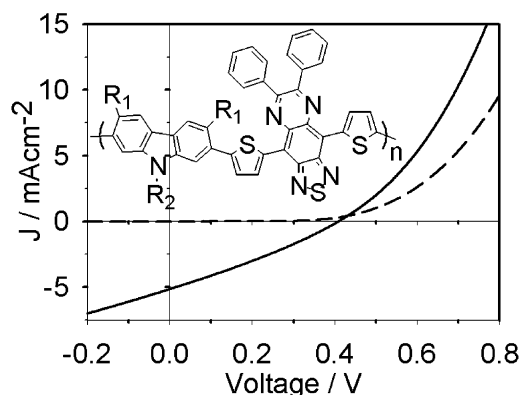


Narrow Energy Gap Polymers with Absorptions up to 1 200 nm and their Photovoltaic Properties^a

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A series of donor/acceptor carbazole copolymers comprising alternating 6,7-diphenyl-4,9-bis-(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline and 3,6-dimethyl-9-alkyl-9*H*-carbazole repeat units (**P1**), or 3,6-dimethyl-9-triarylamino-9*H*-carbazole repeat units (**P2**), or 9-triarylamino-9*H*-carbazole repeat units (**P3**) has been prepared following Suzuki polymerization procedures. **P3** absorbs light up to 1 200 nm and has an energy gap of 1.1 eV, while **P1** and **P2** have energy gaps of 1.3 and 1.25 eV, respectively. Photovoltaic cells with ITO/PEDOT:PSS/**P3**:PCBM (1:1 w/w)/Ca showed an open-circuit voltage of 0.4 V under white light illumination, power conversion efficiency of 0.61%, and short-circuit current of 5.2 mA · cm⁻².



Introduction

Polymer solar cells based on blends of conjugated polymer donors and molecular 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 molecular 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 6%.^[1] 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 lower-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 heterojunction. This energy-difference has important implications on the open-circuit voltage of devices (V_{OC}) with a concomitant impact on device efficiency, necessitating in many cases a trade off between energy gap of the molecular donor and the donor/acceptor HOMO–LUMO.^[2]

Introduction of electron donating and accepting groups 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.^[3] The latter approach has been successfully used in the preparation of narrow energy-gap

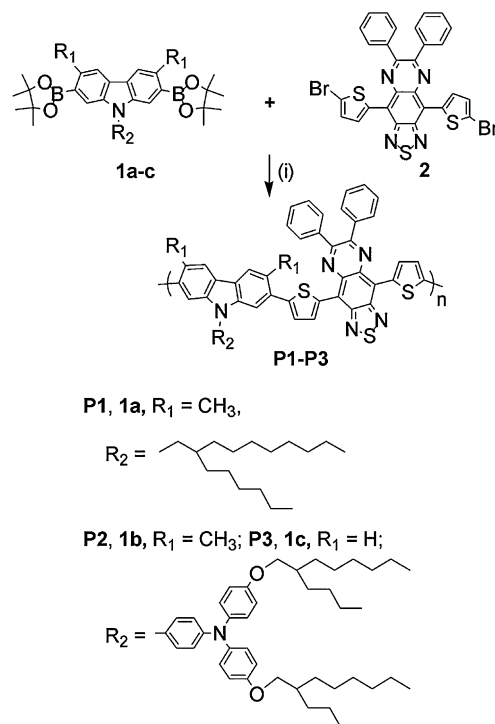
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polymers that better utilize the solar spectrum and a range of polymers within this class have been developed for application in plastic solar cells.^[4] Low energy-gap alternating fluorene copolymers are a class of materials that have attracted a great deal of attention in this area. Alternating copolymers, comprising 9,9-dialkyl-2,5-di-thiophen-2-yl-fluorene units and 2,1,3-benzothiadiazole units which have an energy gap around 1.9 eV have shown great promise when blended with PCBM in solar cells with power conversion efficiency (PCE) up to 2.1% under AM1.5 illumination.^[5] Development of lower energy-gap polymers in this class of materials was achieved by introduction of stronger electron accepting repeat units than the 2,1,3-benzothiadiazole units. Fluorene copolymers with thienopyrazine^[6] or thiadiazolo-quinoxaline^[7] alternate repeat units (APFO-Green2 and APFO-Green1) have narrower energy gaps than the previous polymer with E_g values of 1.6 and 1.3 eV, respectively. While APFO-Green2 afforded good results in PV devices made from blends with PCBM, APFO-Green1 required the use of fullerene derivatives with strong electron accepting groups [(3'-(3,5-bis-trifluoromethyl-phenyl)-1'-(4-nitrophenyl)pyrazolino[60] fullerene (BTPF)) to provide devices capable of photocurrent generation in the near infra-red. Recently, Leclerc et al. developed a range of donor/acceptor copolymers consisting of alternating 2,7-dibenzosilole^[8] or 2,7-carbazole^[9] units which showed very good promise when used with PCBM in bulk heterojunction photovoltaic cells with power conversion efficiencies as high as 3.6% under AM1.5 illumination.^[9a] In this work, we report the preparation and characterization of new classes of donor/acceptor alternating copolymers comprising 2,7-linked carbazole repeat units and thiadiazolo-quinoxaline alternate 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.

Results and Discussion

Two classes of donor/acceptor alternating copolymers were prepared; those with an alkyl group attached at the 9-position of alternate carbazole repeat unit (polymer **P1**) and those where the 9-position of alternate carbazole repeat units are functionalized with a triarylamine functional group (polymers **P2** and **P3**). The preparation of the polymers is outlined in Scheme 1. The polymers were obtained in quantitative yields upon reaction of the bis-boronate ester derivatives **1a-c**^[10] with dibromide **2** using Suzuki type cross-coupling condensation polymerization reactions. Gel permeation chromatography results from the polymerization reactions (using polystyrene standards) have shown weight-average molecular weight



Scheme 1. (i) (a) Pd(II) acetate/*P*(*p*-tolyl)₃ (1/2), NaHCO₃, THF/H₂O, (b) bromobenzene, (c) phenylboronic acid.

values \bar{M}_w ranging from 4400 to 5100 Da with polydispersities around 1.6. The low weight-average molecular weight values obtained for these materials could be linked to their limited solubilities since their 6,7-diphenyl-4,9-bis-(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline repeat units do not have any solubilizing alkyl chains. A similar finding was observed for the fluorene alternating copolymer APFO-Green1 which has the same acceptor repeat unit as our copolymers and which had a number-average molecular weight value \bar{M}_n of 3600 and a weight-average molecular weight value \bar{M}_w of 6200 after fractionation.^[7b]

Figure 1 shows the absorption and photoluminescence spectra of polymer **P1** both in solution in dichloromethane and as a film. The polymer has a maximum absorption at 701 nm in dichloromethane and at 773 nm in films (Table 1). These absorption bands are probably associated with an intramolecular charge transfer process between donor and acceptor units along the polymer chains. The absorption maximum of the polymer in the solid state as well as its optical energy gap are similar to those reported for APFO-Green1 ($\lambda_{\max} \approx 780$ nm in films, E_g of 1.3 eV^[7]). This is despite the fact that polymer **P1** has methyl-substituents at the 3,6-positions on carbazole alternate repeat units ortho to the linkage position with dithienyl thiadiazolo-quinoxaline alternate repeat units which could be expected to induce a certain degree of twisting on the backbone and a lower electronic conjugation when

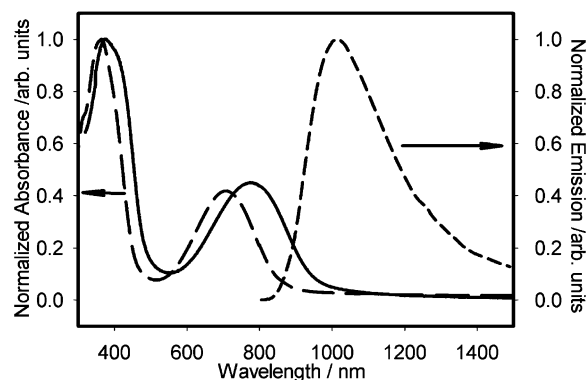


Figure 1. UV-vis spectra of **P1** in dichloromethane (dashed line), and as a film (solid line). PL spectra of **P1** as a film (short dashed line).

compared to the same situation with fluorene alternate repeat units in APFO-Green1. The similar degrees of electronic conjugation between polymer **P1** and APFO-Green1 could be explained by the fact that its carbazole alternate repeat units are stronger electron donating groups than fluorene alternate repeat units in APFO-Green1 which compensate for the steric hindrance of its methyl-substituents ortho to the linkage positions. The fluorescence spectra of films of **P1** (Figure 1 and Table 1) showed an emission band at a λ_{max} value of 1016 nm which is also similar to that reported for APFO-Green1.^[7]

Alternating copolymer **P2** which has triaryl amine-substituents rather than alkyl-substituents was prepared in order to increase the hole mobilities in this class of materials. **P2** displayed slightly red-shifted electronic spectra to those of polymer **P1** both in solution and in the solid state (Table 1). It also displayed a slightly narrower optical energy gap with a value of 1.25 eV for **P2** as compared to 1.3 eV for polymer **P1** indicating that the triaryl amine-substituents have a minimal effect on the net HOMO–LUMO energy gap in this class of materials. The fluorescence spectra of films of **P2** (Table 1) showed an emission band at a λ_{max} value of 1001 nm which is similar to that of **P1**. Polymer **P3** has a maximum absorption at

847 nm in dichloromethane and at 867 nm in films (Table 1). These absorption maxima indicate a more extended electronic conjugation in **P3** than in **P1** and **P2** in view of the fact that **P3** has no methyl-substituents on alternate carbazole repeat units. This permits the polymer to adopt a more planar conformation both in solution and in the solid state. It is also worth noting that the red shift in absorption of the polymer between solution and solid state (20 nm) is much smaller than that of **P1** and **P2** (≈ 60 nm) indicating little structural difference of the polymer in solution and in the solid state. Polymer **P3** absorbs light up to 1200 nm and displays an optical energy gap E_g of 1.1 eV making it one of the very few examples of processable conjugated polymers with similar low energy gaps. The fluorescence spectra of films of **P3** showed an emission band at a λ_{max} value of 1001 nm which is surprisingly similar to those of polymers **P1** and **P2** despite the difference in their energy gaps. It is difficult to explain at this stage the reasons as to the similarity in the PL spectra of all three polymers.

Cyclic voltammetry studies were conducted on drop-cast polymer films in acetonitrile with tetrabutylammonium perchlorate as the electrolyte. The electrochemical data of the polymers are listed in Table 1. Polymer **P1** displays a reversible oxidation wave (p-doping) at a half-wave potential of +0.61 V (vs. Ag/Ag⁺) and two quasi-reversible reduction waves (n-doping) at –1.09 and –1.52 V. 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) and estimated at 3.8 eV (on the basis that ferrocene/ferrocenium is 4.8 eV below the vacuum level^[11]). The HOMO value of polymer **P1** determined similarly from its onset of oxidation was found as 5.1 eV giving an electrochemical energy gap of 1.3 eV which is in accordance with the value of the optical energy gap. Polymer **P2** displays a quasi-reversible oxidation wave (p-doping) at a half-wave potential of +0.47 V (vs. Ag/Ag⁺) and two quasi-reversible reduction

Table 1. GPC data, U-vis–Near IR data, energy gaps, redox potentials (vs. Ag/Ag⁺), and energy levels of polymers **P1–3**.

Polymer	Absorption		Emission	Energy Gap ^{a)}	E_{ox}^0	E_{red}^0	LUMO ^{b)}	HOMO ^{c)}
	λ_{max} (CH ₂ Cl ₂)	λ_{max} (film)	λ_{max} (film)	E_g	V	V	eV	eV
	nm	nm	nm	eV				
P1	701	773	1016	1.30	+0.61	–1.09, –1.52	3.80	5.10
P2	713	772	1001	1.25	+0.47	–1.08, –1.53	3.80	5.05
P3	847	867	1001	1.10	+0.46	–1.06, –1.52	3.70	4.80

^{a)}Determined from the onset position of the absorption band; ^{b)}LUMO position (vs. vacuum) determined from onset of reduction; ^{c)}HOMO position determined from the difference of optical energy gap and LUMO position.

waves (n-doping) at -1.08 and -1.53 V. The LUMO level of the polymer was determined from its onset of reduction at 3.8 eV. The HOMO value of polymer **P2** as determined from its LUMO position and optical energy gap was estimated at a value of 5.05 eV. The LUMO level of polymer **P3** as determined from its onset of reduction from cyclic voltammetric studies was estimated at 3.7 eV which is closer to the vacuum level than those of **P1** and **P2**. The HOMO level determined from the energy difference between the optical energy gap and the LUMO level is estimated at 4.8 eV.

Photoluminescence quenching studies were conducted on examination of the spectra of blends of polymers **P1–P3** with PCBM. Introduction of 6% w/w of PCBM into **P1** films induces a 50% drop in the PL intensity indicating a degree of quenching as a result of some electron transfer between **P1** and PCBM. Introduction of 6% w/w of PCBM into films of **P2** results in a less pronounced degree of fluorescence quenching with only a 17% drop in PL intensity. The fluorescence of polymer **P3** was almost fully quenched when 6% w/w of PCBM was introduced into films of the polymer indicating that it is the most efficient electron donor to PCBM in this class of materials. These results could be due to the fact that the LUMO of PCBM is much closer in energy ($3.8^{[12]}$ – 4.3 eV $^{[2]}$) to those of polymers **P1** and **P2** which both have LUMO levels of 3.8 eV. However, the LUMO of PCBM is further offset in energy from that of polymer **P3** (3.7 eV) which explains the easier electron transfer between polymer **P3** and PCBM. Photovoltaic measurements were made on a series of ITO/PEDOT:PSS/**P3**:PCBM/Ca devices using blends of **P3**:PCBM in a w/w ratio of 1:1. The results of these studies are outlined in Table 2 and Figure 2.

Device 1 (Table 2) is based on an ITO/PEDOT:PSS/**P3**:PCBM/Ca/Ag multilayer-structure in which the active layer was not annealed. Such devices provided relatively low PCE (0.09%) together with a low fill factor (FF) of (16%). Work described in the literature has shown that annealing

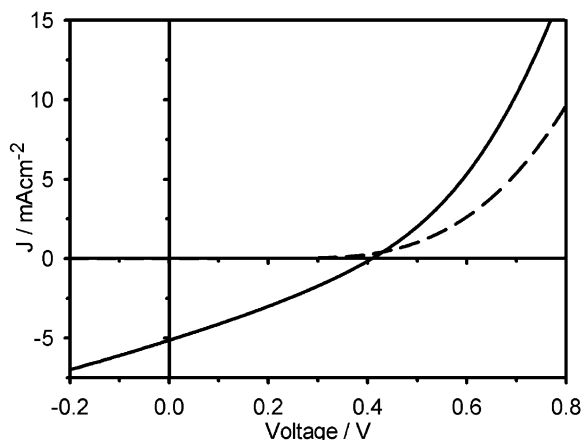


Figure 2. J - V characteristics of **P3**/PCBM 1:1 w/w device under illumination from an AM 1.5 solar simulator ($100 \text{ mW} \cdot \text{cm}^{-2}$) after annealing at 150°C (solid line), and in the dark (dashed line).

of the active layers in bulk heterojunction devices plays a vital role in the improvement of device performance, as a result of a phase-separation and self-assembly of polymer chains and crystallization of the fullerene dopants that increases charge mobility and facilitates charge extraction. Devices were therefore annealed at different temperatures for set periods of time (10 min) and their performances were compared. As can be seen in Table 2, a progressive increase in PCE, FF, and short-circuit current density (J_{SC}) is observed as the annealing temperature is increased. From the series of devices studied, device 6 (in which the active layer was annealed at 150°C) has the best performance, with a PCE of 0.61%, open-circuit voltage V_{OC} of 0.41 V, J_{SC} of $5.2 \text{ mA} \cdot \text{cm}^{-2}$, and FF of 29%. We note that there is a marked increase in J_{SC} and FF that occurs above the glass-transition temperature (determined as 123°C from differential scanning calorimetry). This suggests that the formation of micro-/nano-structures resulting from self-assembly may have an important role in facilitating charge transport and extraction in this material system. $^{[13]}$

Table 2. Performance of ITO/PEDOT:PSS/**P3**:PCBM/Ca/Ag bulk heterojunction photovoltaic devices under a simulated photovoltaic light with $1000 \text{ W} \cdot \text{m}^{-2}$ illumination (AM1.5).

Device	Annealing Temperature ^{a)}	$V_{\text{OC}} (\pm 0.01)$	$J_{\text{SC}} (\pm 0.2)$	PCE (± 0.02)	FF (± 0.5)
	$^\circ\text{C}$	V	$\text{mA} \cdot \text{cm}^{-2}$	%	%
1	— ^{b)}	0.39	1.31	0.09	16
2	70	0.36	2.41	0.19	22
3	90	0.38	2.69	0.23	22
4	110	0.42	3.37	0.32	23
5	130	0.41	4.37	0.50	28
6	150	0.41	5.16	0.61	29

^{a)}Devices annealed at indicated temperature for 10 min; ^{b)}No annealing.

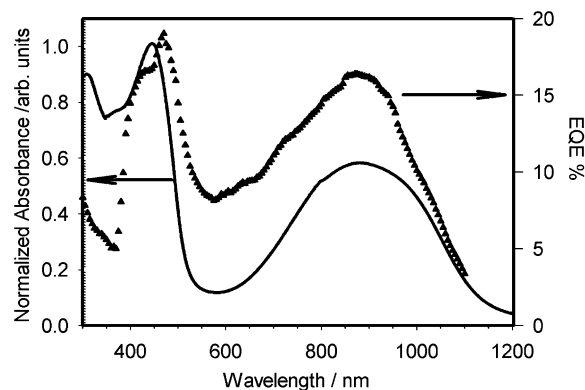


Figure 3. UV-vis spectrum of **P3** as a film (solid line) and photo-current spectral response (EQE) of a solar cell based on **P3**:PCBM (ITO/PEDOT:PSS/**P3**:PCBM/Ca/Ag) annealed at 150 °C (triangles).

Figure 3 shows the external quantum efficiency (EQE) of the device ITO/PEDOT:PSS/**P3**:PCBM/Ca/Ag annealed at 150 °C alongside the absorption spectrum of a thin film of polymer **P3**. The photocurrent response displays two maxima, having EQE values of 19% at 470 nm and 16.4% at 875 nm. The close similarity between the absorption spectrum of polymer **P3** and the device photocurrent response indicates that the photogeneration of charges originates predominantly following the absorption of light by the polymer. The observation of a photocurrent at wavelengths extending beyond 1 μm confirms that the use of a low energy-gap polymer permits photovoltaic devices to be realized having extended spectral sensitivity at near infra-red wavelengths.

The relatively low power conversion efficiencies obtained using polymer **P3** as the electron donor to PCBM in this study could be due in part to its low energy gap (1.1 eV) which would in turn lead to a relatively small energy difference between its HOMO level (4.8 eV) and that of the LUMO level of PCBM (3.8–4.3 eV) and hence result in the relatively low open-circuit voltage (≈ 0.4 V). These findings are in general agreement with the design rules outlined by Scharber et al.^[2] It is also clear that the relatively low FF observed here is suggestive of losses resulting from limited charge extraction, perhaps owing to non-optimal device thickness. However, the large short-circuit currents detected indicate that this class of material is promising for further device studies.

Conclusion

The preparation of new classes of donor/acceptor conjugated polymers comprising alternating 2,7-linked carbazole repeat units and 6,7-diphenyl-4,9-bis-(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline units has been successfully undertaken using Suzuki polymerization

conditions. Copolymers **P1** and **P2** which are functionalized at the 3,6-positions of carbazole repeat units with methyl-substituents have low energy gaps ($1.25 < E_g < 1.3$ eV). Copolymer **P3** which has no methyl-substituents at the 3,6-positions of carbazole repeat units has an even lower energy gap ($E_g = 1.1$ eV) as a result of a better electronic conjugation and absorbs light at wavelengths up to 1.2 μm . Copolymers **P1** and **P2** which have different 9-substituents (an alkyl-substituent for **P1** and a triaryl amine-substituent for **P2**) were found to have similar LUMO energy levels (3.8 eV). The fluorescence of these two polymers is only partly quenched when blended in films with 6% w/w of added PCBM indicating a partial electron transfer between these polymers and PCBM as they both have similar LUMO energy levels to that of PCBM. The fluorescence of **P3**, was almost fully quenched when 6% w/w of PCBM was introduced into films of the polymer as it has a higher LUMO energy level (3.7 eV) than that of PCBM. Preliminary studies on photovoltaic cells using 1:1 w/w blends of **P3** and PCBM as active layers afforded devices with an open-circuit voltage V_{oc} of 0.4 V and a power conversion efficiencies of 0.61%.

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