

Synthesis and Characterization of novel Thiophene and Carbazole-based Polymers – Optical and Electrochemical Characterization

Abdulaziz Ali B. Alghamdi^{1,*}, Abdelqader Imragaa², Essam S. Abdel-Halim^{1,3} and Ahmed Iraqi⁴

¹ Department of Chemistry, King Saud University, PO Box 2455, Riyadh 11451, Saudi Arabia.

² Department of Chemistry, University of Benghazi, Benghazi, Libya.

³ Textile Research Division, National Research Center, Dokki, Cairo, Egypt.

⁴ Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK.

*E-mail: aalghamdia@KSU.EDU.SA

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A donor/acceptor series of carbazole copolymers, composed of alternating 2,7-linked 3,6-difluoro-9-(1-octyl-nonyl)-carbazole units and bithiophene repeated units [P1], 5,7-bis(5-bromothiophen-2-yl)-2,3-bis(4-(2-ethylhexyloxy) phenyl) thieno[3,4-b]pyrazine repeated units [P2] and bithiophene mixed with 5,7-bis(5-bromothiophen-2-yl)-2,3-bis(4-(2-ethylhexyloxy) phenyl) thieno[3,4-b]pyrazine repeated units [P3] have been prepared following Suzuki polymerisation procedures. The route of synthesis and characterisation techniques of this novel class of materials, together with their photo-physical and electrochemical properties are presented in this study. The polymers were characterised by ¹H NMR, ¹³C NMR and Elemental Analysis. Molecular weights were estimated using gel permeation chromatography (GPC). The thermal stability behaviour for polymers was investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The electronic and photo-physical properties were investigated by use of cyclic voltammetry (CV) and UV-Vis spectroscopy, respectively.

Keywords: Organic solar cell, Conjugated polymer, Band gap

1. INTRODUCTION

Research in organic materials for application in organic solar cells has increased in recent years. Organic solar cells have many advantages when compared with inorganic solar cells. The organic solar cells offer low cost, flexible substrates, very high speed of processing. The focus of the

work in this study is development and characterisation the new low band gap polymer. These low band gap polymers can then be mixed with fullerenes derivatives such as PCBM to make bulk heterojunction device [1-8]. The polymer-bulk hetero-junction solar cells are basically composed of electron-acceptor molecules, like fullerenes and electron-donator conjugated polymers. These solar cells are promising as relatively low-cost flexible and portable photovoltaic devices. Recently, organic solar cells, which utilize conjugated polymers have attracted great attention due to their low processing cost, superior electronic properties, their thin-film flexibility, versatility and ease of processing techniques. All aforementioned factors confirm that organic solar cell, although currently its power conversion efficiency is to some extent low (~7%) [9-12], when compared with the inorganic solar cells, still organic solar cells have great potential to be strong competitor in the future trend of solar cell technology. In order for the utilization of organic solar cells to be economically feasible, their power conversion efficiencies still need more improvement, which is expected to be the subject of extensive research worldwide during the next decades.

The power conversion efficiency of the Bulk heterojunction solar cells which made from a mixture of conjugated polymer as electron donor and soluble fullerene derivatives as acceptor has increased from about 1% to over 11% during 15 years [13]. The first certified reported conjugated polymer was poly-3-hexylthiophene with efficiency about 3% [14]. Recently, several new reported conjugated polymers give efficiencies in the range 9% to 11% when made as a blend with suitable fullerene acceptors [15-17].

In this study we present synthesis routes for the preparation of low band-gap semiconductor materials, based on donor/acceptor alternating copolymers composed of 2,7-linked carbazole units with bithiophene repeated units and 5,7-bis(5-bromothiophen-2-yl)-2,3-bis(4-(2-ethylhexyloxy) phenyl) thieno[3,4-b]pyrazine repeated units. We present also the results we got from the characterisation of these semiconductor materials, as well as discussion for their electrochemical and optical properties.

2. EXPERIMENTAL SECTION

2.1 Chemicals

All the chemicals used in this study were purchased from Sigma-Aldrich and were used as such without any further purification. All reactions involved in this study were performed in inert atmosphere under either argon or nitrogen.

2.2 Measurements

Nuclear magnetic resonance analysis (NMR) of the prepared samples was carried out by use of Bruker 250 MHz, AMX400 400 MHz NMR spectrometers at 22 °C, using chloroform-d solution with TMS as an internal standard. For GPC analysis, 2.5 mg cm⁻³ solutions of the polymer in tetrahydrofuran (THF) were prepared and used as the test samples. The system was calibrated by use

of a series of polystyrene narrow standards and the GPC curves were performed by the RI detection method. CHN elemental analysis for the synthesized compounds was performed by use of a Perkin Elmer 2400 CHN Elemental Analyzer and the anion analysis was carried out by the Schöniger oxygen flask combustion method. UV–visible absorption spectra of the prepared compounds were recorded by use of a Hitachi U-2010 Double Beam UV/Visible Spectrophotometer. Spectrophotometric grade dichloromethane was used to prepare the polymers solutions for the UV absorbance measurements. The UV measurements were recorded at ambient temperature in rectangular quartz cuvettes, in which the light path length is 10 mm. For recording UV–visible absorption spectra of pristine polymer, thin-film samples were prepared by the dip coating of quartz plates in pristine polymer solution in HPLC-grade dichloromethane (1 mg cm^{-3}).

Potentiostat/Galvanostat (Princeton Applied Research model 263A) was used to record the cyclic voltammograms, carrying out the measurements at $25 \text{ }^\circ\text{C}$ under argon atmosphere. The used electrolyte solution was tetrabutylammonium tetrafluoroborate (10 cm^3) in acetonitrile (0.1 mol dm^{-3}). Three-electrode system composed of Ag/Ag⁺ reference electrode, platinum working electrode and platinum counter electrode was used in these measurements. Drop casting of polymer solutions in dichloromethane, followed by air drying was used to prepare polymer thin films onto the working electrode surface. Perkin Elmer Pyris 1 Differential Scanning Calorimeter, equipped with Perkin Elmer CCA7 Subambient Accessory was used to record the DSC curves in this study, the measurements were carried out under nitrogen atmosphere at a scan rate of $10^\circ\text{C}/\text{min}$. Perkin Elmer TGA-7 Thermogravimetric Analyser was used to record the TGA curves in this study. The measurements were carried out under nitrogen, at a scan rate of $10^\circ\text{C}/\text{minute}$. Optical band gaps E_g^{opt} (eV) were evaluated from the UV/Vis absorption spectra, where the wavelengths λ of the absorption onset was substituted in the equation: $[E_g \text{ (eV)} = 1240 / \lambda^{\text{abs}}_{\text{onset}} \text{ (nm)}]$. Electrical band gaps E_g^{ec} (eV) were evaluated from the cyclic voltammogram graphs (CV), where the onset of the oxidation potential E_{ox} and the onset of the reduction potential E_{red} , were substituted in the formula: $[E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.8) \text{ (eV)}]$ and the formula $[E_{\text{LUMO}} = -e(E_{\text{red}} + 4.8) \text{ (eV)}]$. The electrical band gap E_g^{ec} (eV) is obtained from the difference between E_{HOMO} and E_{LUMO} .

2.3 Synthesis

2,7-Dibromo-3,6-difluoro-9-(heptadecan-9-yl)-9H-carbazole (1)

2,7-Dibromo-3,6-difluoro-9-(heptadecan-9-yl)-9H-carbazole (**1**) was synthesized using the modified procedure described by Leclerc et al [18]. Pre-synthesized 2,7-Dibromo-3,6-difluoro-9H-carbazole [19-21] (4.97g, 0.013mol) and KOH powder (3.85 g, 0.067 mol) were dissolved in dried DMSO (60 cm^3). A solution containing 9-Heptadecane-p-toluenesulfonate (8.48 g, 0.020 mol) in (26 cm^3) of dry DMSO was added dropwise very slow (over 2 hour). The mixture was stirred at room temperature for 6 hours, after which, the reaction mixture was added onto distilled water (300 cm^3) and the resulting mixture was extracted three times with hexane (300 cm^3 each). The organic layer was left to dry over MgSO_4 and then the solvent was removed by drying in vacuum oven. The dry product was purified by column chromatography (silica gel, hexane) to give 2,7-Dibromo-3,6-difluoro-9-

(heptadecan-9-yl)-9H-carbazole (**1**) as a white solid (5.90 g, 75.71 % yield). The product was observed to give a single spot on TLC ($R_f = 0.43$ in 100% hexane), m.p. 78 °C. Mass (EI); (m/z): 597,599,601 ($M^{•+}$). 1H -NMR ($CDCl_3$); δH / ppm: 7.75 (bm, 2H); 7.57 (d, 2H); 4.39 (m, 1H); 2.18 (bm, 2H); 1.92 (bm, 2H); 1.21 (bm, 20H); 0.95 (bm, 4H); 0.85 (t, 6H). ^{13}C -NMR ($CDCl_3$); δC / ppm: 153.99 (2C); 139.49 (2C); 135.85 (1C); 122.56 (1C); 121.34 (1C); 115.58 (1C); 113.36 (1C); 107.42 (1C); 106.85 (2C); 57.32 (1C); 33.54 (2C), 31.72 (2C); 29.24 (4C); 29.08 (2C); 26.69 (2C); 22.59 (2C); 14.02 (2C). The Calculated Elemental Analysis values, (%) for $C_{29}H_{39}NF_2Br_2$: C, 58.11; H, 6.56; N, 2.34; Br, 26.66. The Found values, (%) were: C, 58.17; H, 6.59; N, 2.25; Br, 26.52.

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

The synthesis of 3,6-Difluoro-9-(1-octyl-nonyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**2**) was also carried out according to the modified procedure described by Leclerc *et al* [18]. Mixture of 2,7-Dibromo-3,6-difluoro-9-(1-octyl-nonyl)-9H-carbazole (**1**) (4 g, 6.67 mmol), bis(pinacolato)diboron (5.93 g, 23.34 mmol), potassium acetate (3.92 g, 39.94 mmol) and $Pd(dppf)Cl_2$ (0.32 g, 0.39 mmol) in 100 cm^3 DMF was heated to 100 °C for 36 hours then cooled down to room temperature. Then poured into H_2O (100 cm^3) and extracted with diethyl ether (3 \times 100 cm^3). The diethyl ether layer was separated and washed twice with distilled water (100 cm^3 each), and then dried over anhydrous $MgSO_4$. The dried product was purified by the recrystallization technique, by dissolving it in the smallest amount of acetone, then precipitating in hot methanol. The precipitate was collected by filtration and dried under vacuum to give 3,6-Difluoro-9-(1-octyl-nonyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**2**) as light brown solid (3.50 g, 87.5% yield) Melting point: 139-142 °C. Mass (EI); (m/z): 693, 694 ($M^{•+}$) (calculated for $C_{41}H_{63}B_2NF_2O_4$: 693.56). 1H NMR ($CDCl_3$) δH /ppm: 0.83 (t, 6H, $J = 6.59$ Hz); 0.90-0.97 (m, 4H); 1.11-1.29 (b, 20H); 1.45 (s, 24H); 1.94 (bm, 2H); 2.28 (bm, 2H); 4.62 (m, H); 7.56 (b, 2H); 7.67 (d, H, $J = 8.79$); 7.89 (b, H). ^{13}C NMR ($CDCl_3$) δC /ppm: 14.01(2C); 22.56(2C); 24.58(4C); 24.84(4C); 26.60(2C); 29.14(2C); 29.34(2C); 31.71(2C); 32.72(2C) 33.81(2C); 56.53(1C); 83.86(4C); 105.76(1C); 114.65(1C); 116.51(1C); 118.97(1C); 124.33(1C); 123.77(1C); 126.30(1C); 127.74(1C); 136.05(1C); 139.44(1C); 159.83(1C) (d, $J_{C-F} = 293.92$ Hz); 161.74(1C) (d, $J_{C-F} = 239.92$ Hz). The Calculated Elemental Analysis values, (%) for $C_{41}H_{63}B_2NF_2O_4$ were: C, 71.00; H, 9.16; N, 2.02. The Found values (%) were: C, 70.93; H, 9.26; N, 1.88.

5, 5'-Bis(tri-n-butylstannyl)-2, 2'-bithiophene (3)

Synthesis of 5, 5'-Bis(tri-n-butylstannyl)-2, 2'-bithiophene (**3**) was obtained using a procedure by Joussemme *et al* [22]. A solution of 2,2'-bithiophene (2.00 g, 12.02 mmol) in THF (80 mL) was cooled to -78°C and 1.6 M solution of *n*-butyllithium (15.6 mL, 24.96 mmol) was then added by the drop-wise. The mixture was warmed up to room temperature and stirred. After 1 h Tri-*n*-butyltin chloride (6.6 mL, 24.4 mmol) was added dropwise and the mixture was reflux for 1 hour then cooled down to room temperature, hexane (300 mL) the organic phase was washed with an aqueous sodium bicarbonate solution (5%, 80 mL) then water (80 mL) and then dried over anhydrous $MgSO_4$. The solvent was removed by drying in vacuum oven to give the product in the form of oily material, which was further purified by use of silica gel column chromatography 50:1 petroleum ether / triethylamine.

5,5'-Bis(tri-*n*-butylstannyl)-2,2'-bithiophene (**3**) was obtained as yellow oil (8.46 g, 94.47% yield). Mass (EI); (m/z): 742, 744 (M^{•+}) (calculated for C₃₂H₅₈S₂Sn₂: 744.35). ¹H NMR (CDCl₃) δH/ppm: 0.93 (t, 18H, J = 7.34 Hz); 1.14 (t, 12H, J = 8.20 Hz); 1.38 (m, 12H); 1.60 (m, 12H); 7.08 (d, 2H, J = 3.17 Hz); 7.34 (d, 2H, J = 3.43 Hz). ¹³C-NMR: (CDCl₃) δ_C/ppm: 10.87 (6C), 13.65(6C), 27.25 (6C), 28.95 (6C), 124.69 (2C), 136.05 (4C), 143.04 (2C). The Calculated Elemental Analysis values, (%) for C₃₂H₅₈S₂Sn₂ were: C, 51.63; H, 7.85; S, 8.62. The Found values, (%) were: C, 52.14; H, 8.17; S, 8.72.

5,5'-Dibromo-2,2'-bithiophene (**4**)

Synthesis of 5,5'-Dibromo-2,2'-bithiophene (**4**) was carried out using the procedure described by Chen *et al* [23]. To a solution of [2,2']Bithiophenyl (9.96g, 44.4 mmol) in DMF (100 cm³), N-bromosuccinimide (16.67g; 93.66 mmol) was added at 0 °C. After stirring in the dark for 30 min, the mixture was warmed up to room temperature and stirring for 1 hour. The solution was kept under continuous stirring overnight, at room temperature and was then poured over 600 cm³ distilled water. This was followed by extraction in ethylene chloride (3 × 300 cm³) and washing the organic extracts with water (3 × 300 cm³). Finally, the product was dried over anhydrous magnesium sulphate and the solvent was removed by drying in vacuum oven to give the 5,5'-Dibromo-2,2'-bithiophene (**4**) as pale light yellow crystal (15.42 g; yield 91%). Melting point: 143-146 °C. Mass (EI); (m/z): 322, 324, 326 (M^{•+}) (calculated for C₈H₄S₂Br₂: 324.06). ¹H NMR (CDCl₃) δH/ppm: 6.8 (d, 2H); 6.9 (d, 2H). ¹³C-NMR: (CDCl₃) δ_C/ppm: 111.54; 124.16; 130.68; 137.79. The Calculated Elemental Analysis values, (%) for C₈H₄Br₂S₂ were: C, 29.65; H, 1.24; Br, 49.32; S, 19.79. The Found values, (%) were: C, 29.65; H, 0.99; Br, 49.04; S, 19.70.

5,7-bis(5-bromothiophen-2-yl)-2,3-bis(4-(2-ethylhexyloxy)phenyl)thieno[3,4-*b*]pyrazine (**5**)

Synthesis of 5,7-bis(5-bromothiophen-2-yl)-2,3-bis(4-(2-ethylhexyloxy)phenyl)thieno[3,4-*b*]pyrazine (**5**) was performed according to the procedure by Mammo *et al* [24]. The synthesized previously 5,5'-Dibromo-3',4'-dinitro-2,2':5'2''-terthiophene [17-18](2.5 g, 5.04 mmol), iron powder (2.81 g, 50.4 mmol) and glacial acetic acid (150 mL) were mixed and heated at 60 °C for 1 h. The mixture was then cooled to room temperature. The synthesized previously 1,2-bis[4-(2-ethylhexyloxy)phenyl]ethane-1,2-dione [18] (2.6 g, 5.55 mmol) was added and the mixture was heated at 60 °C for 5 h. The formed precipitate was filtered off and washed with water and MeOH. Since, the crude product contained traces of side products; it was purified by flash chromatography over silica gel using toluene as eluent and recrystallized from ethanol. The purity was examined using thin-layer chromatography on silica gel with mixture of DCM and petroleum ether (1:4) as the eluent. Residue was Soxhlet extracted with ethanol to give 5,7-bis(5-bromothiophen-2-yl)-2,3-bis(4-(2-ethylhexyloxy)phenyl)thieno[3,4-*b*]pyrazine (**5**) as red-greenish solid (2.20 g, 54.29%). Melting point: 202-204°C. Mass (EI); (m/z): 864, 866, 868 (M^{•+}) (calculated for C₄₂H₄₆Br₂N₂O₂S₃: 866.83). ¹H NMR (CDCl₃) δH/ppm: 0.85-0.95 (12H, m), 1.35-1.61 (16H, m), 1.75-1.83 (2H, m), 3.90(4H, d), 6.90 (4H, d), 7.05 (2H, d), 7.28 (2H, d), 7.57 (4H, d). ¹³C NMR (CDCl₃) δ_C/ppm: 160.51(2C), 153.10(2C), 137.51(2C), 136.17(2C), 131.48(2C), 131.08(4C), 129.75 (4C), 123.68 (2C), 123.47 (2C), 114.36(4C), 114.21 (2C), 70.61(2C), 39.37(2C), 30.53(2C), 29.10(2C), 23.86(2C), 23.06(2C), 14.11(2C),

11.14(2C). The Calculated Elemental Analysis values, (%) for $C_{42}H_{46}Br_2N_2O_2S_3$: C, 58.19; H, 5.35; N, 3.23; Br, 18.44; S, 11.10. The Found values, (%) were: C, 57.77; H, 5.15; N, 3.15; Br, 16.08; S, 11.74.

2.4 Synthesis of the Polymers

Poly [N-(2-heptadecanyl)-3,6-difluoro-2,7-carbazole-alt-2,2'-(5,5'-bithienylene)] (P1)

Poly [N-(2-heptadecanyl)-3,6-difluoro-2,7-carbazole-alt-2,2'-(5,5'-bithienylene)] (P1) was synthesized according to the modified procedure described by Wakim et al [25]. Toluene (10 mL) was added to a mixture composed of 2,7-Dibromo-3,6-difluoro-9-(heptadecan-9-yl)-9H-carbazole (1), (0.599 g, 1 mmol); 5,5'-bis(tri-*n*-butylstannyl)-2,2'-bithiophene (3), (0.744g, 1 mmol); tri(*o*-tolyl)phosphine, (0.0244 g, 0.08 mmol) and tris(dibenzylideneacetone)dipalladium(0), (0.018 g, 0.0244mmol). The solution was heated to 95°C for 92 hours, then cooled down to room temperature and add (0.37 g, 0.99 mmol) 2-(tributylstannyl)-thiophene were added. The mixture was then refluxed for 2.5 hours before bromobenzene (0.0313 g, 1.99 mmol) was added. The mixture was heated to reflux for 2 hours, before toluene (10 cm³) and CHCl₃ (16 cm³) were added and the mixture kept at 60 °C to solubilise the polymer. The hot solution was precipitated in methanol (500 cm³) under a nitrogen atmosphere and the precipitate was filtered and subjected to soxhlet extraction for 24 hours with methanol, 24 hours with acetone and 18 hours with hexane. It was then extracted with CHCl₃ and the chloroform solution concentrated to 30 cm³ and the polymer precipitated in methanol. The the polymer was collected by filtration and dried under vacuum to give orange solid (0.313 g, 52.5 % Yield). $M_n=7200$ $M_w=10900$; PD=1.51. ¹H NMR (CDCl₃), δ_H /ppm: 7.75(s, 2H); 7.60(d, 2H); 7.50(s, 2H); 7.36(d, 2H); 4.58(b, H); 2.37(m, 2H); 2.05(m, 2H); 1.09-1.37(m, 24H); 0.82(m, 6H). The Calculated Elemental Analysis values, (%) for $C_{37}H_{42}NF_2S_2$ were: C, 73.59; H, 7.18; N, 2.32; S, 10.62; Br, 0. The Found values, (%) were: C, 72.24; H, 6.93; N, 2.16; S, 11.03; Br, 0.

Poly[3,6-difluoro-9-(1-octyl-nonyl)-9H-carbazole-2,7-diyl-alt-(5',7'-di-2-thienyl-2',3'-bis-[4-(2-ethylhexyloxy)-phenyl]-thieno[3,4-b]pyrazine)-5,5-diyl] (P2)

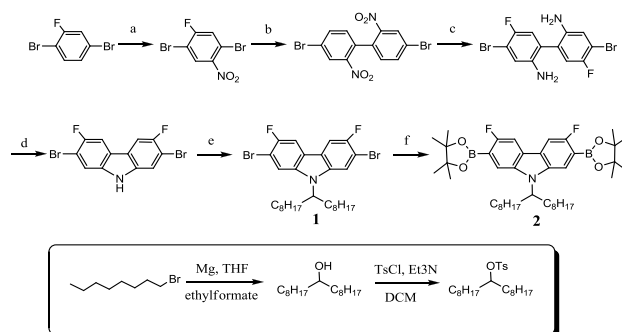
To a mixture of 3,6-difluoro-9-(1-octyl-nonyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (2), (0.30 g, 0.43 mmol) and 5,7-bis(5-bromothiophen-2-yl)-2-(4-(2-ethylheptyloxy)phenyl)-3-(4-(2-ethylhexyloxy)phenyl)thieno[3,4-b]pyrazine (5), (0.38 g, 0.43 mmol) in dry THF 10 cm³, Pd(AcO)₂, (7.92 mg, 0.04 mmol) and tri-*o*-tolylphosphine (32.21 mg, 0.1 mmol) were added and the reaction mixture was stirred for 10 minutes under argon atmosphere. NaHCO₃ solution (1.65 cm³, 20 wt% in water), deoxygenated for 4 hours with argon was added. The mixture was refluxed for 24 hour under argon atmosphere before it was cooled down to room temperature to add bromobenzene (0.10 cm³, 0.95 mmol). The mixture was kept under reflux for 3 hours before adding (0.10 g, 0.82 mmol) phenyl boronic acid and keeping the mixture under continuous reflux overnight. The reaction mixture was allowed to cool to room temperature; and the solution was precipitated in (500 cm³) (10:1) methanol/water mixture. The precipitation mixture was kept under continuous stirring overnight, before it was filtered to separate the polymer. The precipitated polymer was dissolved in chloroform (50 cm³) and then extracted with ammonia solution. Ammonia solution

(50 ml, 35%) was added and the mixture was stirred overnight. The chloroform solution was separated and then washed with ammonia solution and then with distilled water (2×50 ml) by stirring for 2 hour. The organic layer was concentrated and again precipitated in methanol (500 mL) under a nitrogen atmosphere. The solid yield was purified by Soxhlet extraction for 24 hours with methanol, 24 hours with acetone, 18 hours with hexane and 24 hour with toluene. It was then extracted with CHCl_3 , the chloroform and toluene solution concentrated to 20 ml and the polymer precipitated in methanol. The green solid was collected by filtration and dried under vacuum to give (0.45g, 92.54 % Yield). $M_n = 6600$ $M_w = 12000$; PD = 1.82. ^1H NMR (400MHz, CDCl_3), $\delta_{\text{H}}/\text{ppm}$: 7.82 (bs, 2H); 7.70 (m, 2H); 7.62 (bm, 6H); 7.54 (bm, 2H); 6.94 (d, 4H, $J=6.8$ Hz); 4.60 (m, H); 3.92 (m, 4H); 2.38 (m, 2H); 2.01 (m, 2H); 1.78 (m, 2H); 1.55-1.26 (bm, 24H); 1.16-1.07 (bm, 16H); 0.97-0.94 (bm, 12H); 0.81 -0.72 (m, 6H). ^{13}C NMR (CDCl_3), $\delta_{\text{C}}/\text{ppm}$: 11.14; 14.02; 14.10; 22.58; 23.06; 23.87; 26.83; 29.13; 29.33; 30.54; 31.74; 33.98; 39.36; 56.84; 70.62; 95.45; 107.03; 4.15; 121.36; 123.56; 124.16; 125.56; 125.72; 127.54; 128.91; 131.49; 134.42; 135.09; 137.80; 144.82; 152.61; 154.59 ; 160.32. The Calculated Elemental Analysis values, (%) for $\text{C}_{71}\text{H}_{85}\text{N}_3\text{F}_2\text{S}_3\text{O}_2$ were: C, 74.37; H, 7.47; N, 3.66; S, 8.39; Br, 0. The Found values, (%) were: C, 73.34; H, 6.99; N, 3.39; S, 8.98; Br, 0.

Poly[3,6-difluoro-9-(1-octyl-nonyl)-9H-carbazole-2,7-diyl-alt-2,3-bis(4-(ethyl-hexyloxy)-phenyl)-7-bithiophen-5-yl][3,4-b]pyrazine-5,5'-diyl] (P3) [2:4:5] [1:0.5:0.5] (P3)

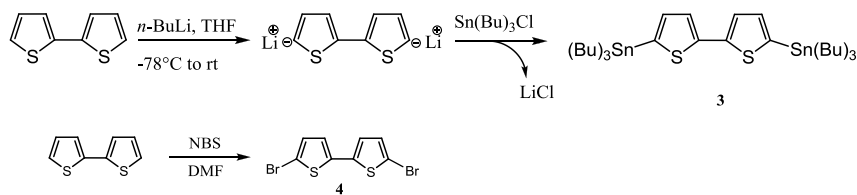
To a mixture of 3,6-difluoro-9-(1-octyl-nonyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**2**), (0.30 g, 0.43 mmol); 5,7-bis(5-bromothiophen-2-yl)-2-(4-(2-ethylheptyloxy)phenyl)-3-(4-(2-ethylhexyloxy)phenyl)thieno[3,4-b]pyrazine (**5**), (0.187 g, 0.216mmol) and 5,5'-dibromo-2,2'-bithiophene (**4**), (0.069g, 0.216mmol) in dry THF 10 cm^3 , a mixture of $\text{Pd}(\text{AcO})_2$ (7.92 mg, 0.04 mmol) and tri-*o*-tolylphosphine (32.21 mg, 0.1 mmol) was added and the whole reaction mixture was stirred for 10 mins under argon atmosphere. NaHCO_3 solution (2.00 cm^3 , 20 wt% in water), deoxygenated for 4 hours with argon was added. The mixture was refluxed for 24 hour under argon atmosphere before it was cooled down to room temperature to add bromobenzene (0.10 cm^3 , 0.95 mmol). The mixture was kept under reflux for 3 hours before adding (0.10 g, 0.82 mmol) phenyl boronic acid and keeping the mixture under continuous reflux overnight. The reaction mixture was allowed to cool to room temperature; and the solution was precipitated in (500 cm^3) (10:1) methanol/water mixture. The precipitation mixture was kept under continuous stirring overnight, before it was filtered to separate the polymer. The precipitated polymer was dissolved in chloroform (50 cm^3) and then extracted with ammonia solution. Ammonia solution (50 ml, 35%) was added and the mixture was stirred overnight. The chloroform solution was separated and then washed with ammonia solution and then with distilled water (2×50 ml) by stirring for 2 hour. The organic layer was concentrated and again precipitated in methanol (500 mL) under a nitrogen atmosphere [2]. The solid yield was purified by Soxhlet extraction for 24 hours with methanol, 24 hours with acetone, 18 hours with hexane and 24 hour with toluene. It was then extracted with CHCl_3 , the chloroform and toluene solution concentrated to 10 ml and the polymer precipitated in methanol. The green solid was collected by filtration and dried under vacuum to give (0.360g, 69.49% Yield). $M_n = 5000$, $M_w = 14200$; PD = 2.84. ^1H NMR (400MHz, CDCl_3), $\delta_{\text{H}}/\text{ppm}$: 7.88-7.43 (m, 20H); 6.95 (d, 4H, $J=6.8$ Hz); 4.61 (m, 2H); 3.92 (m, 4H); 2.35 (m, 4H); 2.01 (m, 4H); 1.79 (m, 2H); 1.60-1.18 (bm, 64H); 0.98-0.94

(bm, 12H); 0.84 -0.81 (m, 12H). ^{13}C NMR (500MHz, CDCl_3) $\delta_{\text{C}}/\text{ppm}$: 11.15, 14.02, 14.10, 22.59, 23.06, 23.88, 26.77, 29.13, 29.32, 30.55, 31.74, 32.74, 33.84, 39.42, 56.81, 70.59, 107.03, 110.09, 114.14, 121.31, 122.86, 124.55, 125.61, 127.27, 128.96, 131.53, 135.07, 136.09, 137.25, 137.63, 137.96, 139.94, 152.58, 154.77, 160.45. The calculated Elemental Analysis values, (%) for $\text{C}_{108}\text{H}_{128}\text{N}_4\text{F}_2\text{S}_5\text{O}_2$ were: C, 74.10; H, 7.37; N, 3.20; S, 9.16. The Found values, (%) were: C, 73.40; H, 7.19; N, 3.09; S, 11.60.

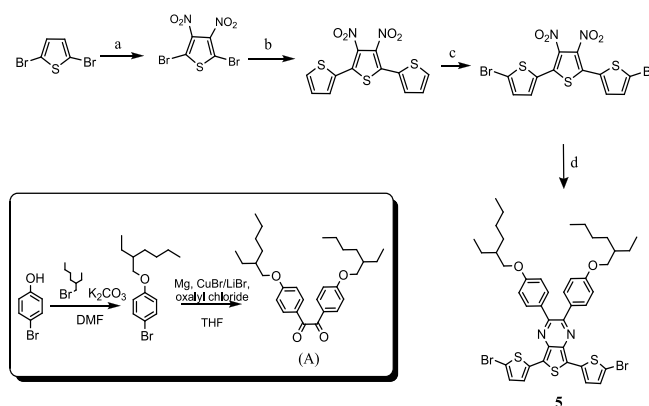


Scheme 1. Synthesis of Monomer 1 & 2

Reaction conditions: a) trifluoroacetic acid / trifluoroacetic anhydride, NH_4NO_2 and DCM; b) Cu / DMF; c) Sn / HCl / EtOH ; d) concentrated phosphoric acid; e) KOH / DMSO , 9-Heptadecane p-Toluenesulfonate; f) Bis(pinacolato)diboron, KOAc , DMF , $\text{Pd}(\text{dppf})\text{Cl}_2$.

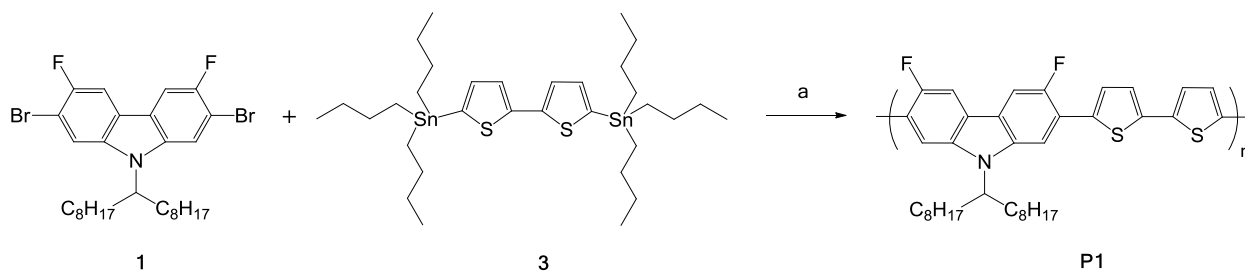


Scheme 2. Synthesis of Monomer 3 & 4

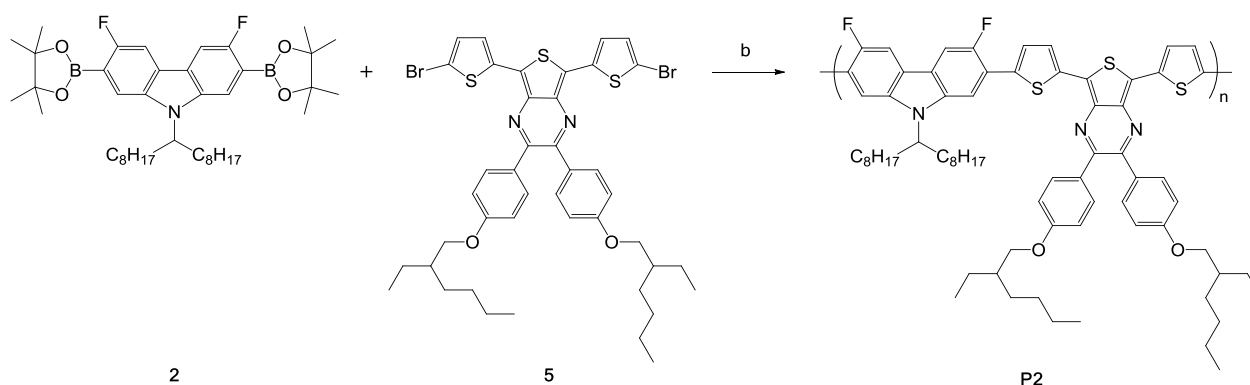


Scheme 3. Synthesis of Monomer 5

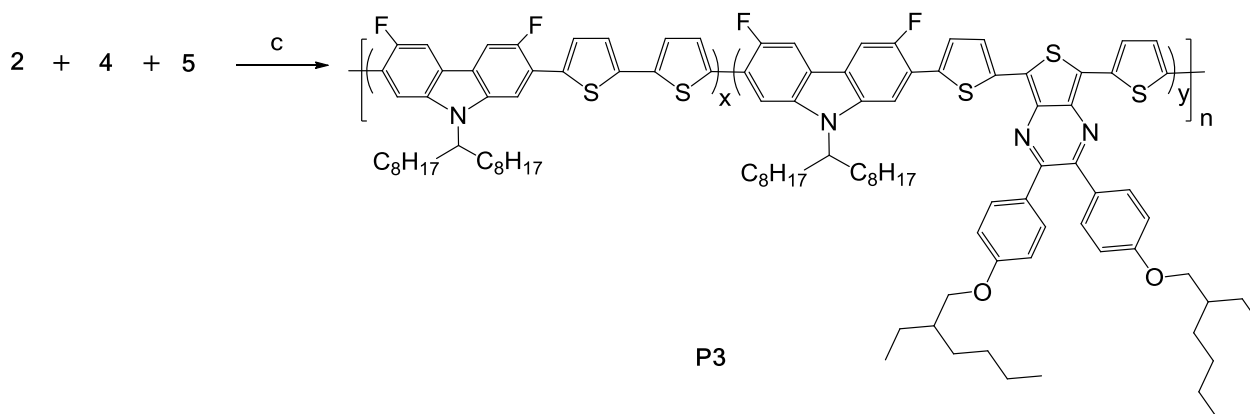
Reaction conditions: a) conc. H_2SO_4 / Fuming H_2SO_4 , Fuming HNO_3 ; b) $\text{PdCl}_3(\text{PPh}_3)_2$ /THF 2-(tributylstannyl)thiophene;; c) NBS/DMF; d) Fe, HAc, 1,2-bis[4-(2-ethylhexyloxy)phenyl] ethane-1,2-dione).



Scheme 4. Synthesis of Polymer 1



Scheme 5. Synthesis of Polymer 2



Scheme 6. Synthesis of Polymer 3

Polymerisation conditions: a) Toluene, $\text{P}(\text{o-tol})_3$, $\text{Pd}_2(\text{dba})_3$; b) THF, $\text{P}(\text{o-tol})_3$, $\text{Pd}(\text{AcO})_2$; c) THF, $\text{P}(\text{o-tol})_3$, $\text{Pd}(\text{AcO})_2$.

3. RESULTS AND DISCUSSION

3.1 Synthesis of the polymers

Poly [N-(2-heptadecanyl)-3,6-difluoro-2,7-carbazole-alt-2,2'-(5,5'-bithienylene)] **P1** was synthesized *via* Stille coupling polymerization according to the modified procedure described by Walkim et al [25]. The reaction was carried out in toluene as show in scheme 4. The reaction was left for 92 hours at reflux, before 2-(tributylstannyl)-thiophene and bromobenzene was added to end – capping reagent the polymer. More toluene and chloroform were added to dissolve the higher molecular weight, where it was not possible to precipitate the solution at room temperature, due to the polymer solubility in the cold solvent that is why the solution was precipitated while hot. The hot solution was precipitated in methanol to remove any palladium and unreacted monomer. The crude polymer obtained was the transferred into thimble and washed thoroughly in a soxhlet apparatus with different solvents. First, it was washed with methanol in order to remove any residual tributyl-tin end group, second washed with acetone and hexane to remove the small oligomer chains. The purified polymer was then extracted with chloroform and precipitated again in methanol.

GPC analysis gave the $M_w = 10,900$ and $M_n = 7,200$ with polydispersity index (PDI) value of 1.51 and degree of polymerisation (DP) value of 12. Poly[3,6-difluoro-9-(1-octyl-nonyl)-9H-carbazole-2,7-diyl-alt-(5',7'-di-2-thienyl-2',3'-bis-[4-(2-ethyl-hexyloxy)-phenyl]-thieno[3,4-b]pyrazine)-5,5-diyl] **P2** and Poly[3,6-difluor-9-(1-octyl-nonyl)-9H-carbazole-2,7-diyl-alt-2,3-bis(4-(ethyl-hexyloxy)-phenyl)-7-bithiophen-5-yl][3,4-b]pyrazine-5,5'-diyl] **P3** were prepared *via* Suzuki coupling polymerization [26], as show in scheme 5 and scheme 6. The Gel permeation chromatography results for the chloroform fractions (using polystyrene standards) have shown $M_w = 12,700$ and $M_n = 6,600$ for **P2** with a polydispersity 1.82 and $M_w = 14,000$ and $M_n = 5,000$ for **P3** with a polydispersity 2.84.

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

Polymer	Yield (%)	M_w	M_n	PDI	DP
P1	52.5	10900	7200	1.51	12
P2	92.5	12000	6600	1.82	6
P3	69.49	14200	5000	2.84	3

3.2 Thermal properties of P1-P3

The differential scanning calorimetry analysis (DSC) and thermogravimetric analysis (TGA) for **P1**, **P2** and **P3** are show in table 1. The glass transition (T_g) is a function of chain flexibility. In some applications that may experience extremely elevated temperature, it is essential to know how these polymers will be affected when they are exposed to variation in temperature and how this will alter the mechanical properties of such polymers. All polymers show T_g above 90 °C they should show a good tolerance to making devices for solar cell. All polymers exhibit similar degradation. The

degradation occurs at 457 for **P1**, **P2** at 418 and **P3** at 421 the TGA analysis confirm that the polymers are stable at high temperature. All the polymers the alkyl chain directly attached to the carbazole repeat units along polymer chains would be lost first and this corresponds well with percentage weight losses. In the case of **P2** and **P3** the slightly higher percentage loss can be attributed to the loss of the alkyl chains, attached directly to the carbazole as well as the alkoxy groups attached to the 5,7-bis(5-bromothiophen-2-yl)-2-(4-(2-ethylheptyloxy)phenyl)-3-(4-(2 ethylhexyloxy) phenyl)thieno [3,4-b]pyrazine.

Table 2. Summary of **P1**, **P2** and **P3** thermal properties, displaying DSC analysis showing the glass transition (T_g), and TGA analysis showing the onset degradation temperature

Polymer	DSC Analysis	TGA Analysis	
	T _g /°C	degradation T/°C	R _m /wt%
P1	115.4	457	47
P2	144.45	418	51
P3	95.36	421	52

3.3 UV-Visible absorption spectra

Figure 5 show the absorption spectra of **P1**, **P2** and **P3** in solution and figure 6 in solid state. The results of these studies are shown in table 2. For **P1** show two absorption bands at 454 nm and 521 nm in DCM and 459, 485 and 521 nm in the solid state. A slight shift of λ_{\max} from the solution and the solid is expected due to aggregation and formation of more planar structure in the solid state. This is expected, as the freedom of movement is reduced in thin film, causing less twisting of polymer chain, which leads in turn to a better overlap of P_z-orbital and to the observed red shift. The optical band gap of **P1** in solid state is 2.13 eV. **P1** having lower band gap due to more planar structure. Crouch et al [26] prepared series of thiophene copolymer; their work showed that the materials have higher electronic conjugation, the reasons for these results to their adoption of more planar in solid state.

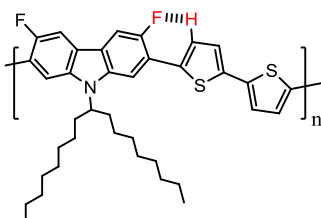


Figure 1. Displaying the H-F electrostatic interactions of **P1** leading to a more planar structure.

Single crystal X-ray studies revealed hydrogen-fluorine electrostatic interaction, it is therefore possible this type of interaction in **P1** (Figure 1). Comparing the absorption spectra of **P1** and those of the polyfluorene equivalent F6T2 [27] (Figure 2), which has absorption bands a λ_{\max} 456 nm a optical

band gap of 2.41 eV do also point to the fact that **P1** has a more extended electronic conjugation due to fluorine-hydrogen interactions.

In addition, the Comparison of photophysical properties of **P1** to another analogue polymer **PF-CDTBT** [28] (Figure 3) which has benzothiadiazole inserted between thiophene groups and its optical band gap was 1.73 eV which is lower than **P1** band gap due to that benzothiadiazole works as good acceptor units for electrons that come from the donor carbazole units, thus more conjugation.

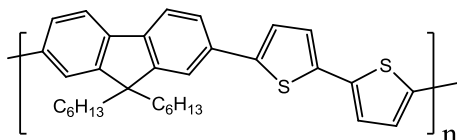


Figure 2. Structure of F6T2

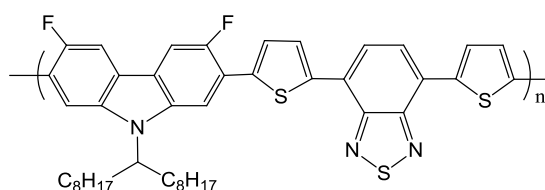


Figure 3. Structure of PF-CDTBT

The UV-Visible spectra (Figure 5,6) of **P2** shows two broad absorption peaks at λ_{\max} 448 nm and 658 nm in DCM solution and at λ_{\max} 456 and 727 nm in the solid state. From which the optical band gap was calculated to be 1.55 eV. When comparing **P2** with **P1** we can see how its absorption is red shifted. The alkoxy electron donating groups which are attached to the phenyl groups of the diphenyl-thieno[3,4-b] pyrazine repeat units might have been expected to reduce the electron accepting properties. The red shifted absorption of **P2** and its lower band gap could be explained by its higher weight average molecular weight when compared to that obtained for **P1**. Comparison of the absorption spectra of **P2** and those of the polyfluorene equivalent APFO-Green5 [29] (Figure 4) which has absorption bands a λ_{\max} 430 nm and 660 nm and a band gap of 1.6 eV do also point to the fact that **P3** has a more extended electronic conjugation due to fluorine-hydrogen interactions in **P2**.

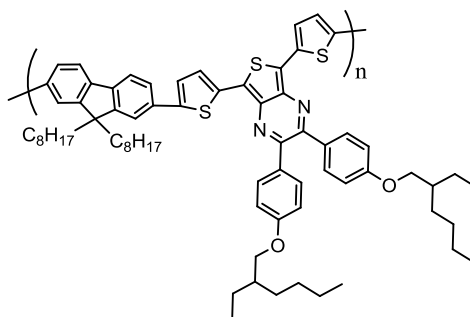


Figure 4. Structure of APFO Green 5

On the other hand, the Comparison of photophysical properties of **P2** to the other analogue polymer **PF-CDTBT** [28] which has benzothiadiazole instead of bis(ethylhexylphenyl)pyrazine

groups. The **PF-CDTBT** showed higher optical band gap (1.73 eV) comparing to 1.55 eV of the **P2**. This means that the bis(ethylhexylphenyl) units increase the electron acceptance, thus more conjugation along the polymer chain and lower optical band gap.

The UV-Visible spectra (Figure 5,6) of **P3** shows two broad absorption peaks at λ_{max} 445 nm and 640 nm in DCM solution and at λ_{max} 451 and 669 nm in the solid state. The red shift observed in the absorption spectra of polymer **P3**, when compared to that present in the absorption spectra of polymer **P1**, can be explained in terms of the alternation of acceptor units on polymer **P3** chain. This leads to relatively low band gap polymer estimated at $E_g = 1.62\text{eV}$ as is determined from its onset of absorption in the solid state. The blue shift presented in the absorption spectra of polymer **P3**, when compared to that presented in the absorption spectra of polymer **P2**, can also be interpreted in terms of the alternation of thiophene monomer on polymer **P3** leading to a relatively higher band gap polymer. The very close values of absorption maxima in the spectra of polymers **P2** and **P3** indicate the little differences in their structures.

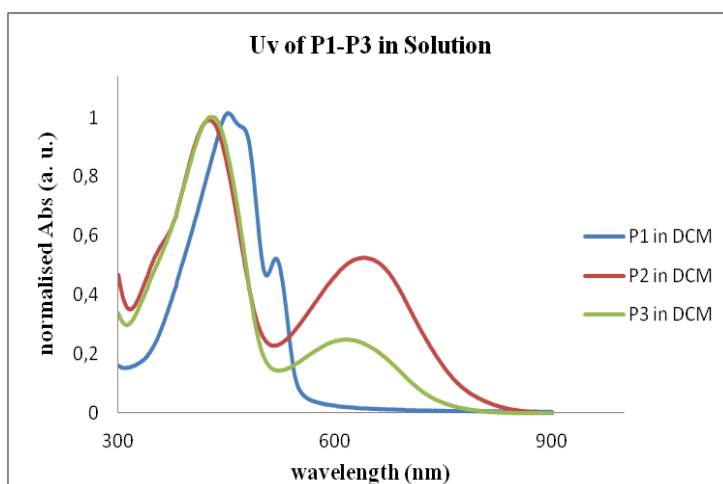


Figure 5. Normalised absorption spectra of **P1**, **P2** and **P3** in DCM (blue line-**P1**) , (brown line-**P2**) and (green line-**P3**).

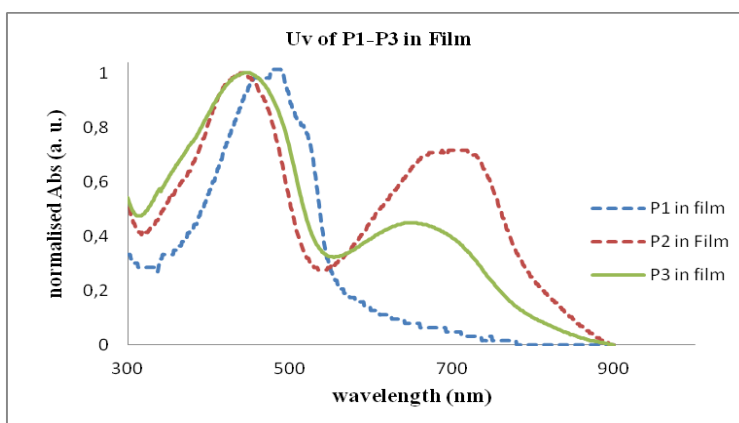


Figure 6. Normalised absorption spectra of **P1**, **P2** and **P3** in solid (blue line-**P1**) , (brown line-**P2**) and (green line-**P3**)

Table 3. UV-Vis data and Optical Band gap of **P1**, **P2** and **P3**

polymer	Absorption		E_g^{opt} (eV)
	λ_{max} (nm) (Solution)	λ_{max} (nm) (Film)	
P1	454, 521	459, 485, 521	2.13
P2	448, 658	456, 727	1.55
P3	457, 643	486, 468	1.62

3.4 Electrochemical studies

The studies of electrochemical properties of polymers were carried out on Princeton potentiostats/galvanostats 263A Electrochemical Workstation. A three-electrode setup, with platinum disc was used as the working electrode, platinum wire as the counter electrode and the used reference electrode was Ag /Ag⁺.

The cyclic voltammetry measurements were performed on drop-cast polymer film in solution of tetrabutylammonium perchlorate as the electrolyte and acetonitrile as the solvent. The lowest unoccupied molecular orbital; LUMO level (or the electron affinities EA) was evaluated from the onset reduction, while the highest occupied molecular orbital; HOMO level (or the ionization potentials IP) was evaluated from the oxidation respectively. The electrochemical band gap (E_g^{ec}) can be calculated from the difference between LUMO and HOMO levels. The electrochemical data of the investigated polymers are listed in Table 4 and the oxidation reduction cyclic voltammograms of both polymers are shown in Figure 7.

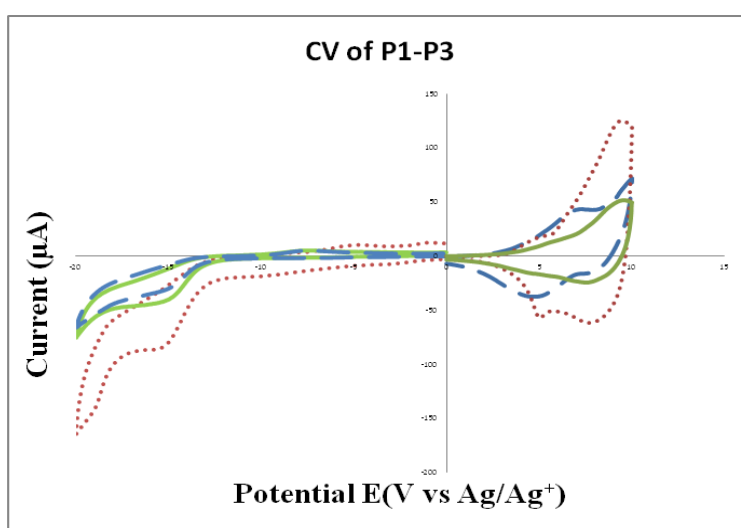


Figure 7. Cyclic voltammograms of polymer **P3** (solid line, green), **P1** (dashed line, blue) and **P2** (dashed line, brown) films cast on platinum disc (0.00314 cm^2) in $\text{Bu}_4\text{NPF}_6/\text{acetonitrile}$ at 100 mV/s .

The Cyclic voltammogram of **P1** exhibits an oxidation wave at anodic peak potential (E_{pa}) of +0.75 V and a reduction wave at $E_{pa} = -1.59$ V, and their associated reduction wave at cathodic peak potential (E_{pc}) of +0.46 V and oxidation waves at $E_{pc} = -1.25$ V. From the onset of oxidation (+0.64 V), the HOMO level is -5.36 eV and from the onset of reduction (-1.36 V), the LUMO level is -3.30 eV for **P1** (on the basis that ferrocenium/ferrocene has an $I_p = 4.8$ eV below the vacuum level, and the oxidation takes place at 0.082 V relative to Ag/Ag⁺), thus the electrochemical band gap of the polymer is 2.06 eV. The CV of **P2** exhibits an oxidation wave at $E_{pa} = +0.88$ V and a reduction wave at $E_{pa} = -1.51$ V, and their associated reduction wave at $E_{pc} = +0.76$ V and oxidation waves at $E_{pc} = -1.23$ V. From the onset of oxidation (+0.32 V), the HOMO level is -5.03 eV and from the onset of reduction (-1.24 V), the LUMO level is -3.48 eV, thus the electrochemical band gap of the polymer is 1.55 eV, which is the same of optical band gap, and lower than electrochemical band gaps of **P1** and **P3**, this decline in E_g indicates that the bis(ethylhexylphenyl)pyrazine units accept electrons better than the bithiophene units due to their electron-deficient nature.

The Cyclic voltammogram of **P3** also exhibits an oxidation wave at $E_{pa} = +0.97$ V and a reduction wave at $E_{pa} = -1.51$ V, and their associated reduction wave at $E_{pc} = +0.75$ V and oxidation waves at $E_{pc} = -1.32$ V. From the onset of oxidation (+0.40 V), the HOMO level is -5.11 eV and from the onset of reduction (-1.24 V), the LUMO level is -3.44 eV, thus the electrochemical band gap of the polymer is 1.67 eV, which comes between of those of **P1** and **P2** as expected, as shown in Table 4. The difference between optical and electrochemical band gaps is common in literatures; in many studies the electrochemical band gap is normally higher than the optical band gap [30].

Table 4. Electrochemical data of **P1**, **P2** and **P3**

	[O] (V)		[R] (V)		E_{ox} (V)	E_{red} (V)	HOMO (eV)	LUMO (eV)	E_g^{ec} (eV)
	E_{pa}	E_{pc}	E_{pa}	E_{pc}					
P1	+0.75	+0.46	-1.59	-1.25	+0.64	-1.38	-5.36	-3.30	2.06
P2	+0.88	+0.76	-1.51	-1.23	+0.32	-1.24	-5.03	-3.48	1.55
P3	+0.97	+0.75	-1.51	-1.32	+0.40	-1.28	-5.11	-3.44	1.67

The comparison of electrochemical properties of **P1** to its two analogous reported polymers, F6T2 and PF-CDTBT indicates that electrochemical band gap of **P1** is lower than that of F6T2 due to the presence of H-F electrostatic interactions, which increase the planarity of the polymer and the electrons conjugation. However, PF-CDTBT has lower electrochemical band gap (1.79 eV) which indicates that the bithiophene units were not a strong acceptor of electron [31], while the benzothiadiazole is one of the best comonomer with electron-deficient. [32] (Table 5).

On the other hand, the comparison of electrochemical properties of **P2** to its analogous polymers APFO-Green5 and PF-CDTBT indicates that it has the lowest band gap. this due to the H-F electrostatic interactions which support the planarity of the polymer and the presence of

bis(ethylhexylphenyl)pyrazine groups has an positive impact on the accepting of electrons as well as the solubility of the polymer [33] (Table 5).

Table 5. Optical and electrochemical energy gaps of **P1**, **P2** and **P3** with their analogues polymers

Polymer	E_g^{opt} (eV)	E_g^{ec} (eV)
P1	2.31	2.06
F6T2	2.41	2.89
PF-CDTBT	1.73	1.79
P2	1.55	1.55
APFO-Green5	1.60	2.00
PF-CDTBT	1.73	1.79
P3	1.62	1.67

4. CONCLUSION

Three novel conjugated polymers were synthesized, successfully via the Suzuki cross-coupling polymerisation technique. The electrochemical and photo-physical properties of the synthesized polymers show that **P2** has the narrowest band gap among other polymers, which still narrower than those of an analogous polymer APFO-Green5. This is due to the induced electrostatic interaction occurring between the fluorine substituents present in the carbazole repeated units and the hydrogen atoms present in position (4) of the neighbour thiophene rings. This assumption supports the planarity of these polymers and the presence of electronic conjugation along their polymeric chains. **P1** also has narrower band gap than those of an analogous polymer F6T2 due to the same reason. **P3** shows a bandgap comes between those of **P1** and **P2** as expected.

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