# Aryl amine substituted low energy gap carbazole polymers: preparation and photovoltaic properties<sup>†</sup>

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The preparation of a series of donor/acceptor copolymers comprising alternating 2,7-linked 3,6dimethyl-9-arylamino-carbazole units and 5,7-bis-(thiophen-2-yl)-2,3-diphenyl-thieno[3,4-b]pyrazine units is presented. The triarylamine substituents are attached to the carbazole repeat units either through the *para-* or *meta-*positions. The effect of the linkage position of triaryl amine substituents in this series of polymers as well as the effect of substitution of the phenyl groups at the 2,3-positions of 5,7-bis-(thiophen-2-yl)-2,3-diphenyl-thieno[3,4-b]pyrazine repeat units with alkoxy-substituents are investigated in this work. The polymers were characterized by NMR spectroscopy, UV-Vis absorption spectroscopy and fluorescence spectroscopy, and their molecular weights were estimated using gel permeation chromatography. Polymers **P1–P4** absorb light up to 900 nm and have energy gaps ranging from 1.37 to 1.40 eV. Photovoltaic cells with ITO/PEDOT:PSS/P2:PC<sub>70</sub>BM(1/4, w/w)/Al showed an open circuit voltage of 0.60 V under white light illumination, power conversion efficiency of 0.67% and short circuit current of 3.6 mA cm<sup>-2</sup>.

# Introduction

Research into the use of conjugated polymers for application in bulk heterojunction solar cells has been the subject of much interest in recent years in view of their potential technological value for energy generation. Major advances have been achieved, 1 however, new polymer systems with high absorption coefficients and extended absorption spectra are still being sought for use in this area. The design of low energy-gap conjugated polymers can be achieved by introduction of alternate electron donor and acceptor repeat units along the polymer chains which results in intra-molecular charge transfer.<sup>2</sup> This approach proved successful in the preparation of a range of narrow energy gap polymers for application in bulk heterojunction solar cells <sup>3</sup> including low energy gap alternating fluorene copolymers with 2,1,3-benzothiadiazole units <sup>4</sup> and lower energy gap fluorene copolymers with thienopyrazine <sup>5</sup> or thiadiazoloquinoxaline <sup>6</sup> alternate repeat units. Donor/acceptor systems comprising alternating 2,7-dibenzosilole 7 as well as 2,7-carbazole 8 units have also been described by Leclerc et al. and showed great promise when used with PCBM in bulk heterojunction photovoltaic cells with good power conversion efficiencies. We have reported recently the preparation of a series of donor/acceptor alternating copolymers comprising dithienyl thiadiazoloquinoxaline and 2,7-linked carbazole repeat units with energy gaps ranging from 1.1 and 1.3 eV. <sup>9</sup> Photovoltaic devices with a power conversion efficiency of 0.61% and short circuit current of 5.2 mA cm<sup>-2</sup> were obtained from one polymer in the series that had an energy gap of 1.1 eV. Besides the magnitude of the energy gap of the polymer donors, the design rules for the development of efficient polymers for photovoltaic applications should also take into account the relative positions of the HOMO and LUMO energy levels with respect to those of the acceptor materials in order to have efficient electron transfer as well as optimum open circuit voltage in devices. <sup>10</sup>

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 dithienyl thienopyrazine alternate repeat units in which triarylamine substituents are attached to the carbazole units either through *para-* or *meta-*linkages. An investigation into the properties of a series of carbazole-based copolymers is conducted in order to probe; (i) the effects the linkage positions of aryl amine substituents to the backbone of polymer chains, and (ii) the effect of attaching electron-donating alkoxy substituents to acceptor repeat units along the polymer chains. We also present an investigation into the physical properties of the polymers including a study of their performance in bulk heterojunction solar cells when blended with two different fullerene electron-acceptors.

# **Results and discussion**

In this study, a series of four donor acceptor conjugated polymers comprising alternate 2,7-linked-3,6-dimethyl carbazole repeat units bearing triaryl amine substituents at the 9-position and dithienyl thienopyrazine alternate repeat units were prepared. The use of triaryl amines as substituents in these materials is aimed at obtaining materials with good hole mobilities which is an important factor in solar cell applications. <sup>11</sup> The

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Device metrics for annealed devices and for films from blends of **P1–P4** with PC<sub>60</sub>BM or PC<sub>70</sub>BM at different percentage ratios. See DOI: 10.1039/c0jm01335h

different classes of donor/acceptor alternating copolymers prepared consist of polymers where the triarylamine substituents are either linked to the polymer backbone at the 9-position of carbazole repeat units through the *para*-position (polymers **P1** and **P2**) or through the *meta*-position (polymers **P3** and **P4**). Furthermore, introduction of electron-donating alkoxy substituents on the acceptor repeat units in polymers **P2** and **P4** also allows a comparison to be made with polymers **P1** and **P3** which do not have such substituents.

Preparation of polymers P3 and P4 required the preparation of the carbazole bis-boronic ester derivative 5 in which the triarylamine substituent is *meta*-linked to the 9-position of the carbazole ring. Intermediate 5 was prepared in four steps according to Scheme 1, starting from 3,6-dimethyl-9*H*-carbazole 1 upon displacement of fluorine from 3-fluoro-nitrobenzene in the presence of a base to afford 2 in good yields. Intermediate 2 was then reduced with tin(1) chloride to afford amino intermediate 3. An Ullmann-type condensation of 3 with 1-(2-butyloctyloxy)-4-iodobenzene in the presence of copper(1) iodide and [1,10]phenanthroline, afforded 4 in good yield. Further reaction of 4 with bis(pinacolato)-diboron in the presence of Pd(dppf)Cl<sub>2</sub> and potassium acetate gave the bis-boronate ester derivative 5 in reasonable yield.

Polymers P1-P4 were prepared using Suzuki cross-coupling condensation polymerisation reactions according to Scheme 2 upon reaction of bis-boronate ester derivative 5 or the known bis-boronate ester derivative 6 9 with known dibromides 7 5 or  $8.^{3}$  End-capping of the polymers with phenyl groups was then undertaken upon addition of bromobenzene and then phenylboronic acid at the end of the polymerisation reactions. All polymers were obtained in good yields. Gel permeation chromatography results from the polymerisation reactions (using polystyrene standards) have shown weight average molecular weight values  $M_{\rm w}$  ranging from 65 300 to 132 000 Da (Table 1) with polydispersity index values ranging from 5.1 to 8.3. These polydispersity index values are rather large especially given the fact that all the materials were fractionated at the work-up stage by Soxhlet extraction with acetone and diethyl ether in order to remove oligomers and low molecular weight chains.



Scheme 1 (i) 3-Fluoro-nitrobenzene,  $K_2CO_3$ , DMF, 85%, (ii) (a)  $SnCl_2 \cdot 2H_2O$ , EtOH, (b) NaOH, 84%, (iii) 1-(2-butyl- octyloxy)-4-iodobenzene Cu(I)I, [1,10]phenanthroline DMF, 84%, (iv) bis(pinacolato)diboron, KOAc, Pd(dppf)Cl<sub>2</sub>, DMF, 68%.



**Scheme 2** (i) (a) Pd(II) acetate/P(*p*-tolyl)<sub>3</sub> (1/2), NEt<sub>4</sub>OH, toluene/H<sub>2</sub>O. (b) Bromobenzene. (c) Phenylboronic acid.

#### Solution and solid-state electronic and fluorescence spectra

Absorption spectra of polymers P1-P4 both in chloroform solutions and as thin films are shown in Fig. 1. The polymers have absorption maxima between 616 and 635 nm in solution and between 638 and 661 nm in the solid state (Table 1). Polymers where the triarylamine substituents are linked through the meta-position to the polymer backbone (P3 and P4) display a slight red shift in their absorbance maxima both in solution and in the solid state when compared to the corresponding polymers where the triarylamine substituents are linked through the paraposition to the polymer backbone (P1 and P2 respectively). The optical energy gaps of polymers P3 and P4 (Table 1) as determined from the onset of their absorption in the solid state are also slightly lower than those of corresponding polymers P1 and **P2**. This finding indicates that the triarylamine substituents exert different stereoelectronic effects on the polymer backbones when they are linked through the meta-position or through the paraposition. A comparison of the absorption spectra of polymers P1 and P2 which only differ by the presence of electron-donating alkoxy substituents on the acceptor repeat units on P2 show similar absorption maxima both in solution and in the solid state. They also show the same optical energy gap indicating little effect resulting from substitution of acceptor repeat units with alkoxy substituents. No major difference is shown between the optical energy gaps of polymers P3 and P4 which have meta-linked arylamine substituents and in which alkoxy substitution of acceptor repeat units has no major bearing on their optical band gaps.

Polymer	$M_{ m n}$	$M_{ m w}$	PDI	Yield (%)	Absorption		Emission		
					$\lambda_{\rm max}/\rm nm~(CHCl_3)$	$\lambda_{\rm max}/{\rm nm}$ (film)	$\lambda_{\rm max}/{\rm nm}$ (CHCl <sub>3</sub> )	$\lambda_{\rm max}/\rm nm$ (film)	Energy gap <sup><i>a</i></sup> $E_{g (op)}/eV$
P1	15 800	132 000	8.3	84	620	642	795	934	1.40
P2	12 700	65 300	5.1	88	616	638	774	946	1.40
P3	13 100	85 700	6.5	80	624	658	789	910	1.39
P4	13 400	80 200	6.0	81	635	661	783	999	1.37

Table 1 GPC data, UV-vis-near IR, fluorescence data and energy gaps of polymers P1-P4



Fig. 1 Absorption spectra in chloroform solutions (solid lines), films (dashed lines) and photoluminescence spectra in chloroform solutions (dash-dot lines) and films (dash-dot-dot lines) of (a) P1, (b) P2, (c) P3 and (d) P4.

The absorption maxima of polymers **P1–P4** are similar to those of a donor–acceptor alternating copolymer comprising 2,7-linked 9-alkyl carbazole units and bis-(3-octylthien-2-yl)-2,3-diphenyl-thieno[3,4-b]pyrazine <sup>12</sup> which showed an absorption maximum of 675 nm. However, the absorption maxima of polymers **P1–P4** are all red-shifted in comparison to those of the alternating poly[9,9'-dioctylfluorene-2,7-diyl-*alt*-5,7-di (thien-2-yl)-2,3-diphenyl-thieno[3,4-b]pyrazine] **APFO-Green2** <sup>5</sup> (615 nm). Their band gap is also lower than that of **APFO-Green2** (1.5 eV) reflecting a higher electron-donating character of alternate carbazole repeat units in **P1–P4** in comparison to alternate fluorene repeat units in **APFO-Green2**.

In our previous studies on 2,7-linked carbazole main chain polymers with dialkylamino-phenyl N-functional groups <sup>13</sup> or with triarylamino N-functional groups <sup>14</sup> linked through the para-position to the polymer backbones, we have found that while the solvent polarity did not affect their electronic spectra, it did have a marked effect on their fluorescence spectra. Major differences were observed in their spectral features in solvents like toluene and dichloromethane. For instance, the 2,7-linked carbazole main chain polymer with 4-dialkylamino-phenyl N-functional groups displayed one main emission band at 417 nm with a shoulder at 441 nm in toluene, while it displayed a weak emission band at 417 nm and a more prominent broad emission band at 486 nm in dichloromethane. A possible explanation for these observations was attributed to intramolecular charge-transfer states <sup>15</sup> associating the strongly electron donating 4-dialkylamino phenyl substituents and the carbazole repeat units on the polymer chains. In other studies, Kijima et al. <sup>16</sup> have also found marked differences in the properties of 2,7linked carbazole polymers with triarylamino substituents linked to the polymer chain either through the meta- or para-positions.

Photoluminescence studies were conducted on polymers P1– P4 in solution in both toluene and chloroform as well as in thin films to investigate the effect of the linkage position of arylamine substituents on their physical properties (Fig. 1). For all polymers, there was no clear difference as to the values of their emission maxima in solution in toluene or in chloroform. Emission maxima varied from 774 to 795 nm in chloroform solutions and 910 and 999 nm in films (Table 1) with Stokes shifts ranging from 148 to 175 nm in solution and 252 to 338 nm in films indicating the large structural differences of the polymers in their ground and excited states.

#### **Electrochemical studies**

Cyclic voltammetry measurements on drop-cast polymer films of **P1–P4** were conducted in acetonitrile with tetrabutylammonium perchlorate as an electrolyte. The cyclic voltammograms of polymers **P1** and **P3** are shown in Fig. 2a and those of **P2** and **P4** in Fig. 2b. The redox potentials of the various polymers as well as their respective HOMO and LUMO levels (*vs.* vacuum) are shown in Table 2. All polymers show reversible oxidation and reduction waves. A comparison of the redox behaviour of polymers **P1** and **P3** indicates that the oxidation potential of polymer **P1** which has arylamine substituents linked through the *para*-position to the polymer **P3** where the arylamine substituents



 Table 2
 Redox potentials and energy levels of polymers P1–P4

-1.0

-0.5

Potential /V (vs. Ag/Ag<sup>+</sup>)

0.0

0.5

Polymer	$E^{0}_{ox}/V$	$E^{0}_{red}/V$	HOMO <sup>a</sup> /eV	LUMO <sup>a</sup> /eV	$E_{g (ec)}^{b}/eV$
P1	0.53	-1.42	-5.10	-3.60	1.50
P2	0.57	-1.44	-5.10	-3.60	1.50
P3	0.59	-1.41	-5.10	-3.60	1.50
P4	0.64	-1.42	-5.00	-3.60	1.40

<sup>*a*</sup> HOMO and LUMO positions (vs. vacuum) determined from onset of oxidation and reduction, respectively. <sup>*b*</sup>  $E_{g (ec)}$ , electrochemical band gap determined from the difference of the onset of oxidation and reduction of the polymers.

are linked to the polymer backbone through the *meta*-position (+ 0.59 V vs. Ag/Ag<sup>+</sup>).

The same finding is observed in respect to polymers P2 and P4 where the oxidation potential of polymer P2 is also lower than that of polymer P4 (0.57 V and 0.64 V vs. Ag/Ag<sup>+</sup>, respectively). Single oxidation waves are observed for both the arylamine substituents and the polymer backbone for all this series of polymers. The fact that the polymers with arylamine substituents that are linked through the para-position to polymer backbones (P1 and P3) have lower oxidation potentials than the corresponding polymers with *meta*-linked aryl amine substituents (P2 and P4) could possibly arise as a result of the electronic delocalization between the arylamine substituents and the polymer backbone when the arylamine substituents are linked through the para-position. The potentials of the reduction waves of all polymers are of comparable values (-1.41 to -1.44 V vs. Ag/ Ag<sup>+</sup>). The HOMO and LUMO levels (vs. vacuum) of polymers P1-P4 were respectively estimated from the onset of their oxidation and reduction waves from cyclic voltammetry experiments. The HOMO levels varied from -5.00 eV for polymer P4 to -5.10 eV for polymers P1, P2 and P3 while all polymers had

the same LUMO level of -3.6 eV. The electrochemical band gaps  $(E_{g (ec)})$  of the polymers were all in good agreement with their optical band gaps  $(E_{g (op)})$  as shown in Table 1.

#### Photovoltaic device characterization

Various preparation and thermal annealing protocols were explored in an attempt to find the processing conditions necessary to fabricate optimized PV devices with active layers consisting of polymer/fullerene blends. Device characterization results are presented in Table 3. In an attempt to optimize efficiency, active layers were thermally annealed after cathode deposition at 110 °C, 130 °C and 150 °C for set periods of 30 min to encourage self-organization of donor-acceptor domains. The fullerene derivative PC70BM was also used (at a relative concentrations of 50, 66 and 80% w/w) to enhance light absorption and improve charge transport It was found that thermal annealing at 150 °C and the use of PC<sub>70</sub>BM at a weight concentration of 80% lead to optimal device performance.

EQE and J-V data from the most efficient device that was prepared from polymer P2 are presented in Fig. 3(a) and (b), respectively. A significant rectification is obtained in the J-Vcurve recorded in the dark. However under illumination, the J-Vcurve is symmetric around  $V_{OC}$ , hence resulting in a relatively low device low fill factor of 31%, a value that could not be improved by annealing at higher temperatures. In fact, thermal annealing at 180 °C resulted in no improvement over an untreated device owing to PCBM crystallization. Such low fill factors are indicative of a large series resistance that most likely adversely affects the charge transport and extraction thus reducing short circuit current  $(J_{SC})$  and power conversion efficiency (PCE). 1,17

The efficiency of this series of polymers when fabricated into devices compares well to those determined in other studies on materials with similar energy gaps 8,9,18 particularly the analogous APFO-Green2:PC<sub>60</sub>BM blend which had  $J_{SC} = 1.6$  mA cm<sup>-2</sup> under 1 Sun AM1.5G simulated solar irradiation.<sup>5</sup> Through careful optimization of processing parameters, we determine optimized device metrics of PCE = 0.67%,  $J_{SC}$  = 3.6 mA cm<sup>-2</sup>,  $V_{\rm OC} = 0.60$  V and FF = 31% measured from a 1 : 4 P2/PC<sub>70</sub>BM device processed from chlorobenzene. By contrast, the performance metrics of a  $1:4 P2/PC_{60}BM$  device (fabricated for the sake of comparison and again characterized under 1 Sun AM1.5G illumination) were: PCE = 0.34%,  $J_{SC} = 1.8$  mA cm<sup>-2</sup>,  $V_{\rm OC} = 0.57$  V and FF = 32%. It is clear that this improved

Table 3 P1-P4 OPV device performance metrics as measured under 1 Sun simulated AM1.5G illumination

Material	PCE (%)	$J_{\rm SC}/{ m mA~cm^{-2}}$	V <sub>OC</sub> /V	FF (%)	Thickness/ $\pm$ 5 nm
P1 P2 <sup>a</sup> P3 P4	0.58 0.67 0.38 0.65	3.4 3.6 2.7 3.5	0.59 0.60 0.50 0.65	29 31 28 29	55 70 67 63
P4	0.65	3.3	0.65	29	03

<sup>a</sup> By contrast, the performance metrics of a 1:4 P2/PC<sub>60</sub>BM device which was processed from chlorobenzene for comparison measured under equivalent conditions are: PCE = 0.34%,  $J_{SC} = 1.8$  mA cm<sup>-2</sup>,  $V_{\rm OC} = 0.57$  V and FF = 32%.



**Fig. 3** Device data from **P2**. (a) EQE and absorption spectra from a thermally annealed  $1 : 4 \text{ P2}/\text{PC}_{70}\text{BM}$  device; part (b): J-V spectra of the same device in the dark (dashed line) and under 1 Sun simulated AM1.5 illumination (solid line).

efficiency partly results from improved light absorption that occurs as a result of using  $PC_{70}BM$  instead of  $PC_{60}BM$ . It is apparent however that low fill factors (suggestive of serial resistive losses) play a significant role in limiting the efficiency of our devices <sup>1,17</sup> and effectively preclude the use of thicker active layers. It is presently unclear whether the reduced fill factor and PCE in our devices is contact or transport related. Clearly, studies addressing charge extraction through the ITO/PEDOT:PSS/polymer interface and electron and hole transport through our polymer/fullerene thin films would help to resolve this issue.

# **Experimental section**

## Materials

2,7-Dibromo-3,6-dimethyl-9*H*-carbazole **1**, <sup>19</sup> *N*,*N*-bis-(4-(2butyloctyloxy)phenyl)-4-(3,6-dimethyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazol-9-yl)aniline **6**, <sup>9</sup> 5,7-bis-(5-bromo-thiophen-2-yl)-2,3-diphenyl-thieno[3,4-b]pyrazine **7**<sup>5</sup> and 5,7-bis-(5-bromo-thiophen-2-yl)-2,3-bis-[4-(2-ethylhexyloxy)-phenyl]-thieno[3,4-b]pyrazine **8**<sup>3</sup> were prepared according to literature procedures. Toluene was distilled over sodium under an inert nitrogen atmosphere. *N*,*N*-Dimethylformamide (DMF) was dried and distilled over calcium hydride before use. Acetonitrile (HPLC grade) was dried and distilled over phosphorus pentoxide under an inert argon atmosphere, then stored over molecular sieves 3 Å.

#### Measurements

NMR spectra were recorded on Bruker 250 MHz, AMX400 400 MHz or DRX500 500MHz NMR spectrometers at 22  $^\circ C$  in

chloroform-d<sub>1</sub> solutions with TMS as the internal standard. GPC curves were recorded on the equipment consisting of a Waters Model 515 HPLC Pump, GILSON Model 234 Autoinjector, MILLIPORE Waters Lambda-Max Model 481 LC Spectrometer, Erma ERC-7512 RI Detector, PLgel 5m 500A Column, and PLgel 10m MIXED-B Column using chloroform as the eluent at a rate of 1 cm<sup>3</sup> min<sup>-1</sup>. Polymer solutions in chloroform (2.5 mg cm<sup>-3</sup>) were used as samples for 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 with a Perkin Elmer 2400 CHN Elemental Analyzer for CHN analysis and by a Schöniger oxygen flask combustion method for anion analysis. UV-visible absorption spectra were measured using a Hitachi U-2010 Double Beam UV/Visible Spectrophotometer or a Perkin-Elmer Lambda 45 UV/Vis Spectrometer. The absorbance of polymers was measured in solution in chloroform at ambient temperature using rectangular quartz cuvettes (light pathlength = 10 mm). Samples of pristine polymer thin films for UV-visible absorption spectra measurements were prepared by dip coating quartz plates into 1 mg cm<sup>-3</sup> polymer solutions in chloroform with measurements carried out at ambient temperature.

Samples of polymer thin films for photoluminescence (PL) spectroscopy measurements were prepared by either spin-coating or drop casting onto glass substrates from polymer solutions in chlorobenzene (HPLC grade). PL spectroscopy measurements were performed by imaging the emission from the sample into a JY SPEX 1/4m monochromator using a silicon photodiode to detect light from 2.2 eV to 1 eV and thereafter with an InSb detector. Samples were optically excited using the 488 nm line of an Ar<sup>+</sup> laser that was mechanically chopped. Photodiode signals were amplified by an EG&G current voltage amplifier and a Stanford Research Systems SR830 Lockin-Amplifier. Solutions were prepared from polymers dissolved in chloroform or toluene (HPLC grade) decanted into glass cuvettes (light pathlength = 10 mm). Absorption spectra were obtained using JY Fluoromax 4 Fluorimeter. Absorption and PL measurements were carried out at ambient temperature in air.

Cyclic voltammograms were recorded using a Princeton Applied Research Model 263A Potentiostat/Galvanostat. Measurements were carried out under argon at  $25 \pm 2$  °C. 10 cm<sup>3</sup> of a tetrabutylammonium perchlorate (TBAClO<sub>4</sub>) solution in acetonitrile (0.1 mol dm<sup>-3</sup>) was used as the electrolyte solution. A three-electrode system was used consisting of an Ag/Ag<sup>+</sup> reference electrode (silver wire in 0.01 mol dm<sup>-3</sup> silver nitrate solution in the electrolyte solution), a platinum working electrode (2 mm diameter smooth platinum disc, area =  $3.14 \times 10^{-2}$  cm<sup>2</sup>), and a platinum counter electrode (platinum wire). Polymer thin films were formed by drop casting 1.0 mm<sup>3</sup> of polymer solutions in dichloromethane (HPLC grade) (1 mg cm<sup>-3</sup>) onto the working electrode, then dried in air. Ferrocene was employed as a reference redox system according to the recommendation of IUPAC.<sup>20</sup>

Photovoltaic devices were fabricated using the basic architecture ITO(50 nm)/PEDOT:PSS(30 nm)/Active Layer(60–80 nm)/ Al(100 nm) where the active layer was a thin film of polymer blended with 80% PC<sub>70</sub>BM by weight. To fabricate OPV devices, a thin film of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) was first coated on the ITO patterned substrates. The active layer solutions and thin films were prepared in an inert N<sub>2</sub> atmosphere maintained in a glove box. Solutions were prepared at a concentration of 20 mg ml<sup>-1</sup> in chlorobenzene then heated overnight at 60 °C. To ensure that each material was dissolved, they were passed through a 0.45  $\mu$ m PTFE syringe mounted filter. All films were spin cast in a glove box at 2000 rpm prior to the thermal deposition of the cathode. Thermal annealing at 150 °C for 30 min was carried out at this point. Devices were then encapsulated in nitrogen using a UV curable epoxy that was used to stick a glass slide to the device surface. The device active area was 0.045 cm<sup>2</sup> as defined by the overlap of ITO anode and the evaporated cathode.

Finished devices were characterized under 1 Sun (100 mW cm<sup>-2</sup>) simulated AM1.5G solar radiation delivered by a Newport Class-A solar simulator whose output was first checked with an NREL calibrated silicon photodiode. Performance metrics were calculated from a J-V sweep taken with a Keithley 237 Source-Measure Unit. For EQE measurements, light from a home-built setup consisting of a tungsten lamp coupled with a Spectral Instruments DK240 monochromator was focused onto the devices with a  $10 \times$  objective. The incident power was first measured with a calibrated reference Newport photodiode before the test photodiode was characterized.

### Preparation of monomers

All reactions were carried out under an inert nitrogen atmosphere.

2,7-Dibromo-3,6-dimethyl-9-(3-nitro-phenyl)-9*H*-carbazole 2. A mixture of 2,7-dibromo-3,6-dimethyl-9H-carbazole 1 (7 g, 19.95 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub>, (13.76 g, 0.10 mol), 3-fluoronitrobenzene (10 g, 70.87 mmol) and DMF (95 cm<sup>3</sup>) was heated at reflux for 24 h under an inert atmosphere. After cooling to room temperature the solution was poured onto warm (40  $^{\circ}$ C) water (500 cm<sup>3</sup>). The dark green solid was collected by filtration and the crude material was washed with several portions of warm (40 °C) water (3  $\times$  300 cm<sup>3</sup>), then recrystallised from toluene to obtain 2 as bright green crystals (7.98 g, 85%), mp 266-269 °C. Mass (EI); (m/z): 472, 474, 476 (M<sup>•+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\rm H}$ /ppm: 2.56 (s, 6H); 7.51 (s, 2H); 7.82 (m, 1H); 7.85 (m, 1H); 7.92 (s, 2H); 8.35 (m, 1H); 8.40 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_{\rm C}$ /ppm: 23.10; 113.03; 121.70; 121.8; 122.56; 122.62; 123.10; 130.31; 131.19; 132.73; 138.44; 139.75; 149.52. IR (KBr): 3038.8; 2919.6; 2856.3; 1605.3; 1527.8; 1450.1; 1343.1; 1304.0; 1234.9; 1081.8; 1041.7; 1000.4; 957.4; 869.6 cm<sup>-1</sup>. Calcd. for  $C_{20}H_{14}N_2Br_2O_2$ : C, 50.66; H, 2.98; N, 5.91; Br, 33.70. Found: C, 50.85; H, 2.69; N, 5.76; Br, 33.41.

**2,7-Dibromo-3,6-dimethyl-9-(3-amino-phenyl)-9H-carbazole 3.** A mixture of 2,7-dibromo-3,6-dimethyl-9-(3-nitro-phenyl)-9H-carbazole **2** (6.39 g, 13.54 mmol),  $SnCl_2 \cdot 2H_2O$  (18.22 g, 80.75 mmol), and ethanol (250 cm<sup>3</sup>) was heated at reflux for 24 h and then cooled to room temperature. The solvent was removed *in vacuo* and the resulting residue washed with a 10% (w/w) aqueous solution of sodium hydroxide (300 cm<sup>3</sup>). The organic material was extracted with diethyl ether (3 × 300 cm<sup>3</sup>) and the combined organic phases dried over MgSO<sub>4</sub>, filtered and the solvent was removed *in vacuo*. The crude product was recrystallised from

toluene to give **3** as ivory crystals (5.01 g, 84%), mp 198–200 °C. Mass (EI); (*m*/*z*): 442, 444, 446 (M<sup>++</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\rm H}$ /ppm: 2.53 (s, 6H); 5.10 (br s, 2H); 6.77 (d, 1H, *J* = 7.6Hz); 6.82 (m, 1H); 6.86 (m, 1H); 7.35 (m, 1H); 7.59 (s, 2H); 8.12 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta_{\rm C}$ /ppm: 23.09; 112.88; 113.66; 114.49; 116.65; 121.33; 122.06; 122.65; 128.93; 130.87; 137.93; 140.32; 148.09. IR (KBr): 3402.8; 3316.6; 3208.4; 2969.7; 2491.2; 2857.5; 1907.9; 1602.1; 1498.1; 1451.6; 1361.5; 1323.9; 1302.8; 1235.8; 1125.6; 1041.1; 995.9; 956.7; 942.0; 855.2; 839.1 cm<sup>-1</sup>. Calcd. for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>Br<sub>2</sub>: C, 54.08; H, 3.63; N, 6.31; Br, 35.97. Found: C, 54.27; H, 3.38; N, 6.12; Br, 35.88.

Bis-(4-(2-butyloctyloxy)phenyl)-3-(2,7-dibromo-3,6-dimethyl-9H-carbazol-9-yl)aniline 4. A mixture of 2,7-dibromo-3,6dimethyl-9-(3-amino-phenyl)-9H-carbazole 3 (2.69 g, 6.09 mmol), 1-(2-butyl-octyloxy)-4-iodobenzene (7.21 g, 18.58 mmol), [1,10]phenanthroline (0.06 g, 0.33 mmol), copper(I) chloride (0.03 g, 0.30 mmol) and potassium hydroxide (2.88 g, 51.33 mmol) in toluene (20 cm<sup>3</sup>) was refluxed under an inert atmosphere for 48 h. The reaction mixture was then cooled to ambient temperature and poured onto water (200 cm<sup>3</sup>). The resulting mixture was extracted with dichloromethane  $(3 \times 200 \text{ cm}^3)$  and the combined organic phases were washed with water (200 cm<sup>3</sup>), dried over MgSO<sub>4</sub> and the solvent removed in vacuo to give the crude product as an oil. The product was purified by chromatography on silica gel using petroleum ether in a first stage, then a more polar solvent mixture petroleum ether/ethyl acetate (10/ 1). Product 4 was obtained as a light brown solid (4.82 g, 84%), mp 94–98 °C. Mass (EI); (*m*/*z*): 963, 965, 967 (M<sup>•+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\rm H}$ /ppm: 0.89 (m, 12H); 1.30 (m, 32H); 1.75 (m, 2H); 2.54 (s, 6H); 3.80 (d, 4H, J = 6.4 Hz); 6.87 (d, 4H, J = 9.15 Hz); 6.95 (dd, 1H, J = 6.41Hz; 2.14 Hz); 7.15 (d, 4H, J = 8.54 Hz); 7.28 (m, 1H); 7.32 (m, 1H); 7.35 (m, 1H); 7.60 (s, 2H); 7.87 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_{\rm C}$ /ppm: 14.15; 22.72; 23.06; 23.10; 26.86; 29.1; 29.73; 31.09; 31.39; 31.90; 38.01; 71.06; 113.71; 113.99; 115.55; 116.96; 117.17; 118.12; 121.29; 122.12; 122.66; 124.56; 126.92; 128.97; 130.25; 139.97; 150.68; 156.18. IR (KBr): 2923.7; 2855.6; 1592.9; 1505.4; 1469.3; 1447.2; 1362.7; 1301.8; 1278.5; 1236.8; 1167.8; 1125.3; 1104.1; 1031.8; 996.7; 951.0; 866.5; 831.6 cm<sup>-1</sup>. Calcd. for C<sub>56</sub>H<sub>72</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 69.70; H, 7.52; N, 2.90; Br, 16.56. Found: C, 69.66; H, 7.52; N, 2.76; Br, 16.60.

N,N-Bis-(4-(2-butyloctyloxy)phenyl)-3-(3,6-dimethyl-2, 7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazol-9-yl)aniline 5. A mixture of bis-(4-(2-butyloctyloxy)phenyl)-3-(2,7-dibromo-3,6-dimethyl-9H-carbazol-9-yl)aniline 4 (3.41 g, 3.60 mmol), bis(pinacolato)diboron (3.41 g, 13.43 mmol), potassium acetate (2.22 g, 22.62 mmol) and Pd(dppf)Cl<sub>2</sub> (0.19 g, 0.26 mmol) in DMF (100 cm<sup>3</sup>) was heated to 100 °C for 24 h. The reaction mixture was then cooled to room temperature, poured into water (100 cm<sup>3</sup>) and extracted with diethyl ether (3  $\times$  100 cm<sup>3</sup>). The organic phases were combined, then washed with water  $(2 \times 100 \text{ cm}^3)$  and dried over MgSO<sub>4</sub>. The crude product was purified by chromatography on silica gel using petroleum ether/dichloromethane/pyridine (30/30/1) as eluent. Product 5 was separated as a white solid (2.60 g, 68% yield), mp 81-83 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\rm H}$ /ppm: 0.82 (m, 12H); 1.21 (m, 32H); 1.31 (s, 24H); 1.66 (m, 2H); 2.63 (s, 6H); 3.71 (d, 4H, J = 5.34 Hz); 6.85 (m, 2H); 6.81 (d, 4H, J = 8.17 Hz); 7.00 (s, 1H) 7.12 (d, 4H,  $J = 8.79 \text{ Hz}); 7.24 (m, 1\text{H}); 7.78 (\text{br s}, 4\text{H}). {}^{13}\text{C NMR} (\text{CDCl}_3) \delta_{\text{C}}/\text{ppm: } 14.15; 22.47; 22.71; 23.09; 24.96; 26.86; 29.09; 29.73; 31.08; 31.39; 31.89; 38.03; 71.02; 83.36; 115.46; 117.02; 117.38; 117.86; 121.11; 124.96; 127.29; 129.95; 133.74; 135.26; 139.17; 139.9; 143.99; 149.98; 151.36; 156.11. IR (KBr): 2924.4; 2854.9; 1740; 1593; 1505.5; 1485.4; 1447.1; 1372.5; 1362.8; 1302.4; 1278.9; 1237; 1167.9; 1125.3; 1104.6; 1031.5; 997.2; 951.1; 831.6 \text{ cm}^{-1}. Calcd. for C<sub>68</sub>H<sub>96</sub>B<sub>2</sub>N<sub>2</sub>O<sub>6</sub>: C, 77.11; H, 9.14; N, 2.64. Found: C, 77.21; H, 9.21; N, 2.54.$ 

#### Preparation of the polymers

Polymer P1. Toluene (11 cm<sup>3</sup>) was added to mixture of palladium(II) acetate (13.86 mg, 0.0617 mmol) and tri-p-tolylphosphine (31.84 mg, 0.105 mmol) and the vessel was heated to 50 °C for 30 min. The solution was then cooled to room temperature and transferred via a syringe to a separate flask containing N,N-bis-(4-(2-butyloctyloxy)phenyl)-4-(3,6-dimethyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazol-9-yl)aniline 6 (0.40 g, 0.3776 mmol) and 5,7-bis-(5-bromothiophen-2-yl)-2,3-diphenyl-thieno[3,4-b]pyrazine 7 (230.53 mg, 0.3776 mmol) under an inert atmosphere. A deoxygenated tetraethylammonium hydroxide solution (2 cm<sup>3</sup>, 20% w/w in water, 2.61 mmol) was then added to the solution and the resulting mixture heated at 95 °C for 43 h. The mixture was then cooled to room temperature and bromobenzene (0.11 cm<sup>3</sup>, 0.49 mmol) was added under an inert atmosphere and the mixture heated at 95 °C for 2 h. The mixture was then cooled to room temperature and phenylboronic acid (0.10 g, 0.82 mmol) was added under an inert atmosphere and the mixture heated at 95 °C for 4 h, then cooled to room temperature. The reaction mixture was then poured onto a mixture of methanol/water (10/1, 250 cm<sup>3</sup>). The resulting precipitate was collected by filtration and purified by Soxhlet extraction with acetone for 24 h, diethyl ether for 24 h then toluene. The toluene fraction was concentrated to ca. 50 cm<sup>3</sup> and the polymer precipitated from methanol (250 cm<sup>3</sup>), filtered and dried to afford P1 as a deep dark green solid (0.40 g, 84%).  $M_{\rm p} =$ 15 800,  $M_{\rm w} = 132\ 000$ , PDI = 8.3. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\rm H}$ /ppm: 0.75-0.95 (m, 12H), 1.10-1.50 (m, 30H), 1.65 (m, 2H), 2.70 (s, 6H), 3.55–3.80 (m, 4H), 6.65–7.80 (m, 30H), 8.00 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ<sub>C</sub>/ppm: 13.09, 20.57, 21.64, 22.03, 25.81, 28.06, 28.65, 30.05, 30.82, 36.99, 70.08, 110.49, 114.4, 119.04, 120.84, 121.61, 123.89, 126.19, 126.46, 126.63, 127.06, 128.09, 129.00, 131.17, 133.51, 136.55, 137.98, 138.18, 139.61, 144.58, 147.30, 151.76, 155.10. Calcd. for C<sub>82</sub>H<sub>86</sub>N<sub>4</sub>O<sub>2</sub>S<sub>3</sub>: C, 78.43; H, 6.90; N, 4.46. Found: C, 77.22; H, 6.60; N, 4.13.

**Polymer P2. P2** was prepared following the same experimental procedure as that adopted for the preparation of **P1** and on the same scale using *N*,*N*-bis-(4-(2-butyloctyloxy)phenyl)-4-(3,6-dimethyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazol-9-yl)aniline **6** and 5,7-bis-(5-bromo-thiophen-2-yl)-2,3-bis-[4-(2-ethyl-hexyloxy)-phenyl]-thieno[3,4-b]pyrazine **8** as the coupling partners. It was obtained as a deep dark green solid (0.50 g, 88%).  $M_n = 12$  700,  $M_w = 65$  300, PDI = 5.1. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_H$ /ppm: 0.85–1.05 (m, 24H), 1.15–1.50 (m, 48H), 1.65 (s, 4H), 2.70 (s, 6H), 3.65–3.98 (m, 8H), 6.71–7.75 (m, 26H), 8.05 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_C$ /ppm: 11.1, 14.0, 21.5, 22.61, 23.00, 23.85, 26.78, 29.03, 29.62, 30.45, 30.52, 30.87, 31.8, 39.40, 37.96,

70.57, 71.04, 111.58, 114.12, 115.37, 119.97, 121.68, 122.59, 124.00, 124.50, 127.08, 127.18, 127.48, 127.72, 131.40, 132.30, 134.85, 137.54, 140.13, 140.56, 145.13, 148.32, 152.44, 156.09, 160.31. Calcd. for  $C_{98}H_{118}N_4O_4S_3$ : C, 77.84; H, 7.87; N, 3.70. Found: C, 77.96; H, 7.89; N, 3.51.

Polymer P3. P3 was prepared following the same experimental procedure as that adopted for the preparation of P1 and on the same scale using N,N-bis-(4-(2-butyloctyloxy)phenyl)-3-(3,6dimethyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazol-9-yl)aniline 5 and 5,7-bis-(5-bromo-thiophen-2-yl)-2,3-diphenyl-thieno [3,4-b]pyrazine 7 as the coupling partners. It was obtained as a deep dark green solid (0.38 g, 80%).  $M_{\rm n} = 13\ 100,\ M_{\rm w} = 85\ 700,\ {\rm PDI} = 6.5.\ {}^{1}{\rm H}\ {\rm NMR}\ ({\rm CDCl}_{3})\ \delta_{\rm H}/$ ppm: 0.70-0.95 (m, 12H), 1.10-1.50 (m, 30H), 1.60 (m, 2H), 2.70 (s, 6H), 3.55–3.80 (m, 4H), 6.60–7.80 (m, 30H), 8.00 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_{\rm C}$ /ppm: 13.09, 20.71, 21.67, 22.04, 25.89, 28.11, 28.69, 30.06, 30.37, 37.08, 69.76, 110.57, 114.3, 116.05, 121.0, 121.80, 123.79, 124.04, 126.40, 126.73, 127.89, 128.12, 129.03, 131.12, 133.47, 136.68, 138.00, 138.80, 139.26, 144.68, 149.41, 151.84, 155.06. Calcd. for C82H86N4O2S3: C, 78.43; H, 6.90; N, 4.46. Found: C, 75.42; H, 6.55; N, 4.06.

Polymer P4. P4 was prepared following the same experimental procedure as that adopted for the preparation of P1 and on the same scale using N,N-bis-(4-(2-butyloctyloxy)phenyl)-3-(3,6dimethyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazol-9-yl)aniline 5 and 5,7-bis-(5-bromo-thiophen-2-yl)-2,3-bis-[4-(2-ethyl-hexyloxy)-phenyl]-thieno[3,4-b]pyrazine 8 as the coupling partners. It was obtained as a deep dark green solid (0.46 g, 81%).  $M_{\rm n} = 13400$ ,  $M_{\rm w} = 80200$ , PDI = 6.0. <sup>1</sup>H NMR  $(CDCl_3) \delta_H/ppm:, 0.70-1.00 (m, 24H). 1.10-1.50 (m, 48H), 1.55$ (s, 4H), 2.75 (s, 6H), 3.60-4.05 (m, 8H), 6.60-7.45 (m, 22H), 7.50–7.70 (m, 4H), 8.05 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_{\rm C}$ /ppm: 10.11, 13.09, 20.7, 22.03, 22.81, 22.88, 25.88, 28.08, 28.68, 29.55, 30.06, 30.37, 30.85, 37.09, 38.36, 70.57, 71.04, 110.58, 113.14, 114.33, 115.96, 121.68, 120.92, 121.76, 123.04, 123.69, 126.06, 126.72, 130.45, 131.23, 133.76, 136.68, 136.89, 138.78, 139.03, 144.31, 149.4, 151.59, 155.06, 159.32. Calcd. for C<sub>98</sub>H<sub>118</sub>N<sub>4</sub>O<sub>4</sub>S<sub>3</sub>: C, 77.84; H, 7.87; N, 3.70. Found: C, 76.77; H, 7.61; N, 3.47.

# Conclusions

A new class of donor/acceptor conjugated polymers comprising alternating 2,7-linked carbazole repeat units and 5,7-bis-(thiophen-2-yl)-2,3-diphenyl-thieno[3,4-b]pyrazine units have been successfully prepared using Suzuki cross-coupling condensation polymerisation reactions. Polymers P1-P4 were obtained in good yields with weight average molecular weight values  $M_{\rm w}$ ranging from 65 300 to 132 000 Da. Polymers absorb light up to 900 nm and have energy gaps ranging from 1.37 to 1.40 eV. Polymers where the triarylamine substituents are linked through the meta-position to the polymer backbone (P3 and P4) display a slight red shift in their absorbance maxima both in solution and in the solid state when compared to the corresponding polymers where the triarylamine substituents are linked through the paraposition to the polymer backbone (P1 and P2, respectively) indicating that the triarylamine substituents exert different stereoelectronic effects on the polymer backbones when they are linked through the *meta*-position or through the *para*-position. Attachment of alkoxy substituents to the phenyl groups of acceptor repeat units on these polymers does not affect their absorption maxima and has no marked effect on the electronic delocalisation along their backbones. In contrast to previous studies on wide band gap carbazole-based polymers with triarylamine substituents, the solvent polarity has little effect on the photoluminescence of this series of low band gap polymers and both polymers with *meta* and *para*-linked aryl amine substituents display similar emission maxima in toluene and chloroform solutions. The Stokes shifts in this class of polymers ranged from 252 to 338 nm in films indicating large structural differences of the polymers in their ground and excited states.

Cyclic voltammetry measurements indicate that the oxidation potential of polymers which have arylamine substituents linked through the *para*-position to the polymer backbone (**P1** and **P2**) are lower than those of polymers where the arylamine substituents are linked to the polymer backbone through the *meta*position (**P3** and **P4**) possibly as a result of the electronic delocalization between the arylamine substituents and the polymer backbone when the arylamine substituents are linked through the *para*-position.

Studies on photovoltaic cells using 1:4 (weight: weight) blends of the polymers and PC<sub>60</sub>BM as active layers on films cast from chlorobenzene afforded devices with power conversion efficiencies ranging from 0.26 and 0.34%. An optimized device was obtained for a 1:4 **P2**/PC<sub>70</sub>BM device processed from chlorobenzene having a PCE = 0.67%,  $J_{SC} = 3.6$  mA cm<sup>-2</sup>,  $V_{OC} = 0.60$  V and FF = 31% under 1 Sun AM1.5G simulated solar irradiation.

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