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Synthesis and Properties of Alternating Vinylene-Benzothiadiazole-Based Copolymers with Carbazole and Fluorene Derivatives for Photovoltaic Applications

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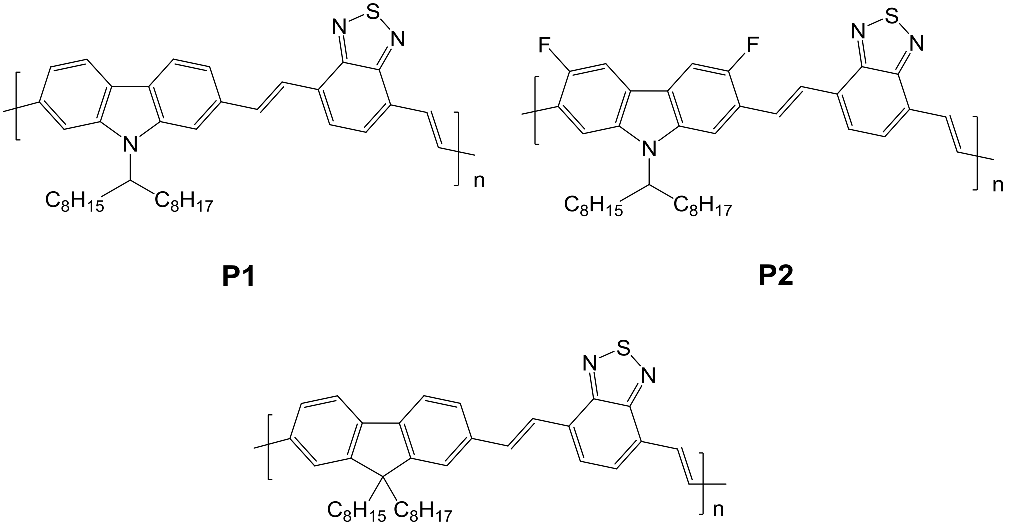
Three vinylene-benzothiadiazole based alternating copolymers with carbazole, 3,6-difluoro carbazole and fluorene were prepared via Suzuki coupling polymerisation in the presence of catalytic amounts of palladium (II) acetate $Pd(OAc)_2$ and tri-ortho-tolylphosphine. $P(o\text{-}tol)_3$. The molecular weights measured by gel permeation chromatography and copolymers were characterised by NMR, UV-Vis spectroscopy and cyclic voltammetry. The physical properties and their band gaps are discussed in relation with their donor units (carbazole and fluorene derivatives).

Keywords: Conjugated polymers; bandgap; organic solar cells.

1. INTRODUCTION

Donor-acceptor alternating copolymers have received a large attention as active materials for photovoltaic devices due to their low bandgaps [1-7]. The lowest bandgap polymer based on donor-acceptor system was prepared by Roncali *et al.* [8], which has a bandgap of 0.36 eV. Carbazole and fluorene derivatives are used widely as donor units, while benzothiadiazole derivatives are used as electron acceptors. The donor and acceptor groups can be linked directly or through thiophene groups such as PCDTBT which is one of the third generations conjugated copolymers and achieved the highest power conversion efficiency of 6 % to date, when combined with PC70BM [9]. The vinylene groups can be used to link the donor and acceptor groups leading to a reduction in the bandgap of the copolymers.

The advantages of incorporating vinylene linkages is that they support the planarity of the polymer backbone by reducing torsional interactions between acceptor and donor rings, thus extending the conjugation, which should lead to a narrow bandgap. In addition, the planar arrangement of the polymer through forming covalent linkage reduces the bandgap, and the H-bonding linkage between the alternating units can also reduces the bandgap of the polymer because it maximizes the extended π-conjugation. The LUMO and HOMO of the polymer should match that of the used acceptor to facilitate the exciton dissociation [10]. Moreover, the incorporation of vinylene linkage into polymer chain provides rotational flexibility, which increases the solubility of the polymer [11].



P1 **P2**

P3

Figure 1. The target polymers P1, P2 and P3

In this work, three novel conjugated copolymers were synthesised, two of them are carbazole, vinylene and benzothiadiazole based copolymers; poly[9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl-alt-4,7-bis(E)-divinylbenzo[c] [1,2,5]thiadiazole)-2,2’-diyl] (**P1**) and poly[3,6-difluoro-9-(1-octyl-nonyl)-*9H*-carbazole-2,7-diyl-alt-4,7-bis(E)-divinylbenzo [c][1,2,5]thiadiazole)-2,2’-diyl] (**P2**). While another one is a fluorene, vinylene and benzothiadiazole based copolymer poly[9,9-dioctyl-9H-fluorene-2,7-diyl-*alt*--4,7-bis(E)-divinylbenzo[c] [1,2,5]thiadiazole)-2,2’-diyl] (**P3**). The comparison of their photophysical and electrical properties illustrated the influence of fluorine substituents on the bandgap, the HOMO and LUMO levels; it also illustrated the difference between carbazole and fluorene units.

2. EXPERIMENTAL SECTION

2.1 Materials

All chemicals were purchased from the commercial suppliers and used as received unless otherwise stated. All solvent used for the reaction were dried except acetone. The reactions for preparing monomers were carried out under Nitrogen atmosphere and the reaction for preparing polymer was carried under Argon atmosphere.

2.2 Measurements

NMR Spectra were recorded on Bruker 250 MHz, AMX400 400 MHz or DRX500 500 MHz NMR spectrometers at 22 °C in chloroform-d_1, acetone-d_6 and 1,1,2,2-tetrachloroethane-d_2 solution with TMS as the internal standard. IR absorption spectra were recorded on the Nicolet Model 205 FT-IR Spectrometer using a Diamond ATR attachment for solid samples analysis. Mass spectra were recorded on Perkin Elmer Turbomass Mass Spectrometer Equipped with Perkin Elmer PE-5MS Capillary Column for GCMS. MS was obtained *via* chemical ionisation (CI) or electron impact (EI) methods. MALDI-TOF spectra were recorded on a Bruker Reflex III in reflection positive ion mode with a DCTB matrix.

Elemental analysis was carried out by the Perkin Elmer 2400 CHN Elemental Analyser for CHN analysis and by the Schöniger oxygen flask combustion method for anion analysis. The weights of the samples submitted for analysis were approx. 5 mg for CHN analysis and approx. 5 mg for each anion analysis. Melting points were measured using a Linkam HF591 heating stage in conjuction with a TC92 controller.

GPC curves were recorded on a equipment consisting of a Hewlett Packard Model 1090 HPLC, a Hewlett Packard Model 1037 Differential Refractive Detector, two Polymer Labs PLgel 5μ Mixed C (300 mm x 7.5 mm) columns and a guard (50 mm x 7.5 mm). using $CHCl_3$ (HPLC grade) as the eluent at a rate of 1 cm^3 min^{-1}. Polymer samples were made up as solutions in chloroform (2.5 mg cm^{-3}) spiked with toluene as a reference. The GPC curves were obtained by the RI-detection method, which was calibrated with a series of narrow polystyrene standards (Polymer Laboratories).

UV-visible absorption spectra were measured by Hitachi U-2010 Double Beam UV / Visible Spectrophotometer. The absorbance of polymers was measured in solution of toluene (spectrophotometric grade) and THF (spectrophotometric grade) at ambient temperature using rectangular quartz cuvettes (light path length = 10 mm) purchased from Sigma-Aldrich. Samples of pristine polymer thin films for UV-visible absorption spectra measurements were prepared by dip coating quartz plates into 1 mg cm^{-3} polymer solutions in chloroform (HPLC grade) and the measurements were carried out at ambient temperature.

Cyclic voltammograms were recorded with a Princeton Applied Research model 263A Potentiostat/Galvanostat. Measurements were carried out under argon at 25 ± 2 ^{o}C. Tetrabutylammonium tetrafluoroborate ($TBABF_4$, 10 cm^3) solution in acetonitrile (0.1 mol dm^{-3}) was used as the electrolyte solution. A three-electrode system was used consisting of an Ag/Ag^+ reference electrode (silver wire in 0.01 mol dm^{-3} silver nitrate solutions in the electrolyte solution), a platinum working electrode (2-mm diameter smooth platinum wire), and a platinum counter electrode (platinum wire). Polymer thin films were prepared by drop casting 1.0 mm^3 of polymer solutions in dichloromethane (HPLC grade) (1 mg cm^{-3}) onto the working electrode then dried in air.

DSC curves were recorded on Perkin Elmer Pyris 1 Differential Scanning Calorimeter equipped with Perkin Elmer CCA7 Subambient Accessory at the scan rate of 10°C/minute under inert nitrogen atmosphere. Aluminium pans were used as sample pans. An empty aluminium pan was used as the reference. TGA curves were obtained by Perkin Elmer TGA-7 Thermogravimetric Analyser at a scan rate of 10°C/minute under inert nitrogen atmosphere.

2.3 Synthesis

All reactions were carried out under inert nitrogen atmosphere. 2,7-Dibromo-9H-carbazole (1) and 2,7-dibromo-3,6-difluoro-9H-carbazole (2) were prepared according to our previous work [12]

Heptadecan-9-ol (3)

Heptadecan-9-ol was prepared according to the procedure by Leclerc *et al*. [13]. In 1L 3-necked flask containing Mg (13.37 g, 549.9 mmol) was heated under high vacuum with stirring for 20 min before adding dry THF (260 ml). Then a solution of 1-bromooctane (96.57 g, 500 mmol) in THF (155 ml) was added drop-wise to a Mg suspension. An *ice bath* was used to maintain the temperature below 25°C. The mixture was then heated to reflux for 2 hours to obtain octylmagnesium bromide as a grey solution (Grignard solution). In another 1L 2-necked flask containing a solution of Ethyl formate (12.35 g, 166.7 mmol) in THF (280 ml) was cooled to -78 °C before Octylmagnesium bromide (0.5 mol, 500 ml of a 1 M solution in THF) was added drop wise and the resulting mixture stirred overnight at room temperature. Methanol and a saturated NH_4Cl solution were then added to quench the reaction. The mixture was extracted with diethyl ether (3 x 400 ml) and washed with a saturated NaCl solution. The organic layer was dried over $MgSO_4$ and the solvent removed in vacuo to obtain heptadecan-9-ol (**1**) as colourless oil *which solidified on* standing (41.50 g, 97% yield). The product gave a single spot on TLC (R_f = 0.53) in 40-60 petroleum ether/ethyl acetate (10:1) and visualised by dipping into p-anisaldehyde and heating.

M.p. = 29 - 32 °C.

^{1}H NMR ($CDCl_3$): (δ_H/ppm) 3.60 (bm, H); 1.43 (m, 8H); 1.30 (m, 21H); 0.898 (t, 6H, *J* = 6.7 Hz).

^{13}C NMR ($CDCl_3$): (δ_C/ppm) 72.0, 37.4, 31.9, 29.7, 29.6, 29.3, 25.6, 22.6, 14.1.

FT-IR (ATR): (cm^{-1}) 3321, 2916, 2872, 2848, 1464, 1375, 1352, 1136, 1089, 1026, 894, 844, 720, 620.

Mass (EI+): (m/z) 255, 256 ($M^{\bullet+}$); (calculated for $C_{17}H_{36}O$: 256.47).

Elemental Analysis (%): calculated for $C_{17}H_{36}O$: C, 79.61; H, 14.15; Found: C, 79.03; H, 14.16.

9-Heptadecane p-toluenesulfonate (4)

9-Heptadecane p-toluenesulfonate (**4**) was obtained by following a procedure of Leclerc *et al* [13]. In 500 ml 2-necked flask containing a solution of p-toluenesulfonyl chloride (27.64 g, 144.9 mmol) in DCM (100 ml) was added to another flask containing heptadecan-9-ol (11) (20.36 g, 79.38

mmol), Et_3N (34 ml, 245 mmol) and $Me_3N.HCl$ (4.26 g, 44.57 mol) in DCM (100 ml) at 0 °C. The reaction mixture was stirred for 90 min before water was added and then the mixture was extracted by DCM (3 x 200 ml). The organic layer was washed with H_2O and brine and then dried over Na_2SO_4. The solvent was removed in vacuo then the crude product was purified *via* silica gel column chromatography, eluting with (89 % hexane, 9 % ethylacetate, 2 % Et_3N) to obtain 9-heptadecane *p*-toluenesulfonate (**2**) as white solid (30.15 g, 92% yield). The product gave a single spot on TLC (R_f = 0.45) in hexane/ethyl acetate (9:1).

M.p. = 33.5 – 35 °C.

^{1}H NMR ($CDCl_3$): (δ_H/ppm) 7.81 (d, 2H, *J* = 8.8 Hz); 7.34 (d, 2H, *J* = 8.1 Hz); 4.55 (qt, H, *J* = 5.9); 2.46 (s, 3H); 1.57 (m, 4H); 1.24 (m, 24H); 0.89 (t, 6H, *J* = 6.8 Hz).

^{13}C NMR ($CDCl_3$): (δ_C/ppm) 144.2, 134.8, 129.6, 127.7, 84.6, 34.1, 31.8, 29.7, 29.3, 29.1, 24.6, 22.6, 21.6, 14.1.

FT-IR (ATR): (cm^{-1}) 2954, 2923, 2851, 1597, 1566, 1354, 1353, 1305, 1185, 1172, 1150, 1096, 1021, 964, 894, 881, 816, 766, 719, 661, 574, 553, 521.

Mass (EI+): (m/z) 410 ($M^{\bullet +}$); (calculated for $C_{24}H_{42}O_3S$: 410.65).

Elemental Analysis (%): calculated for $C_{24}H_{42}O_3S$: C, 70.19; H, 10.31; S, 7.81. Found: C, 70.38; H, 10.65; S, 8.07.

2,7-Dibromo-3,6-difluoro-9-(1-octyl-nonyl)-9H-carbazole (5)

The synthesis of 2,7-dibromo-3,6-difluoro-9-(1-octyl-nonyl)-*9H*-carbazole (**5**) was performed according to a modified procedure by Leclerc *et al* [13]. In dry DMSO (35 ml), 2,7-dibromo-3,6-difluoro-9H-carbazole (**1**) (4.60 g, 12.74 mmol) and KOH (3.60 g, 63.95 mmol) were dissolved. A solution of 9-Heptadecane *p*-toluenesulfonate (**2**) (7.85 g, 19.12 mmol) in dry DMSO (20 ml) was added dropwise to reaction mixture over one hour at room temperature and allowed the reaction to stir overnight at room temperature. Then the mixture poured onto water (400 ml), the product was extracted with hexane (5 x 400) and then dried over $MgSO_4$. The solvent was removed in vacuo then the crude product was purified *via* silica gel column chromatography, eluting with 100 % hexane. Finally the product was recrystallised from methanol to obtain pure product as white crystals (3.10 g, 23% yield). The product gave a single spot on TLC (R_f = 0.45) in 100 % hexane. M.p. = 78.2 – 79.3 °C. ^{1}H NMR ($CDCl_3$): (δ_H/ppm) 7.75 (bm, 2H); 7.57 (d, 2H, *J* = 4.7 Hz); 4.39 (m, 1H); 2.19 (bm, 2H), 192 (bm, 2H); 1.20 (bm, 20H); 0.96 (bm, 4H); 0.85 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$): (δ_C/ppm) 153.0 (d, $^1J_{C\text{-}F}$ = 237 Hz); 139.4; 135.8; 122.7; 121.1; 115.5; 113.3; 107.5 (bm); 106.7 (d, $^2J_{C\text{-}F}$ = 26 Hz); 57.3; 33.5; 31.7; 29.2; 29.0; 26.6; 22.6; 14.0. FT-IR (ATR): (cm^{-1}) 2920, 2852, 1600, 1570, 1466, 1445, 1425, 1333, 1296, 1276, 1245, 1191, 1176, 1159, 1041, 980, 937, 854, 806, 756, 720, 693, 639, 619, 568. Mass (EI+): (m/z) 597, 599, 601 ($M^{\bullet +}$); (calculated for $C_{29}H_{39}Br_2F_2N$: 599.43). Elemental Analysis (%): calculated for $C_{29}H_{39}Br_2F_2N$: C, 58.11; H, 6.56; N, 2.34; Br, 26.66. Found: C, 58.08; H, 6.62; N, 2.32; Br, 26.67.

3,6-Difluoro-9-(1-octyl-nonyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (6)

The synthesis of (**6**) was performed following a modified procedure of Jo *et al* [14]. A mixture of 2,7-dibromo-3,6-difluoro-9-(1-octyl-nonyl)-*9H*-carbazole (**5**) (5.00 g, 8.34 mmol), potassium acetate (4.90 g, 49.93 mmol), bis(pinacolato)diboron (7.42 g, 29.21 mmol), and Pd(dppf)Cl_2 (0.40 g, 0.55 mmol) in DMF (100 ml) was heated to 100 °C for 40 hours. Then the reaction mixture was cooled to room temperature, poured into H_2O (110 ml) and extracted with diethyl ether (3 × 150 ml). The organic layer was washed with H_2O (3 × 120 ml) and dried over $MgSO_4$. The crude product was purified by dissolving it in a minimum amount of acetone and then precipitating in a hot methanol (500 ml) which had been ran through a column of alumina (basic) to remove the acidity. The product was obtained as a light brown powder (3.79 g, 65% yield). M.p. = 140 – 141.5 °C. ^1H NMR ($CDCl_3$): (δ_H/ppm) 7.89 (b, 1H); 7.76 (b, 1H); 7.67 (b, 2H); 4.62 (m, 1H); 2.29 (bm, 2H); 1.94 (bm, 2H); 1.43 (s, 24H); 122 (b, 20H), 0.96 (m, 4H); 0.84(t, 6H, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$): (δ_C/ppm) 160.8 (d, $^1J_{C\text{-}F}$ = 239.0 Hz); 139.4; 136.0; 126.2; 124.8; 119.0; 116.5; 114.8 (b); 106.2 (d, $^2J_{C\text{-}F}$ = 30 Hz); 83.8; 56.5; 33.8; 31.7; 29.3; 29.2; 29.1; 26.6; 24.8; 22.6; 14.0. FT-IR (ATR): (cm^{-1}) 2924, 2854, 1611, 1569, 1442, 1389, 1330, 1291, 1270, 1245, 1213, 1168, 1138, 1067, 968, 881, 853, 808, 735, 720, 698, 665, 613, 579, 533, 499. Mass (EI+): (m/z) 693 ($M^{\bullet+}$); (calculated for $C_{41}H_{63}B_2NO_4F_2$: 693.56). Elemental Analysis (%): calculated for $C_{41}H_{63}B_2NO_4F_2$: C, 71.00; H, 9.16; N, 2.02. Found: C, 69.99; H, 9.03; N, 1.98.

4,7-Dibromo-2,1,3-benzothiadiazole (7)

The synthesis of 4,7-dibromo-2,1,3-benzothiadiazole (**7**) was performed according to a modified procedure by Pilgram *et al* [15]. A mixture of 2,1,3-benzothiadiazole (25.16 g, 184.76 mmol) and hydrobromic acid HBr (48 %, 50 ml, 1.49 g/ml) was heated under N_2 to 100 °C with stirring before Br_2 (28 ml, 3.11 g/ml, 544.93 mmol) was added dropwise over a period of one hour. The product started precipitating then a further amount of HBr (100 ml) was added to facilitate stirring and allowed the mixture to stir under reflux for further 2 hours. The hot reaction mixture was filtered and the precipitate washed with distilled water several time. Then the filtrate was cooled to precipitate further product, filtered and the solid washed with water. The filtrate was poured onto a solution of sodium thiosulphate $Na_2S_2O_3$ (10 % w/w) to destroy the remaining bromine. The obtained orange solid product was recrystallised from ethanol and then recrystallised from a mixture of chloroform / hexane (2:1) to obtain 4,7-dibromo-2,1,3-benzothiadiazole (**5**) as off-white needle crystals (53.54 g, 99% yield). M.p. = 185.5 – 187.5 °C.^1H NMR ($CDCl_3$): (δ_H/ppm) 7.76 (s, 2H). ^{13}C NMR ($CDCl_3$): (δ_C/ppm) 152.9, 132.3, 113.9. FT-IR (ATR): (cm^{-1}) 3079, 3045, 1650, 1587, 1498, 1475, 1375, 1309, 1272, 1183, 1121, 1080, 1019, 934, 873, 842, 824, 793, 743, 730, 705, 686, 656, 632, 615, 585. Mass (EI+): (m/z) 292, 294, 296 ($M^{\bullet+}$); (calculated for $C_6H_2Br_2N_2S$: 293.97). Elemental Analysis (%): calculated for $C_6H_2Br_2N_2S$: C, 24.51; H, 0.69; N, 9.53; Br, 54.36. Found: C, 24.45; H, 0.69; N, 9.39; Br, 54.41.

(2E, 2'E)-3,3'-(Benzo[c][1,2,5]thiadiazole-4,7-diyl)diacrylic acid (8)

The synthesis of the product (**8**) was carried out according to a procedure by Mei *et al* [11]. A mixture of 4,7-dibromobenzo[c][1,2,5]thiadiazole (5.85 g, 20.00 mmol) (7), Pd$(OAc)_2$ (178 mg, 0.80 mmol) and tri(o-tolylphosphine) (488 mg, 1.60 mmol) was degassed under Ar, before a mixture of dry acetonitrile (120 ml), dry THF (28 ml) and triethylamine (Et_3N) (60 ml) was added. Then the reaction mixture was heated to 60 °C before acrylic acid (4.32 g, 60 mmol) was added dropwise, which dissolved the solids in the reaction mixture and turned it into an orange solution. Then the reaction mixture was heated to reflux overnight. A mirror-like layer of palladium was formed on the wall of the flask. The dark hot reaction mixture was concentrated until becoming viscous. A solution of diethyl ether/petroleum ether (1:1) (200 ml) was added to the dark viscous solution. The resulting precipitate was filtered, washed with a solution of diethyl ether/petroleum ether (1:1) and dried to obtain a dark red solid, which dissolved in a mixture of water (1000 ml) and triethylamine (7 ml). After stirring for two hours, the mixture was filtered and the filtrate was acidified by a solution of HCl (100 ml, 1M). The obtained precipitate was filtered and washed with water to obtain the crude product, which was dried under air and dissolved in hot THF (100 ml) and then filtered. The filtrate was precipitated by adding petroleum ether. The resulting precipitate was collected and dried under vacuum to obtain the product (**8**) as an orange solid (5.01 g, 91% yield).

^{1}H NMR (DMSO-d$_6$): (δ_H/ppm) 12.69 (b, 2H); 8.05 (s, 2H); 7.95 (d, 2H, *J* = 16.0 Hz); 7.34 (d, 2H, *J* = 16.0 Hz).

^{13}C NMR (DMSO-d$_6$): (δ_C/ppm) 167.4, 152.8, 138.7, 131.2, 128.1, 124.5.

FT-IR (ATR): (cm^{-1}) 2831, 2578, 2231, 1678, 1623, 1536, 1491, 1419, 1306, 1282, 1249, 1234, 1207, 1080, 1043, 1022, 980, 932, 894, 860, 839, 809, 682, 607.

Mass (EI+): (m/z) 276, 277, 278 ($M^{\bullet +}$); (calculated for $C_{12}H_8N_2O_4S$: 276.27).

Elemental Analysis (%): calculated for $C_{12}H_8N_2O_4S$: C, 52.17; H, 2.92; N, 10.14; S, 11.61. Found: C, 51.81; H, 2.83; N, 9.79; S, 11.49.

4,7-Bis[(E)-2-bromovinyl]benzo[c][1,2,5]thiadiazole (9)

The synthesis of the product (**9**) was carried out according to a procedure by Mei *et al* [11]. A solution of lithium acetate dihydrate (408 mg, 4.00 mmol) in distilled water (15 ml) was added to a mixture of (2E, 2'E)-3,3'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)diacrylic acid (**8**) (1.38 g, 5.00 mmol) and acetonitrile (50 ml). Then NBS (1.87 g, 10.50 mmol) was added before stirring the solution for 3 hours at room temperature. Carbon dioxide was observed in bubbler at once after adding NBS. After adding water (100 ml) the formed precipitate was filtered and then dried under air. The crude product was purified via silica gel column chromatography, eluting with (4 % DCM, 96 % petroleum ether) to obtain the product (**9**) as a yellow solid (1.15 g, 67% yield).

M.p. = 185-189 °C.

^{1}H NMR (CDCl$_3$): (δ_H/ppm) 8.06 (d, 2H, *J* = 13.8 Hz); 7.43 (d, 2H, *J* = 13.9 Hz); 7.41 (s, 2H).

^{13}C NMR (CDCl$_3$): (δ_C/ppm) 152.8, 133.3, 128.3, 128.2, 114.2.

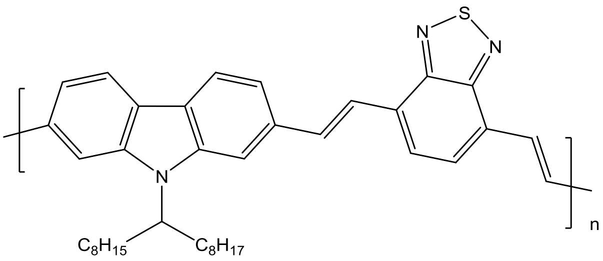
FT-IR (ATR): (cm^{-1}) 3085, 2922, 2852, 1859, 1703, 1602, 1536, 1491, 1388, 1349, 1285, 1269, 1247, 1192, 1168, 939, 896, 850, 777, 745, 719, 623.

Mass (EI+): (m/z) 344, 346, 348 ($M^{\bullet +}$); (calculated for $C_{10}H_6Br_2N_2S$: 346.04).

Elemental Analysis (%): calculated for $C_{10}H_6Br_2N_2S$: C, 34.71; H, 1.75; N, 8.10; Br, 46.18; S, 9.27. Found: C, 35.54; H, 1.68; N, 7.79; Br, 44.15; S, 9.09.

Synthesis of polymers

3.4.8 Poly [9 - (heptadecan – 9 – yl) - 9H – carbazole - 2, 7 –diyl - alt-4,7 – bis (E)-divinylbenzo[c][1,2,5]thiadiazole)-2,2'-diyl] (P1)



A 100-ml one-necked flask under argon containing 2,7-di(1,3,2-dioxaborinan-2-yl)-9-(heptadecan-9-yl)-9H-carbazole (303 mg, 0.461 mmol) and 4,7-bis((E)-2-bromovinyl)benzo[c][1,2,5]thiadiazole (167 mg, 0.483 mmol) (**9**) in dry toluene (12 ml) was degassed. To the mixture tetraethylammonium hydroxide (4 ml, degassed) were added and degassed. Then $Pd(OAc)_2$ (3.3 mg, 0.015 mmol), tri(*o*-tolyl)phosphine (9.0 mg, 0.029 mmol) were added, degassed and heated to 95 ^oC for 5 hours. The mixture was cooled to room temperature and bromobenzene (0.1 ml) were added, degassed and heated 90 ^oC for 1 hour. Again, the mixture was cooled to room temperature and phenylboronic acid (120 mg) was added, degassed and heated to 90 ^oC for 3 hour. After cooling to room temperature, the mixture was dissolved in $CHCl_3$ (200 ml) and to this solution ammonia (28 %) (50 ml) was added, 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 using a Soxhlet extraction with solvents in order methanol (250 ml), acetone (250 ml), hexane (250 ml), toluene (250 ml), chloroform (250 ml) and chlorobenzene (250 ml). The chlorobenzene fraction was concentrated to approximately 50 ml and then poured into degassed methanol (500 ml). The resulting mixture stirred overnight and the solid was collected by filtration through a membrane filter. The fraction was dark red shiny solid (209 mg, 68% yield).

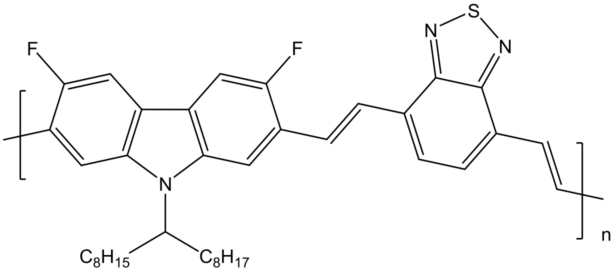
GPC (1,2,4-trichlorobenzene at 100 ˚C): $M_w = 63300$, $M_n = 50400$, PD = 1.3.

Elemental Analysis calculated for $C_{39}H_{47}N_3S$: C, 79.41; H, 8.03; N, 7.12; Br, 0. Found: C, 66.24; H, 7.34; N, 5.23; Br, 0.

^1H NMR ($C_2D_2Cl_4$): (δ_H / ppm) 8.26 (d, 2H); 8.18 (d, 2H); 7.86-7.69 (bm, 8H); 4.77 (br, 1H); 2.48 (br, 2H) 2.17 (br, 2H); 1.53-1.29 (bm, 24H); 0.90 (t, 6H).

FT-IR (ATR): (cm^{-1}) 2955, 2922, 2852, 2185, 1619, 1562, 1527, 1489, 1456, 1435, 1342, 1258, 1226, 1081, 1012, 962, 893, 847, 792, 724, 651, 522.

Poly [3 , 6 – difluoro – 9 - (1 – octyl – nonyl) - 9H – carbazole -2 , 7 – diyl – alt - 4, 7 – bis (E) - divinylbenzo[c][1,2,5]thiadiazole)-2,2'-diyl] (P2)



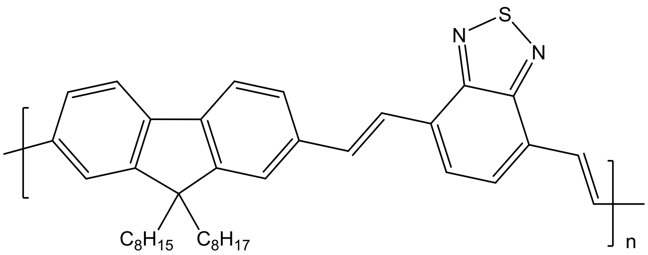
A 100-ml one-necked flask under argon containing 3,6-difluoro-9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**6**) (300.6 mg, 0.433 mmol) and 4,7-bis((E)-2-bromovinyl)benzo[c][1,2,5]thiadiazole (**9**) (150 mg, 0.433 mmol) in dry toluene (9 ml) was degassed. To the mixture tetraethylammonium hydroxide (2.8 ml, degassed) was added and degassed. Then Pd(OAc)$_2$ (2.3 mg, 0.010 mmol) and tri(*o*-tolyl)phosphine (6.4 mg, 0.021 mmol) were added, the system was degassed under argon and heated to 95 ^{o}C overnight. The mixture was cooled to room temperature and another portion of toluene (9 ml) was added, degassed and then bromobenzene (0.1 ml) was added, degassed and heated to 95 ^{o}C for 1 hour. Again, the mixture was cooled to room temperature and phenylboronic acid (83 mg) was added, degassed and heated to 95 ^{o}C for 3 hours. After cooling to room temperature, the mixture was dissolved in CHCl$_3$ (300 ml) and to this solution ammonia (28 %) (50 ml) was added, 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 using a Soxhlet extraction with solvents in order methanol (250 ml), acetone (250 ml), hexane (250 ml), toluene (250 ml). The toluene fraction was concentrated to approximately 50 ml and then poured into degassed methanol (300 ml). The resulting mixture stirred overnight and the solid was collected by filtration through a membrane filter. The fraction was dark red powder (247.1mg, 92% yield). GPC (1,2,4-trichlorobenzene at 100 ˚C): M_w = 32,900, M_n = 14,100, PD = 2.3.

Elemental Analysis calculated for $C_{39}H_{45}F_2N_3S$: C, 75.08; H, 7.40; N, 6.57; Br, 0. Found: C, 70.40; H, 7.48; N, 5.88; Br, 0.

^{1}H NMR ($C_2D_2Cl_4$): (δ_H / ppm) 8.37 (d, 2H). 7.87-7.47 (bm, 8H); 4.73 (br, 1H); 2.39 (br, 2H); 2.12 (br, 2H); 1.52-1.30 (bm, 24H); 0.90 (t, 6H).

FT-IR (ATR): (cm^{-1}) 2922, 2852, 2184, 1611, 1569, 1527, 1452, 1356, 1259, 1173, 1084, 1014, 962, 892, 852, 797, 750, 720, 662, 617.

Poly[9,9-dioctyl-9H-fluorene-2,7-diyl-alt--4,7-bis(E)-divinylbenzo[c] [1,2,5]thiadiazole)-2,2'-diyl] (P3)



A 100-ml one-necked flask under argon containing 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (242.1 mg, 0.434 mmol) and 4,7-bis((E)-2-bromovinyl)benzo[c][1,2,5]thiadiazole (**9**) (150 mg, 0.434 mmol) in dry toluene (8 ml) was degassed. To the mixture tetraethylammonium hydroxide (2.8 ml, degassed) was added and degassed. Then Pd(OAc)$_2$ (2.3 mg, 0.010 mmol) and tri(*o*-tolyl)phosphine (6.4 mg, 0.021 mmol) were added, the system was degassed under argon and heated to 95 ^{o}C. There was precipitate out of solution after one hour and the mixture was cooled to room temperature and another portion of toluene (8 ml) was added, degassed and then heated to 95 ^{o}C for 2 hours. The mixture was cooled to room temperature and another portion of toluene (5 ml) was added, degassed and then bromobenzene (0.1 ml) was added, degassed and heated to 95 ^{o}C for 1 hour. Again, the mixture was cooled to room temperature and phenylboronic acid (84 mg) was added, degassed and heated to 95 ^{o}C for 3 hours. After cooling to room temperature, the mixture was dissolved in $CHCl_3$ (500 ml) and to this solution ammonia (28 %) (50 ml) was added, 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 using a Soxhlet extraction with solvents in order methanol (250 ml), acetone (250 ml), hexane (250 ml), toluene (250 ml) and chloroform (250 ml). The toluene and chloroform fractions were concentrated to approximately 50 ml and then poured into degassed methanol (500 ml), the resulting mixtures stirred overnight and the solid was collected by filtration through a membrane filter. All the fractions were dark red powder.

Toluene fraction (38.5 mg, 15% yield), GPC (1,2,4-trichlorobenzene at 100 ˚C): $M_w = 20000$, $M_n = 8500$, PD = 2.3.

Chloroform fraction (13.1 mg, 5% yield).

(51.6 mg, 20% yield in total including the toluene and chloroform fractions).

Elemental Analysis calculated for $C_{40}H_{48}N_2S$: C, 81.58; H, 8.22; N, 4.76; Br, 0. Found: C, 67.95; H, 8.32; N, 3.24; Br, 0.

A further polymerisation was carried out with short-period polymerisation (one hour) to increase the polymer amount and yield:

A 100-ml one-necked flask under argon containing 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (161.37 mg, 0.288 mmol) and 4,7-bis((E)-2-bromovinyl)benzo[c][1,2,5]thiadiazole (**9**) (100 mg, 0.288 mmol) in dry toluene (6 ml) was degassed. To the mixture tetraethylammonium hydroxide (2 ml, degassed) was added and degassed. Then $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) and tri(*o*-tolyl)phosphine (6.4 mg, 0.021 mmol) were added, the system was degassed under argon and heated to 95 ^{o}C for one hour only. The mixture was cooled to room temperature and another portion of toluene (6 ml) was added, degassed and then bromobenzene (0.1 ml) was added, degassed and heated to 95 ^{o}C for 1 hour. Again, the mixture was cooled to room temperature and phenylboronic acid (70 mg) was added, degassed and heated to 95 ^{o}C for 3 hours. After cooling to room temperature, the mixture was dissolved in $CHCl_3$ (400 ml) and to this solution ammonia (28 %) (50 ml) was added, 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 using a Soxhlet extraction with solvents in order methanol (250 ml), acetone (250 ml), hexane (250 ml), toluene (250 ml), chloroform (250 ml) and chlorobenzene (250 ml). The toluene, chloroform and chlorobenzene fractions were concentrated to approximately 50 ml and then poured into degassed methanol (500 ml), the resulting mixtures stirred overnight and the solid was collected by filtration through a membrane filter. All the fractions were dark red powder.

Toluene fraction: (14.7 mg, 9% yield).

Chloroform fraction: (62.9 mg, 38% yield), GPC (1,2,4-trichlorobenzene at 100 ˚C): M_w = 32500, M_n = 12600, PD = 2.6.

Chlorobenzene fraction: (30.4 mg, 18% yield), GPC (1,2,4-trichlorobenzene at 100 ˚C): M_w = 83400, M_n = 34100, PD = 2.5.

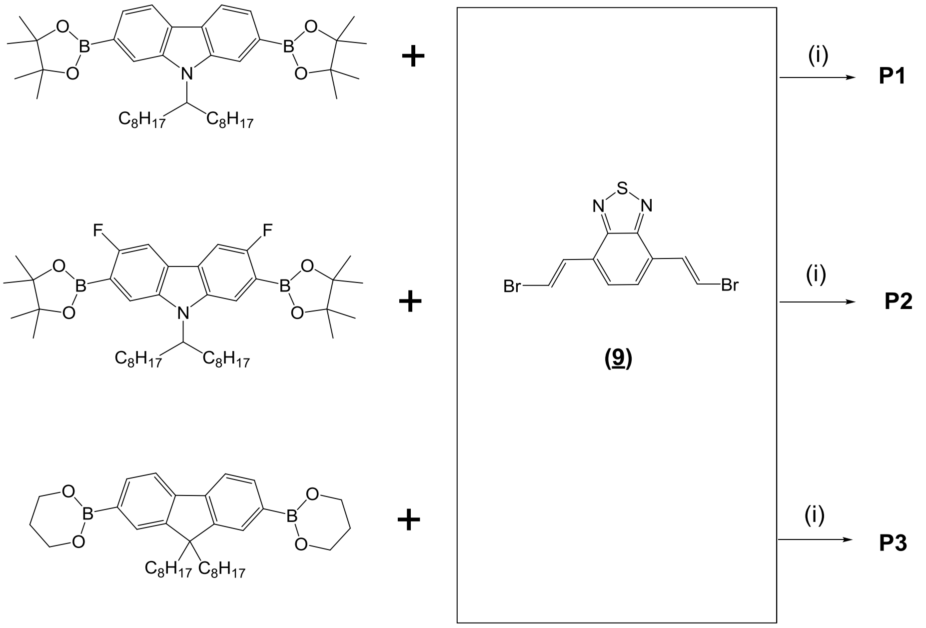
(108 mg, 65% yield in total including the toluene, chloroform and chlorobenzene fractions).

Elemental Analysis calculated for $C_{40}H_{48}N_2S$: C, 81.58; H, 8.22; N, 4.76; Br, 0. Found: C, 57.54; H, 7.74; N, 2.52; Br, 0.

^{1}H NMR ($C_2D_2Cl_4$): (δ_H / ppm) 8.15 (d, 2H); 7.82-7.71 (m, 10H); 2.15 (br, 4H) 1.51 (br, 4H); 1.36-0.97 (m, 20H); 0.89 (t, 6H).

FT-IR (ATR): (cm^{-1}) 3043, 2956, 2923, 2852, 1975, 1623, 1528, 1489, 1462, 1376, 1259, 1206, 1148, 1086, 1015, 965, 891, 865, 796, 741, 698, 661, 626, 553, 502.

3. RESULTS AND DISCUSSIONS



Scheme 1. Preparation of polymers (P1), (P2) & (P3), (i) Pd(AcO)$_2$, tri-o-tolylphosphine, tetraethylammonium hydroxide, toluene

3.1 Synthesis and Analysis of (P1), (P2) and (P3)

Sheme 1 shows the preparation of the series of copolymers, two of them contain polycarbazole poly[9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl-*alt*-4,7-bis(E)-divinylbenzo[c] [1,2,5]thiadiazole)-2,2'-diyl] **(P1)** and poly[3,6-difluoro-9-(1-octyl-nonyl)-*9H*-carbazole-2,7-diyl-*alt*-4,7-bis(E)-

divinylbenzo[c][1,2,5]thiadiazole)-2,2'-diyl] **(P2)**, and one contains polyfluorene poly[9,9-dioctyl-9H-fluorene-2,7-diyl-*alt*--4,7-bis(E)-divinylbenzo[c] [1,2,5]thiadiazole)-2,2'-diyl] **(P3)**.

These copolymers were synthesised using Suzuki cross coupling reaction, in presence of $Pd(OAc)_2$ and tri(o-tolyl)phosphine (1:2) as catalysts, toluene as solvent and tetraethyl ammonium hydroxide as base [16]. The synthesis of **(P3)** was performed twice, the second one was carried out in short period polymerisation (one hour) to increase the amount of polymers and yield. All polymerisations were performed under argon and in degassed systems, and they were stopped when the solutions became viscous. Then another portion of solvent was added to solubilise the formed polymers, and then the end-capping reagents (bromobenzene and phenyl boronic acid) were added to the polymer solutions to increase the stability of the polymer in device operation and to remove bromine and boronic ester end groups from the polymer. Then the polymer solutions were stirred with ammonia to remove catalyst remnants and other impurities.

The palladium impurities, oligomers and unreacted monomers were removed from all the crude polymers, the purifications were carried out by using several methods. At first, the polymers solutions were washed by water several times to remove the ammonia and then concentrated to approximately 50 ml, the polymers were precipitated in methanol to remove end-capping reagents, organic palladium species and unreacted comonomers.

The obtained crude polymers were then collected through filtration on micropore membranes then put inside fiber glass thimbles and cleaned with different solvents using a Soxhlet apparatus. The first solvent was methanol to remove the palladium residues from the copolymer, followed by acetone and hexane, to clean off the low molecular weight oligomers. Then the purified polymers were extracted with toluene, chloroform and chlorobenzene and the solutions precipitated separately in methanol to obtain the different fractions of polymers as dark red powders. The elemental analyses of all fractions did not show any traces of bromine and they gave satisfactory results. All the GPC data are shown in

Table 1, including the polydispersity PD and degree of polymerisation DP.

Table 1. The GPC analysis of (P1), (P2) and (P3)

Polymers		Soxhlet Fraction	Yield (%)	M_w	M_n	PD	DP
P1		chloroform	68	63,300	50,400	1.3	86
P2		toluene	92	32,900	14,100	2.3	23
P3	polymerisation 1	toluene	15	20,000	8,500	2.3	15
		chloroform	5	-	-	-	-
	polymerisation 2	toluene	9	-	-	-	-
		chloroform	38	32,500	12,600	2.6	22

chlorobenzene	18	83,400	34,100	2.5	60

NMR Analysis

All the ^{1}H-NMR analyses for the polymers **(P1)**, **(P2)** and **(P3)** were performed in $C_2D_2Cl_4$ at room temperature at first; but the obtained signals were very broad and not clear especially in the aromatic region (6 – 9 ppm), due to the phenomenon of atropisomerism [17] and polymer aggregation. To solve this problem, the NMR analyses were performed again at 100 ˚C, therefore the broadened peaks at aromatic regions became sharper and more understandable.

Figure 2 shows the ^{1}H-NMR spectra of **(P1)**, the doublet peak at 8.26 ppm corresponds to the two protons at positions a on the carbazole rings, the peak at 8.18 ppm corresponds to the two protons on vinyl group, the other overlapped multi-peak at 7.86-7.69 ppm correspond to the eight protons, two on vinyl groups at positions e, two on benzothiadiazole units at positions f and that two protons at positions c and b on the carbazole. Other peaks on the aromatic region which overlap with others are coming from protons on pheneylene end groups. The broad peak at 4.77 ppm corresponds to methylene hydrogen that is connected directly to the nitrogen atom of the carbazole (position g). The two broad peaks at 2.48 and 2.17 ppm correspond to four protons at positions h on alkyl chains, which they display two different environments due to the rotation around the C-N bond.

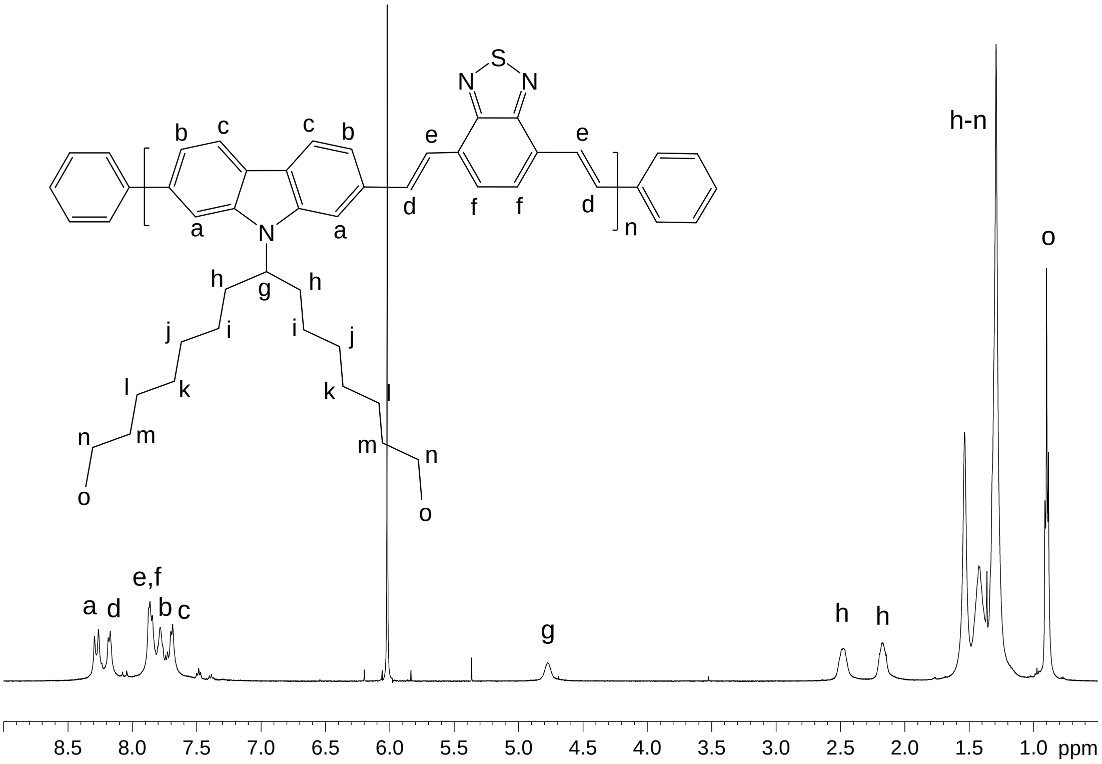


Figure 2. The proton NMR spectra of (P1) in $C_2D_2Cl_4$ at 100 ˚C

Figure shows the ^{1}H-NMR spectra of **(P2)**, the broad signal at 8.37 ppm corresponds to the two protons at positions a on the carbazole rings, the overlapped multi-peaks at 7.87-7.47 ppm correspond to the eight protons on vinyl groups at positions e and d, benzothiadiazole units at positions f and that at positions c on carbazole. Other peaks on the aromatic region which overlap with others are coming from protons on pheneylene end groups. Again the broad peak at 4.73 ppm corresponds to methylene hydrogen that is connected directly to the nitrogen atom of the carbazole (position g). The two broad peaks at 2.39 and 2.12 ppm correspond to the four protons at positions h on alkyl chains, which they display two different environments due to the rotation around the C-N bond.

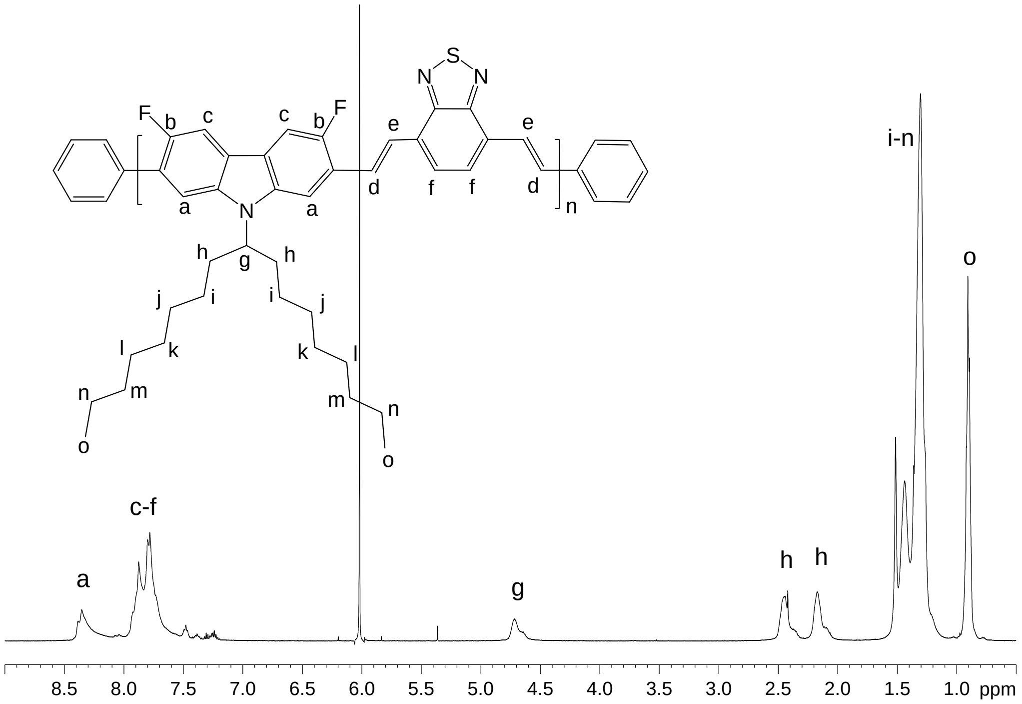


Figure 3. The proton NMR spectra of (P2) in $C_2D_2Cl_4$ at 100 ˚C

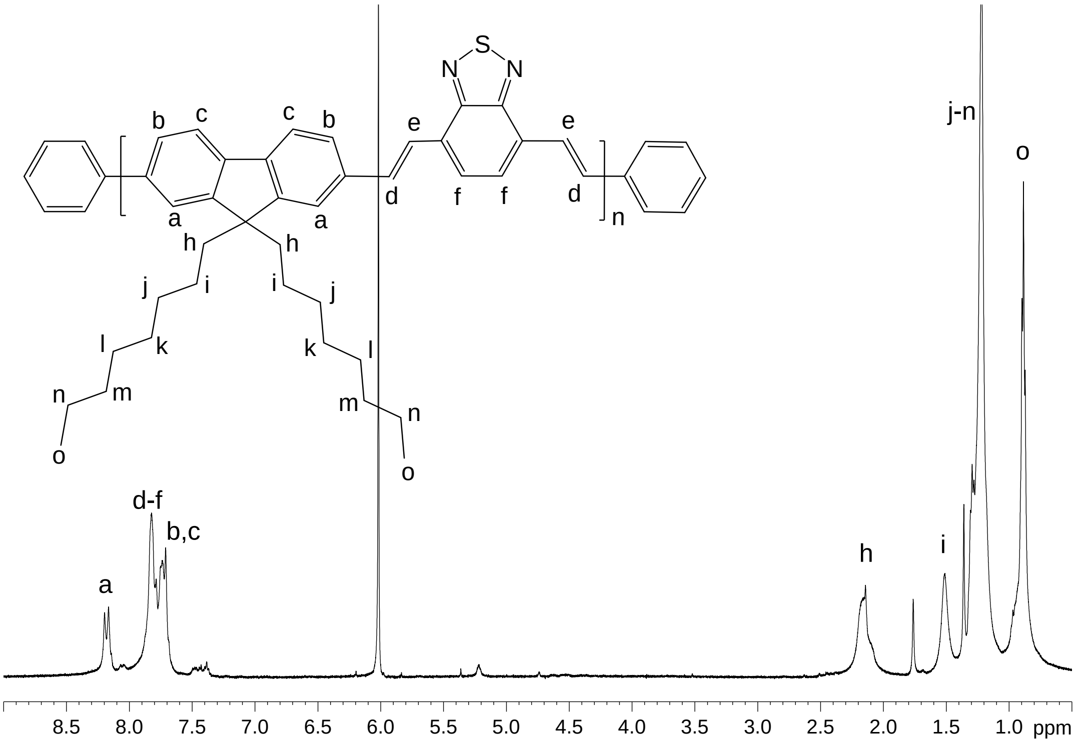


Figure 4. The proton NMR spectra of (P3) in $C_2D_2Cl_4$ at 100 ˚C

Figure shows the ^{1}H-NMR spectra of **(P3)**, the broad signal at 8.15 ppm corresponds to the two protons at position a on the fluorene rings, the overlapped multi-peak at 7.82-7.71 ppm correspond to the ten protons, two on the fluorene units at positions b and c, two on the vinyl groups at positions d and e, two on the benzothiadiazole units at positions f. Other peaks on the aromatic region which overlap with others are coming from protons on pheneylene end groups. The peaks from 2.12 to 0.89 ppm correspond to the two alkyl chains which are connected to fluorene repeat units.

3.2 Photophysical properties of (P1), (P2) and (P3)

UV-Visible absorption spectroscopy analysis

The UV-Visible absorption spectra of the polymers were measured in chloroform and in solid state as thin films. The optical band gaps were calculated from the onset of absorption of the polymers in the solid state, the results of these studies are summarised in Table .

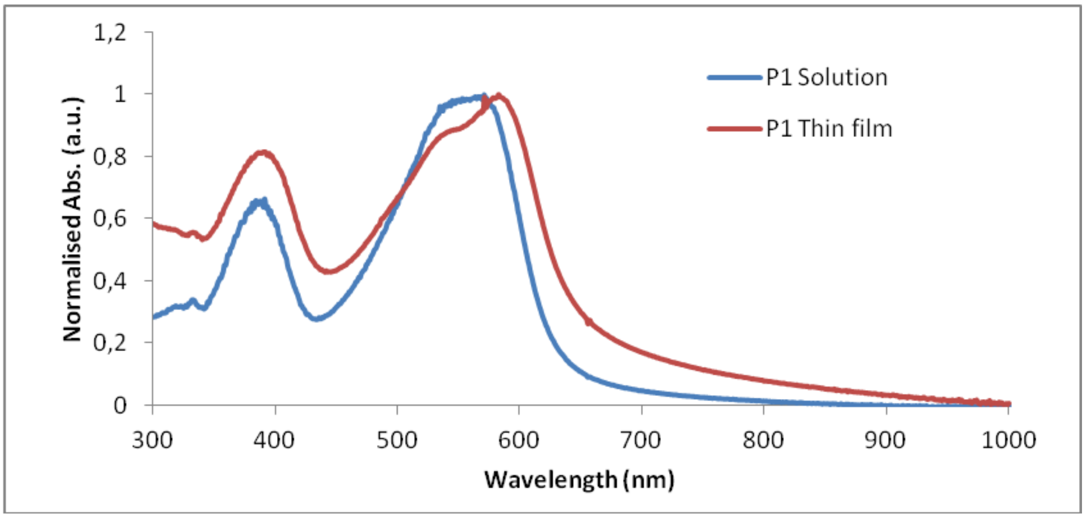


Figure 5. Normalised UV-Vis spectra of (P1) in chloroform (blue line) as a thin film (red line)

UV-Vis analysis of **(P1)** in Figure shows two absorption bands at $\lambda_{max\ 1}$ = 388 nm and $\lambda_{max\ 2}$ = 570 nm in chloroform solution, and at $\lambda_{max\ 1}$ = 390 nm and $\lambda_{max\ 2}$ = 578 nm in solid state. This slight red shift in the solid state for the same polymer was again observed in all polymers and this is because of the structure of polymers in solid state is more planar, thus more conjugation and lower band gap. Therefore, all calculations and comparisons will be based on the solid state results.

UV-Vis analysis of **(P2)** in Figure shows two absorption bands at $\lambda_{max\ 1}$ = 383 nm and $\lambda_{max\ 2}$ = 534 nm in chloroform solution, and at $\lambda_{max\ 1}$ = 386 nm and $\lambda_{max\ 2}$ = 538 nm in solid state, which they are lower than that for **(P1)** as unexpected, therefore the electrostatic interaction between the close hydrogens on vinyl groups and the fluorine substituents on the neighbouring carbazole was not strong enough and did not lead to high conjugation like in the previous two polymer groups.

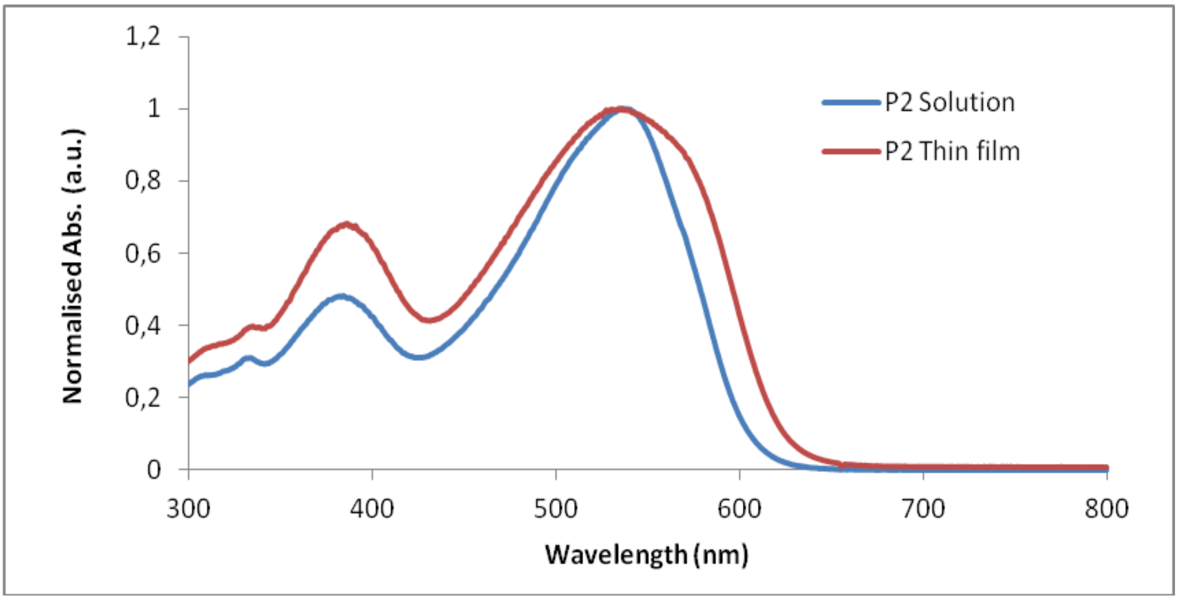


Figure 6. Normalised UV-Vis spectra of (P2) in chloroform (blue line) as a thin film (red line)

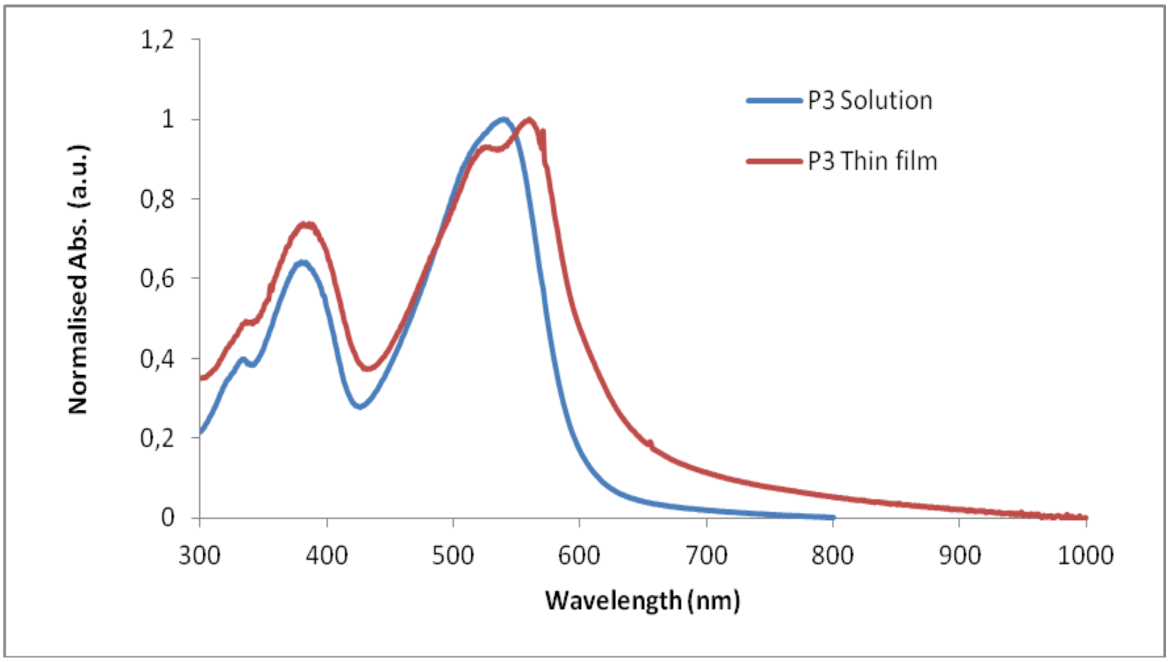


Figure 7. Normalised UV-Vis spectra of (P3) (chloroform fraction) in chloroform (blue line) as a thin film (red line)

UV-Vis analysis of **(P3)** (chloroform fraction) in Figure shows two absorption bands at $\lambda_{max\ 1} = 381$ nm and $\lambda_{max\ 2} = 539$ nm in chloroform solution, and at $\lambda_{max\ 1} = 377$ nm and $\lambda_{max\ 2} = 562$ nm in solid state, the UV-Vis results from solution are very close to that for **(P2)** and lower than those for **(P1)**, while their results from solid state comes between **(P2)** and **(P3)**.

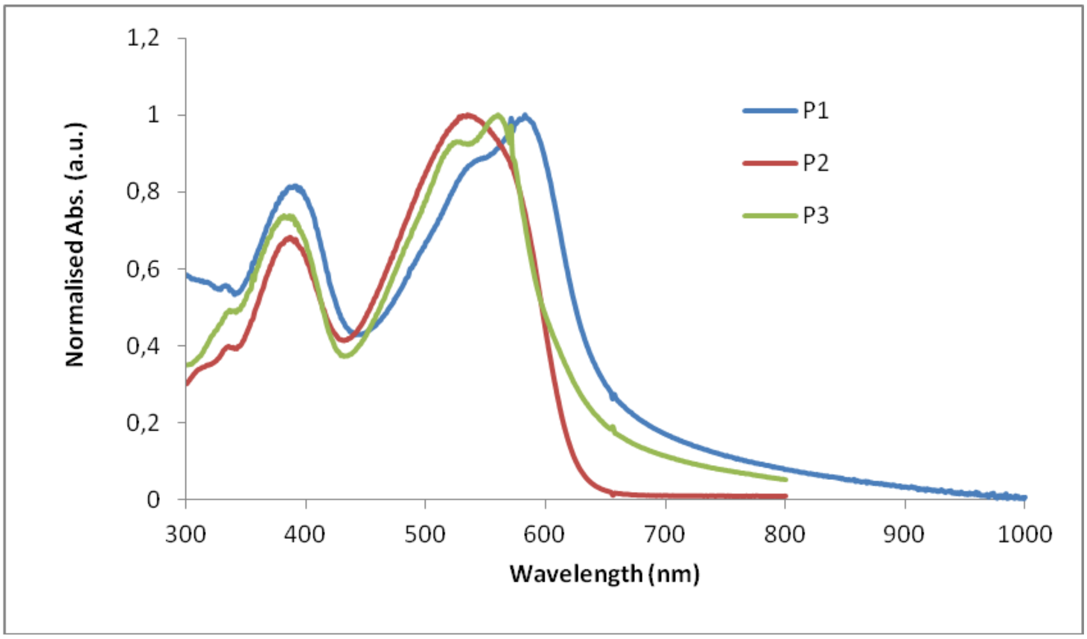


Figure 8. Normalised UV-Vis spectra of (P1), (P2) and (P3) as thin film

Table 2. UV-Vis data of (P1), (P2) and (P3)

Polymers	λ_{max} (nm) Solution		λ_{max} (nm) Thin film		λ Onset Abs. (nm)	E_g Optical (eV)
	1	2	1	2		
P1	388	570	390	578	652	1.91
P2	383	534	386	538	622	2.00
P3	381	539	377	562	620	2.00

Figure shows UV-Vis absorption spectra of **(P1)**, **(P2)** and **(P3)** in solid state. They show two broad bands at different λ_{max} with different absorption onsets, **(P1)** exhibits the narrowest optical band gap (E_g = 1.91 eV) in this type of polymers, this increase in the conjugation is might be because the polymer is more planar than other. **(P2)** and **(P3)** have different $\lambda_{max\ 2}$, but they have the same absorption onset value (620 nm), Therefore their optical band gap is (E_g = 2.00 eV). In addition, the optical band gap of **(P2)** which is based on fluorinated carbazole , is higher than **(P1)** in this type of polymers and is unlike the polymers (P3-P2) and (P6-P5), this is because of the electrostatic interaction between the close hydrogens on vinyl groups and the fluorine substituents on the neighbouring carbazole was not strong enough and did not lead to more planar and higher conjugation like in the previous polymers. The UV-Vis absorption of **(P1)** and **(P3)** show an extended absorption with small shoulder in the solid state, which is properly due to their ability to form crystals and aggregations through the thin film leading to an increase in the conjugation of the copolymers and low optical band gaps.

3.3 Electrochemical properties of (P1), (P2) and (P3)

Cyclic Voltammetry (CV) analysis

Cyclic voltammetry (CV) studies were again performed on drop-cast polymer films in acetonitrile with tetrabutylammonium perchlorate as the electrolyte. The LUMO level and the HOMO level were calculated from the onset reduction and oxidation respectively. Then the electrochemical band gap (E_g) can be calculated from the difference between them. The cyclic voltammogram of the polymers is shown in Figure .

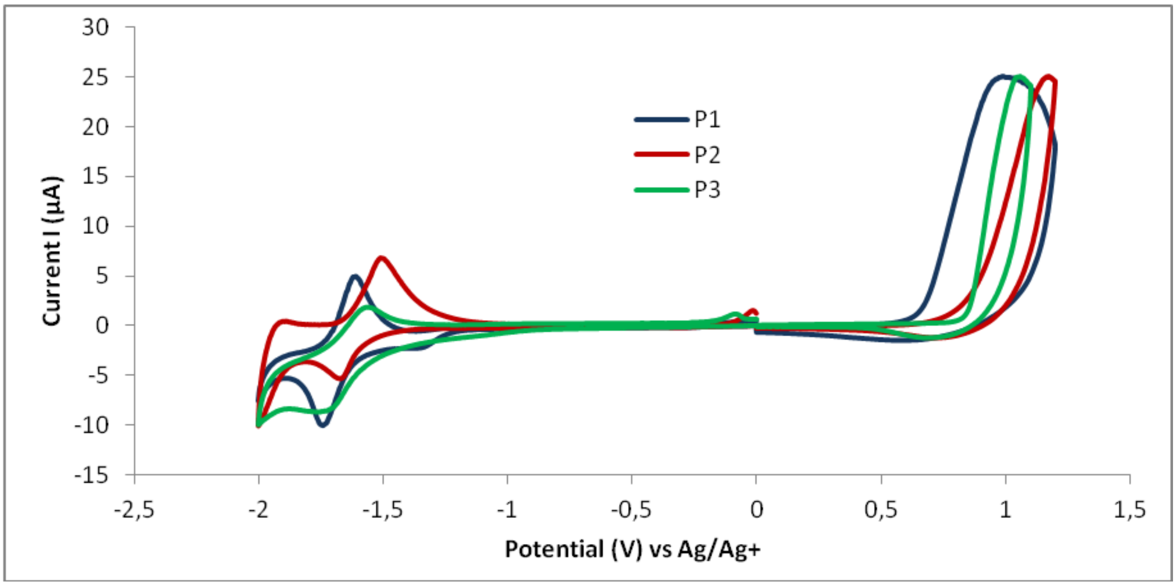


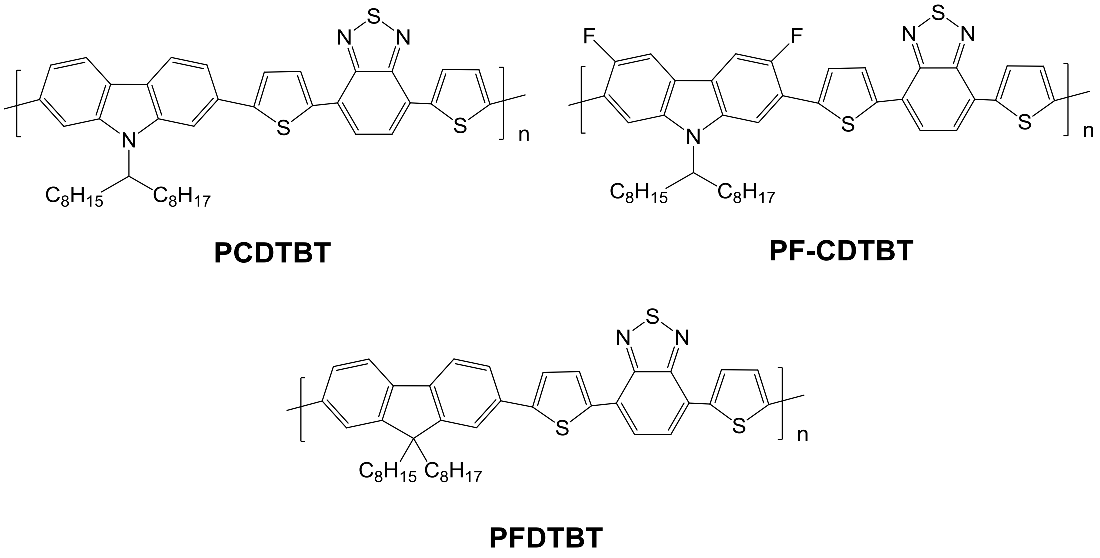
Figure 9. Normalised cyclic voltammogram spectra of the polymers (P1), (P2) and (P3)

The polymer **(P1)** exhibits an oxidation wave at E_{pa} = +0.99 V and a reduction wave at E_{pa} = -1.73 V, and their associated reduction and oxidation substituent in reducing the conjugation of the polymer, the same pattern observed in their optical band gaps. The polymer **(P2)** exhibits an oxidation wave at E_{pa} = 1.16 V and a reduction wave at E_{pa} = -1.66 V, and their associated reduction and oxidation waves at E_{pc} = +0.74 V and E_{pc} = -1.52 V respectively. From the onset of oxidation (+0.86 V) and the onset of reduction (-1.57 V), the HOMO level is at -5.578 eV and the LUMO level is at -3.148 eV for the polymer backbone, therefore the electrochemical band gap of the polymer is 2.43 eV, which is the highest electrochemical band gap in this type of polymers and also is the highest electrochemical band gap in carbazole-based polymers, this increase is might be because the fluorine substituents reduce the planarity of the polymer by forming an electrostatic interaction between the fluorine substituents and hydrogens on other chains. The polymer **(P3)** exhibits an oxidation wave at E_{pa} = +1.04 V and a reduction wave at E_{pa} = -1.71 V, and their associated reduction and oxidation waves at E_{pc} = +0.69 V and E_{pc} = -1.58 V respectively. From the onset of oxidation (+0.85 V) and the onset of reduction (-1.53 V), the polymer HOMO level is at -5.568 eV and the LUMO level is at -3.188 eV for the polymer backbone, therefore the electrochemical band gap of the polymer is 2.38 eV, which is between **(P1)** and **(P2)**.

Table 3. Electrochemical data from CV measurements of (P1), (P2) and (P3)

Polymers	$[O]_1$ (V)	$[R]_1$ (V)	$[R]_2$ (V)		HOMO (eV)	LUMO (eV)	E_g (eV)
	$E_{1/2}$ (V)	$E_{1/2}$ (V)	E_{pa} (V)	E_{pc} (V)			
P1	0.81	-1.67	-	-1.94	-5.378	-3.098	2.28
P2	0.95	-1.59	-	-1.92	-5.578	-3.148	2.43
P3	0.86	-1.64	-	-1.94	-5.568	-3.188	2.38

The comparison of the photophysical and electrochemical properties of (P1), (P2) and (P3) to three analogous reported polymers, PCDTBT [19], PF-CDTBT [20] and PFDTBT [21] (Figure 10), which have thiophene units instead of vinylene units, indicates that the vinylene-based polymers display higher optical and electrochemical band gaps than those of thiophene-based polymers. However, the linkage between carbazole or fluorene repeat units and benzothiadiazole *via* vinylene groups can support polymer solubility and planarity but not the conjugation system through the polymer backbone (Table 4).



PCDTBT

PF-CDTBT

PFDTBT

Figure 10. Three analogous reported polymers, PCDTBT, PF-CDTBT and PFDTBT

Table 4. Optical and electrochemical energy gaps of P1, P2 and P3 with their analogues polymers

Polymer	$E_{g(op)}$ /eV	$E_{g(elec)}$ /eV
P1	1.91	2.28
PCDTBT	1.88	1.93
P2	2.00	2.43
PF-CDTBT	1.73	1.79
P3	2.00	2.38
PFDTBT	1.86	1.90

3.4 Thermal properties of (P1), (P2) and (P3)

Thermo-gravimetric Analysis (TGA)

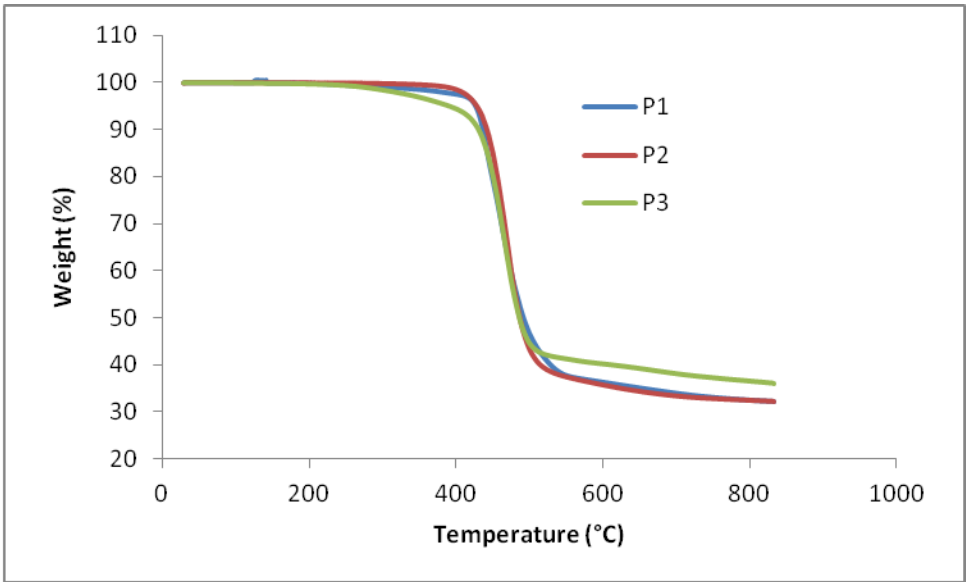


Figure 11. The TGA thermgram of (P1), (P2) and (P3)

Figure 11 shows the TGA curves of the thermal degradation of the polymers **(P1)**, **(P2)** and **(P3)**. The polymers **(P1)** and **(P2)** display very close onset degradation temperature and weight loss. The onset degradation of **(P1)** occurs at 447 ˚C, with a weight loss of 67.9 %, **(P2)** shows one degradation occurs at 438 ˚C and the weight loss at 800 ˚C is 67.6 %. The percentage of the weights loss of **(P1)** and **(P2)** are consistent with percentage weight of two alkyl chains, the two vinylene groups and benzothiadiazole. The onset degradation of **(P3)** occurs at 433 ˚C, with a weight loss of 64.0 %, which is lower than other and originated from the elimination of the two alkyl chains, the two vinylene groups and benzothiadiazole. The TGA analysis confirms that the polymers have a high thermal stability up to 400 ˚C.

Differential Scanning Calorimetry (DSC) analysis

Table 5 summarises the results from the thermo gravimetric analysis (TGA) and the differential scanning calorimetry (DSC). The polymers were subjected to a first heating run, cooling run followed by a further heating run, at the scan rate of 10 ˚C/ minute, and when no T_g was seen, 20 up to 100 ˚C/ minute rates was applied. The glass transitions (T_g) values were estimated and obtained from the first scans as broad peaks, they were above 50 ˚C indicating that all polymers have good tolerance to the stages required in making devices.

Table 5. Summary of the thermal properties of P1, P2 & P3, displaying TGA analysis showing the onset degradation temperature and DSC analysis showing the glass transition (Tg)

Polymers	TGA Analysis		DSC Analysis
	Onset degradation temp. / ˚C	Weight loss at 800 ˚C (wt. %)	T_g / ˚C
P1	447	67.9	73
P2	438	67.6	72
P3	433	64.0	67

4. CONCLUSION

Three vinylene-benzothiadiazole-based copolymers **(P1)**, **(P2)** and **(P3)** were prepared successfully *via* Suzuki cross coupling reactions and gave high degrees of polymerisation. However, the photophysical and electrochemical properties of these materials show that their optical and electrochemical band gaps are higher than those of thiophene containing copolymers. This indicates to that the linkage between carbazole or fluorene repeat units and benzothiadiazole *via* vinylene groups can support polymer solubility but not the same degree of electronic delocalisation along the polymer backbone. **(P2)** has the highest optical and electrochemical band gaps among this series of polymers because of the electrostatic interaction between the close hydrogens on vinyl groups and the fluorine substituents on the neighbouring carbazole was not strong enough and did not lead to more planar and higher electronic conjugation like observed in the previous set of polymers.

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