

## Research Article

# Synthesis and Characterization of novel Carbazole-based Block copolymer for applications in solar cells

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## Abstract

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 is development and characterization 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 devices. The polymer have been synthesised for applications in solar cells. donor/acceptor carbazole block copolymer comprising alternating 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)-alt-2,2'-(5,5'-bithienylene)) P1. Block copolymer P1 have been synthesised following Suzuki cross coupling polymerisation methods. The polymer were characterised by <sup>1</sup>H NMR, <sup>13</sup>C 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 photophysical and electronic properties were investigated using UV-Vis spectroscopy and cyclic voltammetry (CV). Electrochemical and optical absorption show that the band gaps for P1 is 1.58 eV. [1-6].

**Keywords:** Carbazole, block copolymer, solar cells

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## Introduction

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 [5-8]. The polymer-bulk hetero-junction solar cells are basically composed of electron-acceptor molecules, like fullerenes and electron-donor 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%)[8], 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. The first certified reported conjugated polymer was poly-3-hexylthiophene with efficiency about 3%. [9] Recently, several new reported conjugated polymers give efficiencies in the range 9% to 11% when made as a blend with suitable fullerene acceptors. [10, 11]

In this study we present synthesis routes for the preparation of low band-gap semiconductor materials, based on donor/acceptor alternating Block 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.

## Materials and Methods

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. 5,2,3,6-difluoro-9-(1-octyl-nonyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole[1] (**1**), 5, 5'-5,5'-Dibromo-2,2'-bithiophene (**3**) and 5,7-bis(5-bromothiophen-2-yl)-2,3-bis(4-(2-ethylhexyloxy)phenyl)thieno[3,4-b]pyrazine (**2**) [1] were prepared according to literature procedures. [1,2] All other reagents were obtained from commercial sources and used as received.

## Apparatus

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<sup>-3</sup> solutions of the polymer in tetrahydrofuran (THF) were prepared and used as the test samples. The system was calibrated by use Potentiostat/Galvanostat was used to record the cyclic voltammograms, carrying out the measurements at 25 °C under argon atmosphere. The used electrolyte solution was tetrabutylammonium tetrafluoroborate (10 cm<sup>3</sup>) in acetonitrile (0.1 mol dm<sup>-3</sup>). Three-electrode system composed of Ag/Ag<sup>+</sup> 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 °C/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 °C/minute. Optical band gaps  $E_{\text{gopt}}$ (eV) were evaluated from the UV/Vis absorption spectra, where the wavelengths  $\lambda$  of the absorption onset was substituted in the equation: [ $E_{\text{g}}(\text{eV}) = 1240 / \lambda_{\text{abs onset}}(\text{nm})$ ]. Electrical band gaps  $E_{\text{g ec}}$  (eV) were evaluated from the cyclic voltammogram graphs (CV), where the onset of the oxidation potential  $E_{\text{ox}}$  and the onset of the reduction potential  $E_{\text{red}}$ , 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  $E_{\text{g ec}}$ (eV) is obtained from the difference between  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ .

## Synthesis of the Polymer

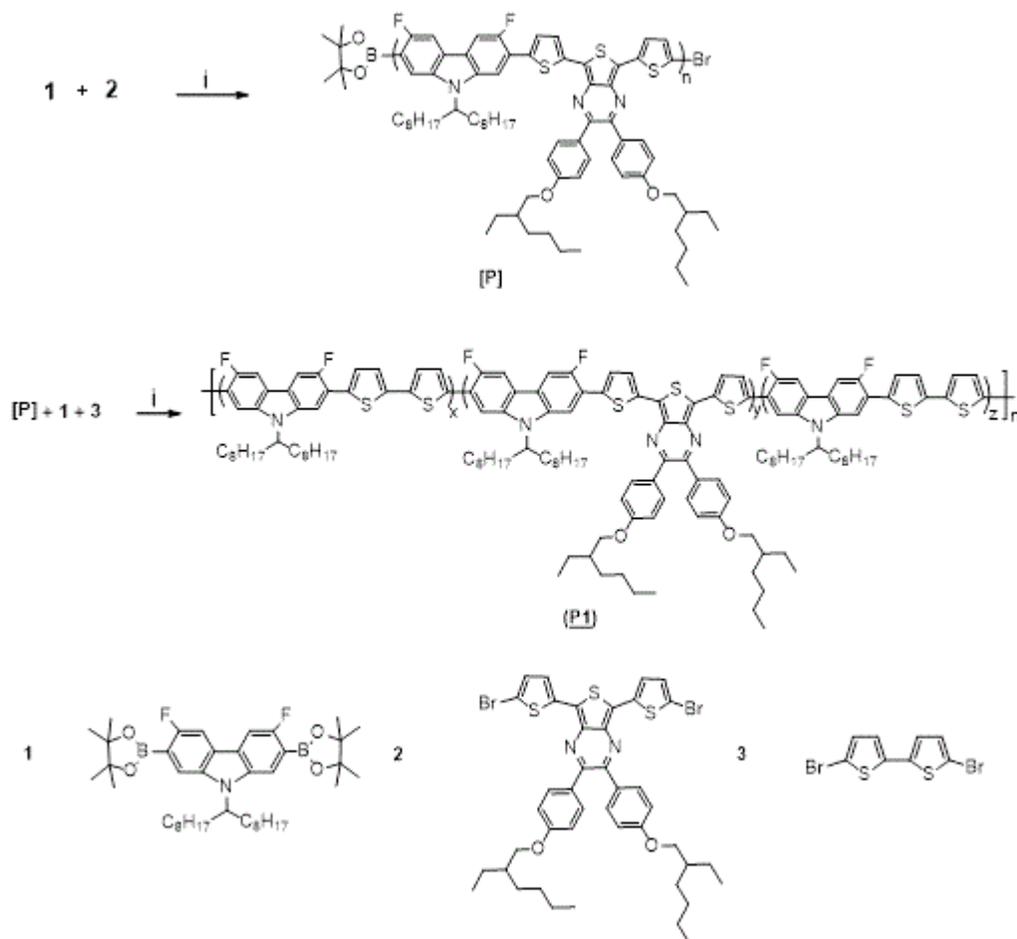
Poly[(3,6-difluoro-9-(1-octyl-nonyl)-9H-carbazole-2,7-diyl-alt-(5',7'-di-2-thienyl-2',3'-bis-[4-(2-ethyl-hexyloxy)-phenyl]-thieno[3,4-b]pyrazine)-5,5-diyl)- alt-2,2'-(5,5'-bithienylene)] (**P1**) To 3,6-difluoro-9-(1-octyl-nonyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**1**) (0.15 g, 0.215 mmol) and 5,7-bis(5-bromo thiophen-2-yl)-2-(4-(2-ethylheptyloxy)phenyl)-3-(4-(2-ethylhexyloxy)phenyl)thieno[3,4-b]pyrazine (**2**) (0.187 g, 0.216 mmol) in dry THF (10 cm<sup>3</sup>) was added Pd(AcO)<sub>2</sub> (7.92 mg, 0.04 mmol) and tri-*o*-tolylphosphine (32.21 mg, 0.1 mmol) the reaction was stirred for 10 mins under argon. NaHCO<sub>3</sub> solution (1.65 cm<sup>3</sup>, 20 wt % in water) deoxygenated for 4 hours with argon was added. The mixture was heated to 90 °C for 2 hour under argon and then cool down to room temperature. 3,6-difluoro-9-(1-octyl-nonyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**1**) (0.15 g, 0.215 mmol) and 5,5'-dibromo-2,2'-bithiophene (**3**) (0.069 g, 0.216 mmol) was added. The mixture was heated to 90 °C for 24 hour under argon before it was cooled down to room temperature to add bromobenzene (0.10 cm<sup>3</sup>, 0.95 mmol) and the mixture was refluxed for 3 hours before phenyl boronic acid (0.10 g, 0.82 mmol) was added and then the mixture was refluxed overnight. The reaction mixture was cooled to room temperature; the solution was precipitate in methanol (500 cm<sup>3</sup>). The solution was stirred overnight and then filtered. The polymer was dissolved in hot chloroform (50 cm<sup>3</sup>) and then extracted with ammonia solution. Ammonia solution (50 cm<sup>3</sup>, 28 %) was added and the mixture stirred overnight. [3] The chloroform solution was separated and then washed with ammonia solution and then with distilled water (2 x 50 cm<sup>3</sup>) each time stirred for 2 hour. The organic layer was concentrated and again precipitated in methanol (500 cm<sup>3</sup>) under a nitrogen atmosphere, subjected to Soxhlet extraction with methanol (24 hours), acetone (24 hours), hexane (18 hours) and then extracted with chloroform, the chloroform solution concentrated to (10 cm<sup>3</sup>) and the polymer precipitated in methanol. The dark green solid was collected by filtration and dried under vacuum to give (0.37 g, 71.32 % Yield).  $M_n = 10900$ ;  $M_w = 24200$  and PD = 2.23. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>);  $\delta_{\text{H}}$ /ppm: 7.86-7.42 (m, 20H); 6.94 (d, 4H,  $J = 6.8$  Hz); 4.58 (m, 2H); 3.90 (m, 4H); 2.57 (m, 4H); 2.33 (m, 4H); 1.75 (m, 2H); 1.54 - 1.15 (bm, 64H); 0.98 -0.92 (bm, 12H); 0.80 - 0.79 (m, 12H). <sup>13</sup>C NMR (500MHz, CDCl<sub>3</sub>);  $\delta_{\text{C}}$ /ppm: 160.33; 156.03; 154.79; 152.88; 152.64; 144.85; 139.95; 137.81; 137.62; 137.27; 136.41; 134.43; 134.35; 131.46; 128.92; 127.90; 127.56; 127.23; 126.45; 125.59; 124.54; 123.58; 121.39; 120.44; 114.16; 112.17;

110.13; 107.56; 107.04; 70.62; 56.81; 47.17; 39.39; 33.83; 32.75; 31.74; 30.53; 29.37; 29.11; 26.75; 23.86; 23.05; 22.58; 14.09; 14.02; 11.11. Elemental Analysis (%) calculated for  $C_{108}H_{128}N_4F_2S_5O_2$ : C, 74.10; H, 7.37; N, 3.20; Br, 0. Found: C, 73.29; H, 7.19; N, 3.18; Br, 0.

## Results and discussions

### Synthesis of the polymers

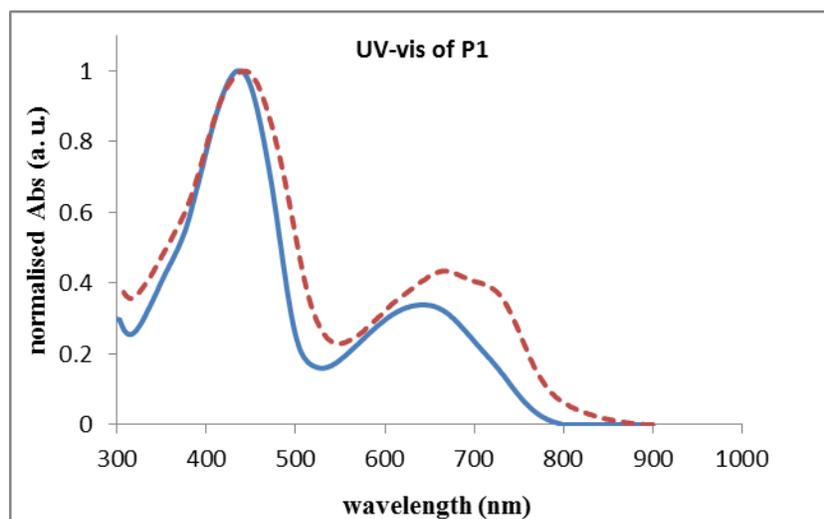
Block copolymer P1 was synthesized by polymerisation reactions using similar experimental conditions in Suzuki cross coupling with two sequential additions of monomers. The first stage in the polymerisation reaction involves, the polymerisation reaction between 3,6-difluoro-9-(1-octyl-nonyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**1**) and 5,7-bis(5-bromothiophen-2-yl)-2-(4-(2-ethylheptyloxy)phenyl)-3-(4-(2-ethylhexyloxy)phenyl)thieno[3,4-b]pyrazine (**2**) in THF, using  $NaHCO_3$  as a base and mixture of palladium(II) acetate and tri(*p*-tolyl)phosphine as catalyst. The mixture was heated to 90 °C for 4 hour, to form intermediate polymer [P] as shown in **Scheme 1** below. The mixture was cooled to room temperature and then 3,6-difluoro-9-(1-octyl-nonyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**1**), 5,5-dibromo-2,2'-bithiophene (**3**) was added and heated to 90 °C for 24 hour. It was purified to remove any palladium remaining and oligomers in the crude product. P1 was obtained in 71.32 % Yield as a green solid, Gel permeation chromatography (GPC) results for the chloroform fractions (using polystyrene standards) have shown  $M_w = 24,200$  and  $M_n = 10,900$  for P1 with a polydispersity 2.23.



**Scheme 1** Preparation of block copolymer (P1) (i)  $Pd(AcO)_2$ , tri-*o*-tolylphosphine,  $NaHCO_3$ , THF

### UV-Visible absorption spectra

The UV-Vis spectra (**Figure 1**) of P1 shows two broad absorption peaks at  $\lambda_{max}$  437 nm and 664 nm in chloroform solution and at  $\lambda_{max}$  445 nm and 669 nm in the solid state. The optical band gap of the polymer was calculated from the onset of absorption in films to be 1.58 eV. Comparison of the absorption spectra of P1 with those of the polycarbazole random equivalent copolymer P3 [5] shows similar features for both copolymers.

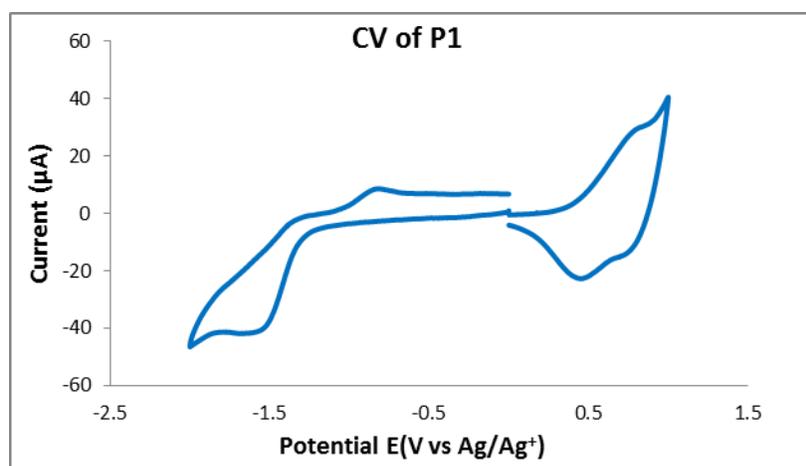


**Figure 1** Normalised absorption spectra of P1 in chloroform solution (blue line) and as thin film (brown line)

### Electrochemical studies

The cyclic voltammograms of polymer P1 is shown in **Figure 2**. The onset of the oxidation wave for P1 is at a potential of  $E_{pa} = 0.37$  V and the reduction wave at potential  $E_{pc} = -1.22$  V, respectively. The estimated HOMO and LUMO energy levels of P1 are  $-5.08$  eV and  $-3.50$  eV. The electrochemical band gap for P1 is  $1.58$  eV. This value is similar to the optical band gap.

The electrochemical band gaps for random copolymer P3[5] and block copolymer P1 are between  $1.57$  and  $1.6$  eV. The band gaps of random copolymer P3 [5] and block copolymer P1 are similar, because the polymers have the same molecular composition except for the ratio of monomer unit. Random copolymer which contains more 5,7-bis(thiophen-2-yl)-2-(4-(2-ethylheptyloxy)phenyl)-3-(4-(2-ethylhexyloxy)phenyl) thieno[3,4-b]pyrazine and less bithiophene unit in the copolymer chain will have stronger band gap. Because 5,7-bis(thiophen-2-yl)-2-(4-(2-ethylheptyloxy)phenyl)-3-(4-(2-ethylhexyloxy)phenyl) thieno[3,4-b]pyrazine has a larger aromatic resonance than bithiophene, this in turn decreases the bond length and increasing the quinoid form. The HOMO - LUMO band gap decreases with increasing the quinoid form in conjugated polymer. The cyclic voltammetry result of the polymer P1 corresponds well to required electronic energy levels for blend with PCBM in bulk heterojunctions.



**Figure 2** Cyclic voltammograms of P1 (blue) films cast on platinum disc ( $0.00314$  cm<sup>2</sup>) in tetrabutyl ammonium perchlorate/acetonitrile at  $100$  mV/s

### Thermal Properties of P1

The thermal properties of P1 were estimated by both Thermal gravimetric analysis (TGA) and Differential scanning calorimetry (DSC) analyses. **Figure 3** shows the Thermal gravimetric analysis (TGA) curves of P1. The onset of the first degradation occurs at  $424$  °C for P1. The block copolymer P1 shows high thermal stability, up to  $400$  °C, which exceeds by far the requirements for solar cells applications. All polymers have alkoxy chains attached to the

thiophene unit and alkyl chains attached to the carbazole unit of the polymer. The degradation and weight loss of block copolymer P1 can be assigned to loss of the alkyl chains and alkoxy chains.

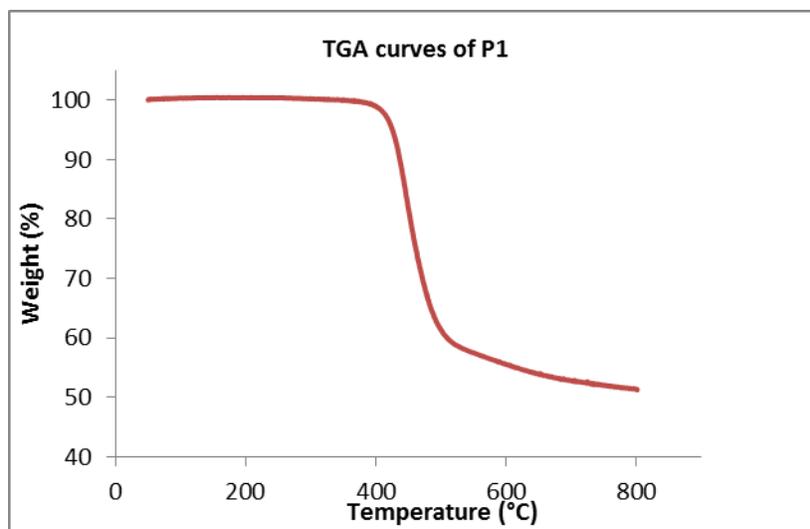


Figure 3 TGA curves of P1

## Conclusion

Novel conjugated block co polymer was synthesized, successfully via the Suzuki cross-coupling polymerisation technique. The electrochemical and photo-physical properties of the synthesized polymers show that P1 has the narrowest band gap among other polymers, which still narrower than those of an analogous polymer P3. 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.

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