***Original research Articles***

# Donor-c Based Polymers for Application in Solar Cells

**Abstract:**

The preparation and characterization of poly[(3,6-difluoro-9-(1-heptadecan-9-yl)-9H-carbazole-2,7-diyl)-alt-(2,3,7,8-tetraphenyl-10-(thiophen-2-yl)pyrazino[2,3-g]quinoxaline)-5,5'-diyl] **P1** and Poly[(3,6-difluoro-9-(1-heptadecan-9-yl)-9H-carbazole-2,7-diyl)-alt-(2,3-diphenyl-8-(thiophen-2-yl)quinoxalin -5-yl)thiophen-2-yl)-5.5'-diyl] **P2** are presented. The polymers were prepared via Suzuki cross-coupling reactions; both polymers provided low-band-gap polymers that absorbs light up to 350 nm of the electromagnetic spectrum. Cyclic voltammetry studies on the two polymers indicate greater electrolytic stability of these new polymers as compared to the polyfluorene equivalent[1,2] . Electrochemical and optical absorption show that the band gaps of **P1** and **P2** range from 1.64 and 1.93 eV.

Keywords: Electroacrive polymer, conjugated polymer, solar cell.

## Introduction:

Polymer solar cells based on blends of conjugated copolymer donors and acceptors are attracting a great deal of interest, as such systems have potential technological value due to their ease of fabrication and their relatively low production costs. While different acceptors have been used in these systems, fullerene derivatives have attracted the greatest research interest. This enabled devices to be produced that have solar power conversion efficiencies approaching 7%[3]. Efficient harvesting of solar energy requires the development of polymers with high absorption coefficients and extended absorption spectra in order to enable photocurrent generation from low energy photons. This in turn will require low energy-gap polymers that absorb at near-IR wavelengths. While the size of the energy gap has great importance in the design of these materials, it is also important to tailor the energy difference between the HOMO of the polymer donor and the LUMO of the fullerene acceptor in the bulk hetero- junction. Introduction of electron donating - accepting units on consecutive repeat units to stimulate intramolecular charge transfer along polymer chains has been shown as a proven alternative method toward controlling the energy gap of conjugated polymers[4].The latter approach has been successfully used in the preparation of low energy-gap polymers that better utilize the solar spectrum and arrange of polymers within this class have been developed for application in plastic solar cells. Low energy-gap alternating fluorene copolymers are a class of materials that have attracted a great deal of attention in this area. Developed a range of donor/acceptor copolymers consisting of alternating 2,7-carbazole[5] units which showed very good promise when used with PCBM in bulk heterojunction photovoltaic cells with power conversion efficiencies as high as 3.6%[6]. In this work, we report the synthesis and characterization of new classes of donor/acceptor alternating copolymers comprising alternate 2,7-linked-3,6-difluoro carbazole repeat units bearing alkyl chain substituents at the 9-position with quinoxaline based acceptor repeat units. We also present studies on the physical properties of the polymers and their ability to act as electron donors to PCBM as well as the performance of one of the polymers in bulk heterojunction solar cells in blends with PCBM.

## Experimental

**Measurements**. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker 250 MHz, AMX400 400 MHz or DRX500 500 MHz NMR spectrometers at 22 °C in chloroform-*d* solutions with TMS as the internal standard. Polymer solutions in THF (2.5 mg cm$^{-3}$) were used as samples for Gel permeation chromatography (GPC) analysis. The GPC curves were obtained by the RI detection method, which was calibrated with a series of polystyrene narrow standards (Polymer Laboratories). Elemental analyses were carried out by the Perkin Elmer 2400 CHN Elemental Analyzer for CHN analysis and by the Schöniger oxygen flask combustion method for anion analysis. UV–visible absorption spectra were measured by Hitachi U-2010 Double Beam UV/Visible Spectrophotometer. The absorbance of polymers was measured in solution in chloroform (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 using a Princeton Applied Research Model 263A Potentiostat/Galvanostat. Measurements were carried out under argon at 25±2 °C. 10 ml of tetrabutylammonium hexafluorophosphate 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 solution in the electrolyte solution), a platinum working electrode (2 mm-diameter smooth platinum disc, area=$3.14\times10^{-2}$ cm$^{2}$), and a platinum counter electrode (platinum wire). Polymer thin films were formed by drop casting 1.0 mm$^{3}$ of polymer solutions in chloroform (HPLC grade) (1 mg cm$^{-3}$) onto the working electrode, then dried in air. Ferrocene was employed as a reference redox system according to IUPAC's recommendation

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**Materials:** 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[7] **(M1)**, 2,3,6,7-tetraphenyl-9,10-di(1'-bromothien-2-yl)pyrazino[2,3-g]quinoxaline[1] **(M2)** and 5,8-bis(5-bromothien-2-yl)pyrazino2,3-diphenyl quinoxaline (**M3**)[1] were prepared according to literature procedures. All other reagents were obtained from commercial sources and used as received.

### *Poly[(3,6-difluoro-9-(1-heptadecan-9-yl)-9H-carbazole-2,7-diyl)-alt-(2,3,7,8-tetraphenyl-10-(thiophen-2-yl)pyrazino[2,3-g]quinoxaline)-5,5'-diyl](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 **(M1)** (0.30 g, 0.43 mmol) and 2,3,6,7-tetraphenyl-9,10-di(1'-bromothien-2-yl) pyrazino[2,3-g] quinoxaline (**M2**) (0.349 g, 0.43 mmol) in dry THF (10 cm$^{3}$) was added Pd(AcO)$_2$ (7.92 mg, 0.04 mmol) and tri-o-tolyphosphine (32.21 mg, 0.1 mmol), the reaction was stirred for 10 mins under argon. 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. The mixture was cooled to room temperature and bromobenzene (0.10 cm$^{3}$, 0.95 mmol) were added and then the mixture heated to 90 $^{o}$C for 3 hours. Again, the mixture was cooled to room temperature and phenylboronic acid (0.10 g, 0.82 mmol) was added and then the mixture was refluxed over night. The reaction mixture was cooled to room temperature, the solution was precipitate in methanol (500 cm$^{3}$). The solution was stirred overnight and then filtered. The polymer was dissolved in chloroform (50 cm$^{3}$) and then extracted with ammonia solution. Ammonia solution (50 cm$^{3}$, 28 %) was added and the mixture stirred over night. The chloroform solution was separated and then washed with ammonia solution and then with distilled water (2 x 50 $cm^3$) each time stirred for 2 hour. The organic layer was concentrated and again precipitated in methanol (500 $cm^3$) 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 $cm^3$) and the polymer precipitated in methanol. The black-green solid was collected by filtration and dried under vacuum to give (0.34 g, 72.22 % Yield). $M_n$ = 3400; $M_w$ = 4100 and PD=1.2. $^1H$ NMR (400MHz, $CDCl_3$); $\delta_H$/ppm: 8.51 (d, 2H, $J$ = 4); 7.85 (m, 2H); 7.80 (m, 8H); 7.47 (d, 2H, $J$ = 5.0); 7.41 (m, 14H,); 7.31 (d, 2H, $J$ = 4.5); 4.60 (m, 1H); 2.35 (m, 2H); 2.01 (m, 2H); 1.51-1.14 (m, 24H); 0.87 (m, 6H). $^{13}C$ NMR (500MHz, $CDCl_3$); $\delta_C$/ppm: 152.70; 152.37; 138.48; 138.48; 138.48; 138.11; 136.40; 136.30; 136.10; 134.88; 129.61; 129.41; 129.20; 128.95; 128.40; 127.23; 126.23; 126.11; 125.94; 119.16; 56.94; 33.95; 31.70; 31.58; 29.96; 29.31; 29.15; 26.80; 22.55; 14.11; 14.00. Elemental Analysis (%) calculated for $C_{71}H_{63}N_5F_2S_2$: C, 78.35; H, 5.83; N, 6.43; Br, 0. Found: C, 74.51; H, 6.03; N, 5.91; Br, 0.

### *Poly[(3,6-difluoro-9-(1-heptadecan-9-yl)-9H-carbazole-2,7-diyl)-alt-(2,3-diphenyl-8-(thiophen-2-yl)quinoxalin-5-yl)thiophen-2-yl)-5.5'-diyl] (**P2**)*

To 3,6-difluoro-9-(1-octyl-nonyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*9H*-carbazole (**M1**) (0.30 g, 0.43 mmol) and 5,8-bis(5-bromothien-2-yl)pyrazino2,3-diphenyl quinoxaline (**M3**) (0.261 g, 0.43 mmol) in dry THF (10 $cm^3$) was added $Pd(AcO)_2$ (7.92 mg, 0.04 mmol) and tri-o-tolyphosphine (32.21 mg, 0.1 mmol), the reaction was stirred for 10 mins under argon. $NaHCO_3$ 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. The mixture was cooled to room temperature and bromobenzene (0.10 $cm^3$, 0.95 mmol) were added and then the mixture heated to 90 °C for 3 hours. Again, the mixture was cooled to room temperature and phenylboronic acid (0.10 g, 0.82 mmol) was added and then the mixture was refluxed over night. The reaction mixture was cooled to room temperature, the solution was precipitate in methanol (500 $cm^3$). The solution was stirred overnight and then filtered. The polymer was dissolved in chloroform (50 $cm^3$) and then extracted with ammonia solution. Ammonia solution (50 $cm^3$, 28 %) was added and the mixture stirred over night. The chloroform solution was separated and then washed with ammonia solution and then with distilled water (2 x 50 $cm^3$) each time stirred for 2 hour. The organic layer was concentrated and again precipitated in methanol (500 $cm^3$) 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 $cm^3$) and the polymer precipitated in methanol. The red solid was collected by filtration and dried under vacuum to give (0.250 g, 65.45 % Yield). $M_n$= 4400; $M_w$= 12000 and PD= 2.73. $^1H$ NMR (400MHz, $CDCl_3$); $\delta_H$ / ppm**:** 8.29 (s, 2H); 8.02 (m, 2H); 7.88 (m, 8H); 7.71 (m, 2H); 7.40 (m, 6H); 4.62 (m, 1H); 2.39 (m, 2H); 2.02 (m, 2H); 1.50-1.08 (m, 24H); 0.81 (m, 6H). $^{13}C$ NMR ($CDCl_3$); $\delta_C$/ppm: 153.98; 152.06; 150.70; 143.52; 140.6; 138.98; 137.17; 136.28; 135.39; 130.16; 129.67; 129.53; 128.01; 128.01; 127.21; 126.34; 125.85; 125.58; 125.43; 124.72; 120.24; 109.15; 106.60; 106.03; 67.28; 63.77; 55.87; 33.05; 30.71; 28.89; 28.45; 28.17; 25.83; 21.55; 12.98; 11.00. Elemental Analysis (%) calculated for $C_{57}H_{55}N_3F_2S_2$: C, 77.43; H, 6.23; N, 4.35; Br, 0. Found: C, 74.86; H, 6.57; N, 4.39; Br, 0

## Results and Discussion

Polymers **P1–P2** were synthesised using Suzuki cross coupling polymerisation reactions as shown in scheme 1, 2. The reaction used Pd(AcO)$_2$ as catalyst, NaHCO$_3$ solution (20 wt % in water) as the base deoxygenated for 4 hours with argon. The reaction was carried out in THF, and was left stirring for 24 hours at reflux. The end–capping reagents used were phenyl boronic acid then bromobenzene. A small amount of chloroform was added to dissolve the higher molecular weight portion of the polymer before the end - capping. The solution was precipitated in methanol to remove any palladium and unreacted monomer. The solution was stirred overnight and then filtered. The polymer was dissolved in chloroform and then extracted with ammonia solution. This treatment is designed to remove any palladium residues. The chloroform solution was separated and then washed with distilled water. The organic layer was concentrated and again precipitated in methanol under a nitrogen atmosphere. The crude polymer obtained was then transferred into a thimble and washed with different solvents in a Soxhlet apparatus. The first wash with methanol is to remove any organic impurities. The small oligomer chains were removed with acetone and hexane. The purified polymer was then extracted with chloroform and precipitated again in methanol, filtered and dried. **P1** was obtained in 72.22 % Yield as black-green solid, Gel permeation chromatography (GPC) results for the chloroform fractions (using polystyrene standards) have shown Mw = 8,200 and Mn = 3,400 . **P2** was obtained in 65.45 % Yield as a red solid, GPC results for the chloroform fractions (using polystyrene standards) have shown $M_w = 12,000$ and $M_n = 4,400$. A similar finding was observed for the fluorene alternating copolymer **APFO-Green 9**[1] and **APFO-18**[2] which has the same acceptor repeat unit as our copolymers and which had similar a number average molecular weight value and a weight-average molecular weight value after fractionation.

Figure 1 show the absorption spectra of polymer **P1** in solution and thin film. Polymer **P1** shows three absorption bands at $\lambda_{max}$ 570, 460 and 363 nm in chloroform and three absorption bands at $\lambda_{max}$ 606, 478 and 372 nm in the solid state. A slight shift of $\lambda_{max}$ 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 the thin film, causing less twisting of polymer chain, which leads in turn to a better overlap of $p_z$-orbital. The optical band gap of **P1** in solid state is 1.64 eV. **P1** having lower band gap due to more planar structure. Comparison of the optical band gap of **P1** and those of the polyfluorene equivalent **APFO-Green 9[1]** which has a optical band gap of 1.75 eV do also point to the fact that **P1** has a more extended electronic conjugation due to fluorine-hydrogen interactions in **P1**.

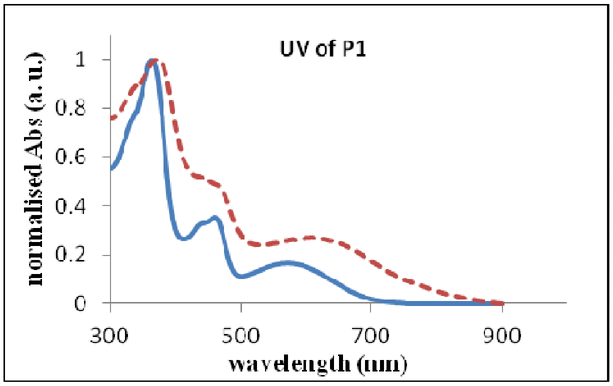


Figure 1: Normalised absorption spectra of P1 in chloroform solution (blue line) and as thin film (brown line)

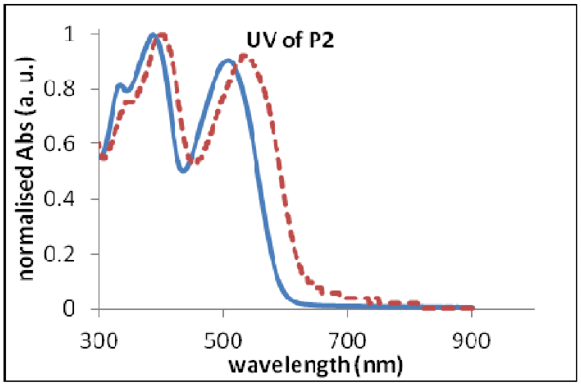


Figure 2: Normalised absorption spectra of P2 in chloroform solution (blue line) and as thin film (brown line)

Figure 2 show the absorption spectra of polymer **P2** in solution and thin film. Polymer **P2** shows two absorption bands at $\lambda_{max}$ 508 and 389 nm in chloroform and two absorption bands at $\lambda_{max}$ 534 and 398 nm in the solid state. A slight shift of $\lambda_{max}$ 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. The optical band gap of **P2** in solid state is 1.93 eV. **P2** having lower band gap due to more planar structure. Comparison of the optical band gap of **P2** and those of the polyfluorene equivalent **APFO-18**[2] and which has optical band gap of 2.00 eV, **APFO-18** having a larger band gap then **P2**. This is also point to the fact that **P2** has a more extended electronic conjugation due to fluorine-hydrogen interactions in **P2**.

**Table 1: Absorption maxima for P1 – P2 in chloroform solution and solid state as a film**

| **Polymers** | **Solution ($\lambda_{max}$/nm)** | | | **Thin Film ($\lambda_{max}$/ nm)** | | | **optical band gap(eV)** |
|---|---|---|---|---|---|---|---|
| | **1** | **2** | **3** | **1** | **2** | **3** | |
| **P1** | 363 | 460 | 570 | 372 | 478 | 606 | 1.64 |
| **P2** | 389 | 508 | - | 398 | 534 | - | 1.93 |

Cyclic voltammetry (CV) studies were conducted on dropcast polymer films in acetonitrile with tetrabutyl ammonium perchlorate as the electrolyte. The electrochemical data of the polymers are listed in Table 2. Polymer **P1** displays a reversible oxidation wave (p-doping) at a half wave potential of +0.61V (vs. $Ag/Ag^+$) and two quasi reversible reduction waves (n-doping) at -1.13 and -1.30V. The LUMO level of the polymer was determined from the onset of reduction of the polymer (taken as the value obtained from the intersection of the two tangents drawn at the rising current and the baseline charging current of the CV curves) (figure 3) and estimated at -3.67eV (on the basis that ferrocene/ ferrrocenium is 4.8 eV below the vacuum level[8]. The HOMO value of polymer **P1** determined similarly from its onset of oxidation was found as -5.31 eV giving an electrochemical energy gap of 1.64 eV which is in accordance with the value of the optical energy gap.

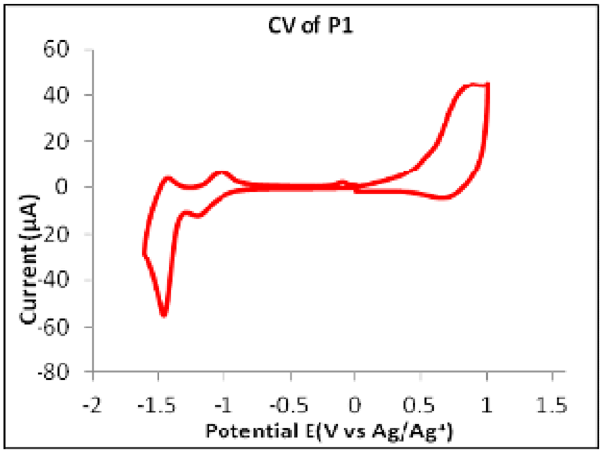


Figure 3: Cyclic voltammograms of P1 films cast on platinum disc (0.00314 $cm^2$) in tetrabutylammonium perchlorate/acetonitrile at 100mV/s

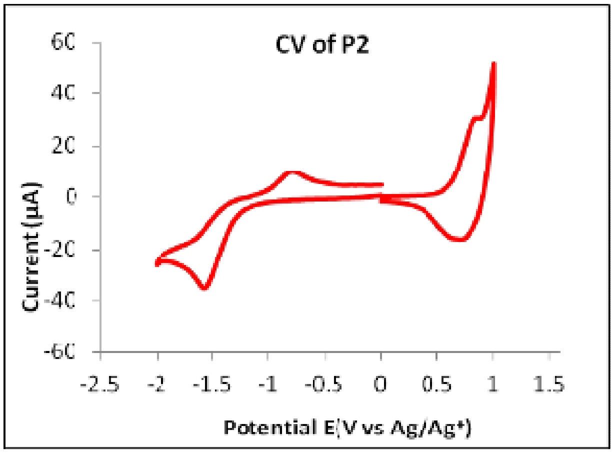


Figure 4: Cyclic voltammograms of P2 films cast on platinum disc (0.00314 $cm^2$) in tetrabutylammonium perchlorate/acetonitrile at 100mV/s

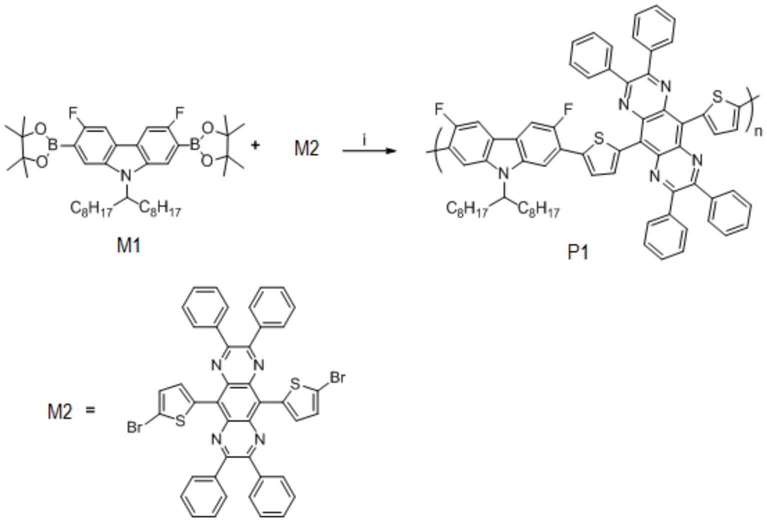
Polymer **P2** displays a reversible oxidation wave (p-doping) at a half wave potential of + 0.66 V (vs. $Ag/Ag^+$) and reversible reduction waves (n-doping) at -1.28V (figure 4). The LUMO level of the polymer was determined from the onset of reduction of the polymer and estimated at -3.44eV. The HOMO value of polymer **P1** determined similarly from its onset of oxidation was found as -5.37 eV giving an electrochemical energy gap of 1.93 eV which is in accordance with the value of the optical energy gap.

**Table 2: Cyclic Voltammetry results and band gaps of P1 – P2**

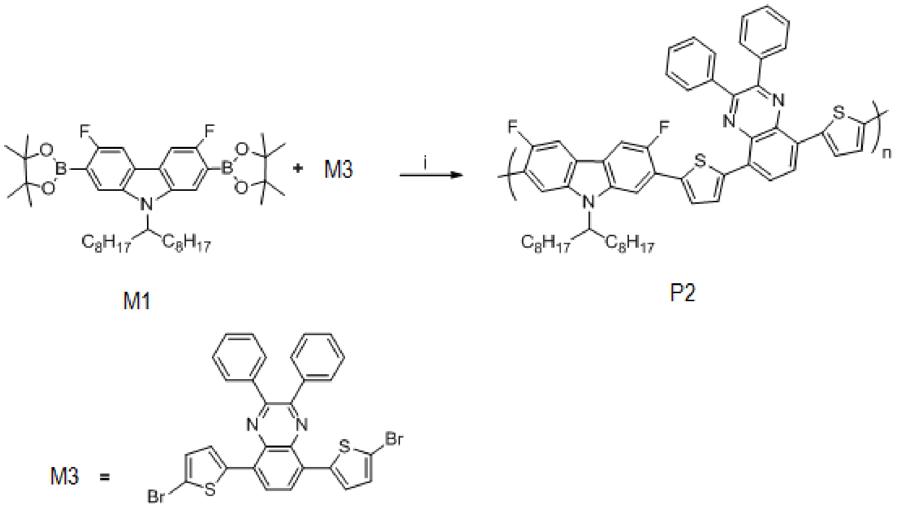
| Polymer | Epa (V) | Epc (V) | HOMO(eV) | LUMO(eV) | Band gap (eV) |
|---|---|---|---|---|---|
| **P1** | 0.60 | -1.13&-1.30 | -5.31 | -3.67 | 1.64 |
| **P2** | 0.66 | -1.28 | -5.37 | -3.44 | 1.93 |

## Conclusions

The preparation of new classes of donor/acceptor conjugated polymers comprising alternating copolymers comprising alternate 2,7-linked-3,6-difluoro carbazole repeat units with quinoxaline based acceptor repeat units has been successfully undertaken using Suzuki polymerization conditions. **P1** composed of alternating carbazole donor unit and acceptor unit were successfully prepared. Gel permeation chromatography results from polymerisation have shown that the **P1** had a weight average molecular weight values Mw of 8,100 Da. UV-Vis analysis showed the polymer absorbed at high wavelengths $\lambda_{max}$ 570 nm in solution and 606 nm in the solid state and the band gap of **P1** in solid state is 1.64 eV. CV measurements estimated the band gap as 1.64 eV from the onset of oxidation and reduction. The HOMO and LUMO levels can be estimated as -5.31 eV and -3.67 eV respectively. **P2** composed of alternating carbazole donor unit and acceptor unit were successfully prepared. Gel permeation chromatography results from polymerisation have shown that the **P2** had a weight average molecular weight values Mw of 12,000 Da. UV-Vis analysis showed the polymer absorbed at high wavelengths $\lambda_{max}$ 508 nm in solution and 534 nm in the solid state and the band gap of **P2** in solid state is 1.93 eV. CV measurements estimated the band gap as 1.93 eV from the onset of oxidation and reduction. The HOMO and LUMO levels can be estimated as -5.37 eV and -3.44 eV respectively.



**Scheme1: Preparation of polymer P1 (i) Pd(AcO)$_2$, tri-o-tolyphosphine, NaHCO$_3$, THF**



**Scheme2: Preparation of polymer P2 (i) Pd(AcO)$_2$, tri-o-tolyphosphine, NaHCO$_3$, THF**

## Reference

**(1) Zhang, F.; Bijleveld, J.; Perzon, E.; Tvingstedt, K.; Barrau, S.; Inganaes, O.; Andersson, M. R. *Journal of Materials Chemistry* 2008, *18*, 5468.**

**(1) Lindgren, L. J.; Zhang, F.; Andersson, M.; Barrau, S.; Hellstrom, S.; Mammo, W.; Perzon, E.; Inganas, O.; Andersson, M. R. *Chemistry of Materials* 2009, *21*, 3491.**

**(3) Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.;Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photonics* 2009, *3*, 297.**

(4) Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nat. Mater.* **2007**, *6*, 497

**(5) Wakim, S.; Blouin, N.; Gingras, E.; Tao, Y.; Leclerc, M. *Macromolecular Rapid Communications* 2007, *28*, 1798.**

**(6) Wakim, S.; Blouin, N.; Gingras, E.; Tao, Y.; Leclerc, M. *Adv. Mater.* 2007, *19*, 2295.**

**(7) Jo, J. H.; Chi, C. Y.; Hoger, S.; Wegner, G.; Yoon, D. Y. *Chemistry-a European Journal* 2004, *10*, 2681.**

**(8) pommerehnce , J.; vestwebew, H. *Adv. Mater.* 2007, *19*, 2295.**