and 2,5-dibromothiophene (6) were obtained from Aldrich Chemical Co.

9,9-Dihexylfluorene.¹ To a solution of 5.0 gm (30.1 mmol) of fluorene in THF (60 ml) at -78°C was added dropwise, 25 ml (62.5 mmol) of n-butyllithium (2.5 M in hexane). The mixture was stirred at -78°C for 1 h, and 11.5 gm (70 mmol) of 1-bromohexane in THF (15 ml) was added dropwise to the mixture. The solution was allowed to warm to room temperature and was stirred for overnight. The mixture was poured into water and extracted with ether (3 X 30 ml). The organic layer was washed with brine solution and dried over anhydrous MgSO₄. The solvent was removed by reduced pressure and excess 1-bromohexane was removed by distillation and obtained yellow viscous oil (9.72 gm, yield 97%).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.71-7.68 (m, 2H), 7.35-7.27 (m, 6H), 1.98-1.92 (m, 4H), 1.07-1.00 (m, 12H), 0.76 (t, *J* = 7.0 Hz, 6H), 0.62 (m, 4H).

2,7-Dibromo-9,9-dihexylfluorene.¹ To a solution of 9,9-dihexylfluorene (5.01 gm, 15 mmol) in CHCl₃ (30 ml) at 0°C were added 36 mg (0.22 mmol) of FeCl₃ and 1.8 ml (35 mmol) of bromine dropwise. The solution was warmed to room temperature and was stirred for 3 h in the dark place. The resulting slurry was poured into water and washed with sodium thiosulphate until the red color disappeared. The aqueous layer was extracted with CHCl₃ (3 X 20 ml), and the combine organic layer was dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure to afford the title compound as a white solid (7.3 gm, yield 99%).

M.P. 65-66°C, ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.46 (brs, 2H), 7.44 (brd, 2H), 1.92 (t, *J* = 4.1 Hz, 4H), 1.15-1.00 (m, 12H), 0.78 (t, *J* = 7.1 Hz, 6H), 0.59 (m, 4H). MS (EI), *m/e*: 492 (M⁺, 100%).

9,9-Dihexyl-2,7-diboronic acid.² To a solution of 2,7-dibromo-9,9-dihexylfluorene (9.84 g, 20 mmol) in dry THF (100 ml), *n*-BuLi (2.5 M in *n*-hexane, 18 ml, 45 mmol) was added dropwise under Ar atmosphere at -78°C within 20 min. After further stirring for 1 h at this temperature, freshly distilled B(OBu)₃ (13 ml, 48 mmol) was added. The cooling bath was removed and stirring was continued for 12 h at room temperature. The reaction mixture was hydrolyzed with 1 M HCl solution (150 ml) and extracted with ether (3 X 70 ml). The organic layer was dried over anhydrous MgSO₄ and the solvent was removed at reduced pressure. The product was obtained as white solid (7.68 g, 18.2 mmol, 91%). M.P. 179-180°C, ¹H NMR (DMSO, 400 MHz, ppm): δ 8.03 (brd, 2H), 7.84 (s, 2H), 7.76 (brd, 2H), 1.95 (t, *J* = 8.0 Hz, 4H), 1.05-0.92 (m, 12H), 0.70 (t, *J* = 7.0 Hz, 6H), 0.50-0.45 (m, 4H).

9,9-Dihexyl-2,7-bis(trimethylene boronate)³(1). To a solution of 9,9-dihexyl-2,7-diboronic acid (6.31 gm, 15 mmol) in toluene (50 ml) was added 1,3-propanediol (2.04 gm, 33 mmol). The reaction mixture was refluxed at 130°C for 24 h under nitrogen. The mixture was poured into water and extracted with ethylacetate (3 X 30 ml) and dried over anhydrous MgSO₄. The solvent was removed at reduced pressure and the crude product was recrystallized from hexane to afford the title compound as a white

solid (5.72 gm, yield 76%).

M. P. 121-122°C (lit. 123-124°C), ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.69 (s, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 4.18 (t, *J* = 5.4 Hz, 8H), 2.07 (t, *J* = 5.3 Hz, 4H), 1.96 (m, 4H), 1.07-0.93 (m, 12H), 0.71 (t, *J* = 7.1 Hz, 6H), 0.54-0.50 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 150.17 (2XC), 143.46 (2XC), 132.33 (2XC), 127.88 (4XC), 119.28 (2XC), 62.56 (4XC), 55.48, 41.11 (2XC), 32.34 (2XC), 30.59 (2XC), 28.25 (2XC), 24.54 (2XC), 23.50 (2XC), 14.94 (2XC).

3-Hexylthiophene.⁴ The Grignard reagent of 1-bromohexane (30.7 mmol, 1 M in THF) was added dropwise at room temperature to a mixture of 3-bromothiophene (5 gm, 30.7mmol) and 1.2 mol % of [1,3-bis(diphenylphosphino)propane]nickel(II)chloride [Ni(dpp)Cl₂] (35 mg). After stirring at 50°C for 15 h, the THF was removed by distillation under atmospheric pressure. The salts were extracted with hexane which was distilled at 760 mmHg after filtration of the mixture. Distillation of the residue thus obtained the title compound as a colorless liquid (4.08 gm, yield 79%).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.25 (brs, 1H), 6.97-6.92 (m, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.65-1.60 (m, 2H), 1.38-1.28 (m, 6H), 0.94-0.88 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 143.23, 128.26, 124.99, 119.72, 31.69, 30.53, 30.28, 29.37, 22.61, 14.08.

2,5-Dibromo-3-hexylthiophene⁵(2). N-Bromosuccinimide (1.9 gm, 10.5 mmol) was added portionwise to a solution of 3-hexylthiophene (840 mg, 5 mmol) in THF (20 ml) under ice-cold water bath. After 3h stirring, THF was removed under reduced pressure and the resulting slurry was filtered over silicagel using hexane. The solvent was removed under reduced pressure and the dibromo compound obtained as a colourless liquid (1.55 gm, yield 95%), ¹H NMR (CDCl₃, 400 MHz, ppm): δ 6.75 (s, 1H), 2.47 (t, *J* = 7.6 Hz, 2H), 1.52 (q, *J* = 6.5 Hz, 2H), 1.32-1.26 (m, 6H), 0.89-0.83 (m, 3H).

3-Hydroxymethylthiophene. To a solution of thiophene-3-carboxaldehyde (3.84 g, 30 mmol) in dry THF (30 ml) was added slowly LiAlH₄ (1.2 g, 32 mmol) under nitrogen atmosphere. The mixture was

stirred at room temperature for 20 min. and then the mixture was refluxed at about 120°C for 4h. It was allowed to cool at room temperature and then kept at ice-cold water bath. The moist ether and then saturated NH₄Cl solution were added to decompose excess LiAlH₄. The complex was decomposed by the addition of concentrated HCl (5 ml) and the resulting mixture was extracted with ether (3 X 20 ml). The organic layer was washed with water (50 ml) and dried over anh. MgSO₄. It was evaporated under reduced pressure and obtained brown color oil 3-hydroxymethylthiophene (3.27 g, yield 85%).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.29 (dd, *J* = 4.9 Hz, 1H), 7.20 (s, 1H), 7.07 (dd, *J* = 4.9 Hz, 1H), 4.67 (s, 2H).

3-Hexoxymethylthiophene. To DMSO (16 ml) was added powdered KOH (1.67 g, 30 mmol). After stirring 5 min., 3-hydroxymethylthiophene (1 g, 8.77 mmol) was added, followed immediately by the 1-bromohexane (2.8 g, 17 mmol), stirring was continued for 40 h at room temperature. After that, the resulting mixture was poured into 150 ml water and extracted with CH₂Cl₂ (3 X 15ml). The organic layer was washed with water (2 X 30ml) and dried over anh. MgSO₄. It was evaporated under reduced pressure to remove excess 1-bromohexane and obtained pure brown color oil 3-hexoxymethylthiophene (1.48 g, yield 83%).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.27 (dd, *J* = 4.9 Hz, 1H), 7.18 (s, 1H), 7.05 (dd, *J* = 4.9 Hz, 1H), 4.48 (s, 2H), 3.43 (t, *J* = 6.7 Hz, 2H), 1.57 (m, 2H), 1.34-1.24 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 139.83, 127.30, 125.82, 122.48, 70.44, 68.07, 31.68, 29.69, 25.83, 22.60, 14.03.

3-Hexoxymethyl-2,5-dibromothiophene⁶ (4). N-Bromosuccinimide (1.12 gm, 6.3 mmol) was added portionwise to a solution of 3-hexoxymethylthiophene (594 mg, 3 mmol) in DMF (10 ml) under ice-cold water bath. After 5h stirring, water (30 ml) was added and the resulting mixture extracted with ethylacetate (3 X 20 ml). The organic phase was dried over anhydrous MgSO₄ and the solvent

evaporated to afford the title compound as light yellow color viscous oil (993 mg, yield 93%).

^1H NMR (CDCl_3 , 400 MHz, ppm): δ 6.95 (s, 1H), 4.34 (s, 2H), 3.41 (t, $J = 6.64$ Hz, 2H), 1.58-1.52 (m, 2H), 1.34-1.24 (m, 6H), 0.86 (t, $J = 6.89$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 139.58, 130.78, 111.15, 109.69, 70.65, 66.51, 31.69, 29.69, 25.84, 22.59, 14.04.

Thiophene-3-carboxylic acid.⁷ To the brown silver oxide, formed from 15 gm of silver nitrate and 7 gm of sodium hydroxide in 60 ml of water, was added 4.75 gm (42.4 mmol) of 3-thiophene carboxaldehyde in small portions with cooling. The addition was completed with 3 min. and the oxidation was completed in 30 min. as evidence by the disappearance of the characteristic aldehyde odor. The silver was removed and washed with 20 ml of water. The solution was concentrated and acidified with concentrated HCl and cooled for 12 h. The desired product was precipitated, filtered and dried. White solid (5.25 gm, yield 97%). M.P. 137-138°C (lit. 137-138°C).

2,5-Dibromo thiophene-3-carboxylic acid.⁸ A solution of 20 gm (121.7 mmol) of bromine in 50 ml of glacial acetic acid was slowly added to a stirred solution of 7 gm (55 mmol) of thiophene-3-carboxylic acid in 75 ml of glacial acetic acid at room temperature. The mixture was stirred for 15 min. and the poured into 400 ml of cold water (ice bath). The mixture was filtered and a white solid was obtained. The crude product was recrystallized from 500 ml of water. White solid (9.9 gm, yield 63%).

M.P. 176-177°C (lit. 177-179°C). ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 7.38 (s, 1H).

Hexyl-2,5-dibromothiophene-3-carboxylate⁸ (3). 2,5-Dibromothiophene-3-carboxylic acid (6 gm, 21 mmol) was dissolved in thionyl chloride (6 ml, 82.2 mmol) and the mixture was refluxed for 1 h. The excess thionyl chloride was distilled under atmospheric pressure and the residue was treated with a solution of 1-hexanol (2.35 gm, 23.1 mmol) in pyridine (4.2 ml). It was further refluxed for 2 h and allowed to cool. The resultant mixture dissolved in CH_2Cl_2 (150 ml) and washed with water (2 X 50 ml), dried (MgSO_4) and concentrated to yield the crude product, which was purified by column

chromatography (silica gel; EtOAc-hexane, 10%). Light yellow viscous oil (7.15 gm, yield 92%).

^1H NMR (CDCl_3 , 400 MHz, ppm): δ 7.32 (s, 1H), 4.24 (t, $J = 6.6$ Hz, 2H), 1.70 (t, $J = 7.4$ Hz, 2H), 1.39 (m, 2H), 1.32-1.27 (m, 4H), 0.90-0.85 (m, 3H).

2,5-Dibromo-3-cyanothiophene (5). To a solution of 3-cyanothiophene (545 mg, 5 mmol) in CHCl_3 (10 ml) at 0°C were added 12 mg (0.08 mmol) of FeCl_3 and 0.54 ml (10.5mmol) of bromine dropwise. The solution was warmed to room temperature and was stirred for 3 h in the dark place. The resulting slurry was poured into water and washed with sodium thiosulphate until the red color disappeared. The aqueous layer was extracted with CHCl_3 (3 X 10 ml), and the combine organic layer was dried over anhydrous MgSO_4 and the solvent was removed under reduced pressure to afford the title compound as brown color viscous oil (1.3 gm, yield 98%).

^1H NMR (CDCl_3 , 400 MHz, ppm): δ 7.08 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 130.91, 122.87, 114.64, 113.29, 112.61. Ms (EI), m/e: 267 (M^+ , 58%), 269 ($\text{M}+2$, 100%).

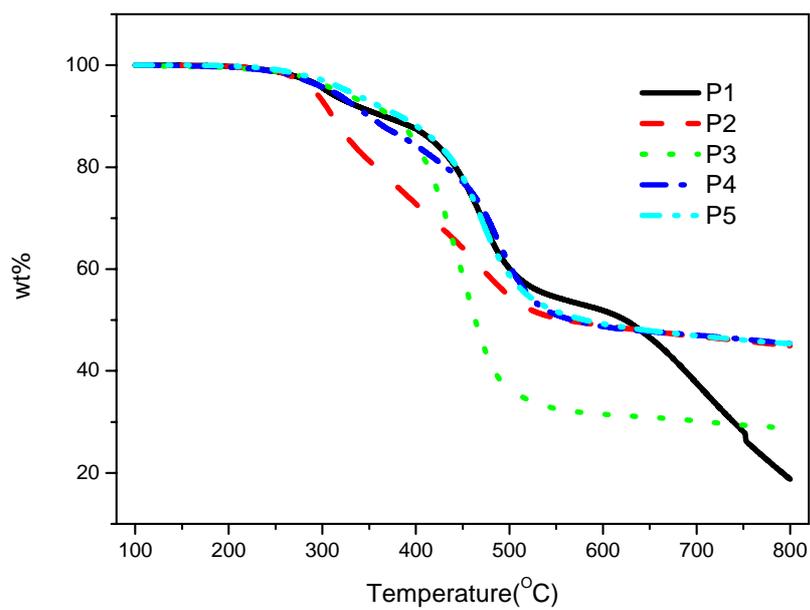


Figure 1. TGA diagrams of copolymers **P1**, **P2**, **P3**, **P4** and **P5**

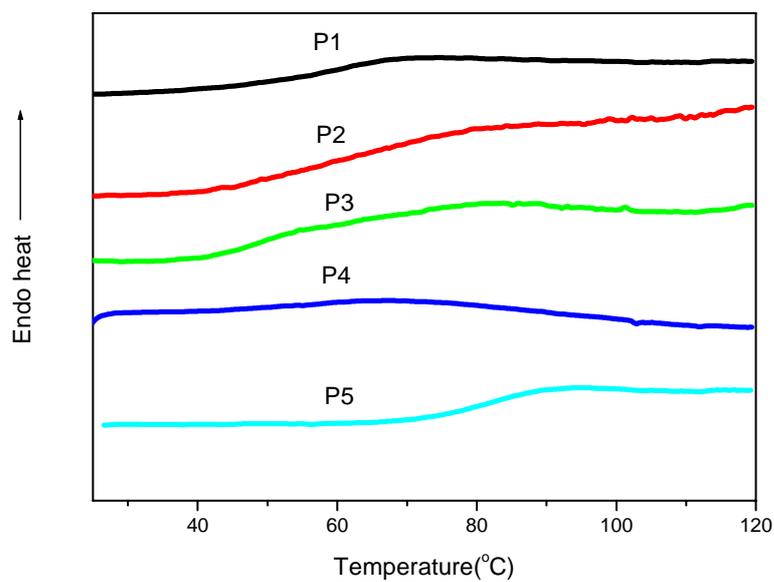


Figure 2. DSC diagrams of copolymers **P1**, **P2**, **P3**, **P4** and **P5**

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