Impact of dithienyl or thienothiophene units on the optoelectronic and photovoltaic properties of benzo[1,2,5]thiadiazole based donor–acceptor copolymers for organic solar cell devices†


We report a comparative study on four donor–acceptor benzothiadiazole-based copolymers containing dithienyl or thienothiophene moieties for application in organic photovoltaic (OPV) devices. Bulk-heterojunction OPV devices are fabricated having power conversion efficiencies ranging between 4 and 6%. Morphological, spectroscopic and charge-transport measurements are used to investigate the influence of either the dithienyl or thienothiophene moieties on the structure and photophysical properties of the copolymer and copolymer:PC71BM blend films and rationalise the solar cell characteristics. Although all copolymer:PC71BM blends exhibit comparable hole polaron yields, solar cell devices with the highest power conversion efficiencies are correlated with increased charge-carrier mobility of the copolymer and enhanced aggregation of PC71BM in the blend.

Introduction

Solution-processable photovoltaic devices are a promising technology for low-cost solar energy conversion, with organic photovoltaic devices (OPVs) attracting significant attention from a wide range of research fields over the past decade.1–4 OPV devices that employ blends of conjugated polymers and fullerene derivatives in the photoactive layer in a bulk-heterojunction (BHJ) architecture have demonstrated a steady rise in efficiency and lifetime in recent years.5–10 This rise has, in part, been due to the large number of novel electron donating semiconductors that have been synthesised. In particular, donor–acceptor copolymers with alternating electron-rich and electron-deficient heterocycles along the conjugated backbone have proven to be promising semiconductor materials that have low optical band-gaps, and can thus efficiently harvest a relatively large portion of the visible and near-IR regions of the solar spectrum.6–9 Benzothiadiazole (BT) is one example of an electron-deficient moiety that can be included in a donor–acceptor copolymer. Many examples exist where this unit is flanked by thiophene moieties and combined with a suitable electron donor such as 2,7-carbazole,9 fluorene,10 cyclopentadithiophene11 and benzothiophene.12,13 When blended with fullerene derivatives such as PCBM or PC71BM in an OPV device, power conversion efficiencies of up to 8% have been achieved under optimised processing conditions.13

One strategy to further improve the light-harvesting efficiency of BT containing copolymers is to reduce their optical band-gaps by altering adjacent units with other heterocycles such as selenophene.14–17 Fused heterocycles may also be used to modify the optical bandgap of the copolymer; an approach that forms the basis of this work. The synthesis of PFDT2BT-8 and PCDT2BT-8 have been reported previously,18,19 with devices incorporating PCDT2BT-8 exhibiting maximum PCEs above 6% after optimisation of the device architecture.18 The copolymer PCDT2BT-8 is similar in structure to the relatively well-studied copolymer PCDTBT.9,20–23 Here, addition of octyloxy groups to the BT unit has been shown to increase the solubility of PCDT2BT-8 in common processing solvents relative to PCDTBT. Furthermore, a reduction in the HOMO level of PCDT2BT-8 in common processing solvents relative to PCDTBT has been shown to aﬀord an increase in device open-circuit voltage.19 Substitution of the two thiophene
units on PCDT2BT-8 and PFDT2BT-8 with thienothiophene moieties provides a further opportunity to modify the structural and optoelectronic properties of the copolymers. Synthesis of these structures affords two new polymers, namely PCDTTBT-8 and PFDTTBT-8. In this work a detailed physical study is undertaken to explore the optical and electronic properties of these four copolymers in order to understand their performance in OPV devices.

Results and discussion

The copolymers PCDT2BT-8 and PFDT2BT-8 were synthesised according to previous reports. Copolymers PCDTTBT-8 and PFDTTBT-8 were prepared using Suzuki coupling conditions upon reaction of 4,7-bis-(5-bromo-thieno[3,2-b]thiophene-2-yl)-5,6-bis-octyloxy-benz[o,1,2,5]thiadiazole with 9-(heptadecan-9-yl)-2,7-bis(4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole and 9,9-dioctylfluorene-2,7-diboron acid bis[1,3-propanediol] ester respectively according to Scheme 1. The structures of all the copolymers studied are shown in Fig. 1.

![Scheme 1](image)

Scheme 1: (i) (a) Pd(OAc)2/2,2'-bipy (1/2), NEt4OH, toluene/H2O, 95 °C, 4 h. (b) PhBr, (c) PhB(OH)2.

![Fig 1](image)

Fig. 1 Chemical structures of the copolymers used in this study.

### Table 1  Physical characteristics of the copolymers used in this study

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M_w/kDa</th>
<th>M_n/kDa</th>
<th>PDI</th>
<th>E_on/V</th>
<th>E_1/2V</th>
<th>HOMO/eV</th>
<th>LUMO/eV</th>
<th>Band gap/eV</th>
<th>ε/L mol⁻¹ cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCDT2BT-8</td>
<td>31.1</td>
<td>57.2</td>
<td>1.84</td>
<td>0.78</td>
<td>−1.72</td>
<td>−5.2</td>
<td>−3.3</td>
<td>1.95</td>
<td>58 500</td>
</tr>
<tr>
<td>PCDTTBT-8</td>
<td>18.6</td>
<td>4.08</td>
<td>2.58</td>
<td>0.79</td>
<td>−1.52</td>
<td>−5.3</td>
<td>−3.5</td>
<td>1.89</td>
<td>67 200</td>
</tr>
<tr>
<td>PFDT2BT-8</td>
<td>64.2</td>
<td>91.6</td>
<td>1.47</td>
<td>0.71</td>
<td>−1.45, −1.74</td>
<td>−5.3</td>
<td>−3.4</td>
<td>1.92</td>
<td>58 600</td>
</tr>
<tr>
<td>PFDTTBT-8</td>
<td>25.4</td>
<td>75.8</td>
<td>2.98</td>
<td>0.81</td>
<td>−1.70</td>
<td>−5.3</td>
<td>−3.2</td>
<td>1.94</td>
<td>58 400</td>
</tr>
</tbody>
</table>

* Determined by GPC against PS standards.  
* Determined by CV.  
* Estimated from the absorption onset in UV-VIS measurements of copolymer thin-films.  
* Measured at peak optical absorption.

Optical properties

Normalised UV-VIS absorption spectra of each copolymer in solution and thin-film are presented in Fig. 2. It can be seen that the structure of the absorption spectra for each copolymer are qualitatively similar, with the onset of absorption for thin-films being around 1.9 eV. These absorption spectra are in general characterised by two broad bands in the wavelength range 520–580 nm and 400–430 nm. At the wavelength of peak absorption, the molar extinction coefficients (ε) of all polymers exceed 58 000 L mol⁻¹ cm⁻¹, with the most absorptive polymer being PCDTTBT-8 which has ε = 67 200 L mol⁻¹ cm⁻¹.

We find a relative red-shift in optical absorption is observed for each copolymer when it is cast from solution into a thin-film. Such effects are likely attributed to an increased aggregation of polymer chains. Comparison of the absorption spectra from thienothiophene-based copolymers show that for the 2,7-carbazole derivatives, a relative red-shift in the onset of absorption is observed for PCDTTBT-8 compared to the polymer PCDT2BT-8. This difference is in qualitative agreement with several reports of band-gap reduction for thienothiophene-containing copolymers relative to their thiophene counterparts. However, no significant difference between the optical band-gap is observed for the fluorene-based copolymers PFDT2BT-8 and PFDTTBT-8. Note here that the absorption band located at approximately 420 nm for PFDT2BT-8 is apparently blue-shifted to 400 nm in the polymer PFDTTBT-8. It is possible that this change originates from variations in the degree of electronic delocalisation along the conjugated backbone of each copolymer, or differences in molecular weight.

Electrochemical properties

Cyclic-voltammetry (CV) measurements were conducted on drop-cast polymer films in acetonitrile with tetrabutylammonium...
perchlorate as an electrolyte (Fig. 3). The redox potentials of the different polymers are presented in Table 1 along with the values of the HOMO and LUMO levels for each copolymer in this study as determined from their onset of oxidation and reduction respectively. It can be seen that all copolymers have very similar HOMO levels which are located between $-5.2$ eV and $-5.3$ eV relative to vacuum, while relatively larger variations in the positions of their LUMO levels (located between $-3.5$ eV and $-3.2$ eV) were observed.

**Photovoltaic, structural & charge transport properties**

Solar cell devices in a standard architecture were fabricated to determine the photovoltaic efficiency of each copolymer when blended with the fullerene derivative PC$_{71}$BM. The device structure in each case was as follows: ITO/PEDOT:PSS (30 nm)/active layer (50–100 nm)/Ca (5 nm)/Al (100 nm). To optimise the morphology of the photoactive semiconductor blend layer for photovoltaic performance, we have explored the influence of the casting solvent, blend composition and the application of post-film deposition annealing treatments. In Fig. 4 and Table 2, the photovoltaic characteristics and efficiency parameters derived from the current–voltage measurements are presented for solar cell devices after active-layer optimisation. Device efficiency metrics for other solar cells prepared during the optimisation process, including the influence of active layer blend ratio, are presented in the ESI.$^\dagger$

As shown in Fig. 4, all optimised devices exhibit relatively efficient photovoltaic behaviour. We find that the optimum weight composition of each photoactive layer is 1 : 4 wt% copolymer:PC$_{71}$BM; a composition comparable to that used for other PCDTBT-derivatives.$^{14,18,19}$ The thickness of the photoactive semiconducting layer in each optimised device was found to be approximately 60 nm. Comparing the two carbazole containing copolymers PCDT2BT-8 and PCDTTBT-8, substitution of the thiophene heterocycles with thienothiophene permits the fabrication of photovoltaic devices having a PCE of 4%. For the best performing devices however, OPV devices utilising PCDT2BT-8 reach a maximum PCE of 4.1% whereas for OPV devices utilising PCDTTBT-8 a slightly higher PCE of 4.5% is determined. From Table 2 it is apparent that the improvement in PCE of the best PCDTTBT-8 devices relative to the PCDT2BT-8 devices.
devices results from increased short-circuit current density ($J_{sc}$) (9.8 mA cm$^{-2}$ and 8.7 mA cm$^{-2}$ respectively).

This can be correlated with the relatively lower optical bandgap and higher molar extinction coefficient of PCDTBT-8. Furthermore, comparison of the photovoltaic performance of PCDTBT-8 (PCE of up to 4.5%) to a similar carbazole-based polymer described in the literature (PCDTBT-C12) (PCE of 3.4%),$^{27}$ with dodecylxoy-substituents rather than octylxoy-substituents, also indicates a superior performance of PCDTBT-8.

Comparing the photovoltaic efficiency of PFDT2BT-8:PC71BM blends with PFDTTBT-8:PC71BM blends, it can be seen that a relatively lower average PCE is obtained for the PFDTTBT-8 based OPV devices (4.1% against 5.8% for PFDT2BT-8:PC71BM). This difference arises from a relatively lower FF and $J_{sc}$ for the PFDTTBT-8 devices as the open-circuit voltage $V_{oc}$ in each system is similar (0.93 compared with 0.91 V for PFDT2BT-8:PC71BM). For OPV devices incorporating PFDT2BT-8 a maximum PCE of 6.2% is determined; the highest value in the material set studied.

A morphological study was undertaken to characterise the nanostructure of the blend films. Specifically, grazing-incidence wide-angle X-ray scattering (GIWAXS) was employed to characterise the degree of nanoscale crystallinity in the blend films. These measurements were complimented by atomic force microscopy (AFM) imaging of the sample surface for each copolymer:PC71BM blend film (see ESI†), with these scans potentially providing evidence for phase-separation at length-scales greater than can be probed via GIWAXS. In Fig. 5, out-of-plane GIWAXS patterns are presented for each copolymer:PC71BM blend thin-film having an identical film composition to that of the best performing OPV devices (1:4 copolymer:PC71BM wt%). 2D GIWAXS images are provided in the ESI† From these measurements it can be seen that X-ray scatter from each blend thin-film is dominated by PC71BM, as evidenced by the relatively broad ring at $q = 1.34$ Å$^{-1}$ which indicates an isotropic distribution of small fullerene clusters within each blend film.$^{28}$

We note that complimentary measurements on as-cast pure copolymer thin-films only evidence weak X-ray scatter in the out-of-plane direction (see ESI†) with signals attributed to π-π stacking of adjacent copolymers chains at $q_z = 1.72$ Å$^{-1}$ ($d = 3.65$ Å) for PFDT2BT-8 and $q_z = 1.62$ Å$^{-1}$ ($d = 3.88$ Å) for the remaining three copolymers.

Our GIWAXS measurements suggest that the blends studied here are characterised by a finely mixed distribution of copolymer and PC71BM domains with little long-range order present. This conclusion is supported by AFM scans of each blend thin-film surface that are apparently smooth (RMS roughness values below 0.5 nm). Significantly however, we find that the intensity of the broad ring at $q = 1.34$ Å$^{-1}$ (associated with PC71BM aggregation) is largest in the fluorene copolymer PFDT2BT-8:PC71BM blend and is greater than that of X-ray scatter from PCDTBT-8:PC71BM and the two fused-thiophene polymer blends PCDTBT-8:PC71BM and PFDTTBT-8:PC71BM. This suggests that the degree of PC71BM crystallisation in the polymer blends is different. However, as the linewidth of the scatter peak at $q = 1.34$ Å$^{-1}$ is similar in all blends, we conclude that the average size of the PC71BM aggregates is constant, although the fraction of molecules that find themselves within such an aggregate is different. We propose that enhanced PC71BM aggregation in PFDT2BT-8:PC71BM facilitates the extraction of electrons through the creation of percolation pathways within the BHJ, hence suppressing non-geminate recombination.$^{29}$ At present, the origin of the enhanced PC71BM aggregation in PFDT2BT-8:PC71BM blends is not understood.

To determine whether any optical or electronic differences exist between each photovoltaic blend in order to rationalise the solar cell characteristics presented earlier, we have performed time-resolved optical spectroscopy to probe distinct stages in the photocurrent generation process. Specifically, the relative yield of free polaron in the copolymers on the µs timescale was probed using transient absorption spectroscopy (TAS). To compliment these studies, organic field-effect transistor (OFET) devices were fabricated to determine the charge-carrier mobility in each copolymer.
To probe the relative yield of charge carriers in the blend, we have performed TAS measurements to monitor the dynamics of hole polarons generated after photoexcitation of the copolymer and subsequent excited state dissociation at a copolymer:PC71BM interface. Note that steady-state photoluminescence (PL) measurements of each copolymer:fullerene blend film indicate efficient (>99%) quenching of photoexcited states (see ESI†). Here, a lower blend concentration of PC71BM (20 wt%) than used in optimised devices was used to slow the recombination of dissociated polarons, as the decay dynamics occurred within a timescale commensurate with the response time of the instrument in blends with compositions corresponding to optimised devices. This data is presented in Fig. 6.

As shown, over the time-range 0.2–2 μs the transient absorption dynamics at 960 nm (corresponding to the peak absorption wavelength by the hole polarons)38 from each blend thin-film exhibit power-law decays, indicative of non-germinate recombination processes of dissociated polarons.31,32 As shown, a similar ΔOD is determined for each copolymer:PC71BM blend. Previous studies have shown that the magnitude of ΔOD provides a reasonable indicator of the quantum yield of dissociated charges, with further reports of this signal correlating with photocurrent generation efficiency in a fabricated OPV device.33 Here however, we do not find sufficient evidence to suggest that variations in polaron yields between each copolymer:PC71BM sample correlate with OPV device efficiency as the different polymers display almost identical charge generation and recombination characteristics. For example, the blend system PFDT2BT-8:PC71BM exhibits the most efficient photovoltaic behaviour, however it displays similar ΔOD transient kinetics to all other blend films studied.

Bottom-gate architecture OFET devices were fabricated to characterise the charge-carrier mobility of each of the copolymers. Transfer and output characteristics for typical copolymer OFETs are presented in the ESI† with extracted charge carrier mobilities detailed in Table 3.

Here it can be seen that the copolymer PFDT2BT-8 exhibits a higher charge carrier mobility than the thienothiophene derivative PFDTTBT-8 (values of 4.3 × 10–3 cm2 V–1 s–1 and 7 × 10–4 cm2 V–1 s–1 respectively). A relatively high on/off ratio of 103 is also determined for PFDT2BT-8. Furthermore, for the carbazole containing copolymers, mobility values of 2.1 × 10–3 cm2 V–1 s–1 and 2.4 × 10–3 cm2 V–1 s–1 are obtained for the PCDT2BT-8 and PCDTTBT-8 copolymers respectively. We therefore correlate the best performing solar cell devices that incorporate PFDT2BT-8 with the superior charge carrier mobility of this copolymer compared to the others studied. This characteristic also correlates well with the relatively higher device FF that suggests low charge recombination within the semiconductor blend layer. For the other copolymer blends studied, the relatively lower PCEs of solar cell devices are not found to be limited by the yield of hole polarons. Note that with the exception of PFDT2BT-8:PC71BM devices, all solar cells exhibit comparable photocurrent densities at relatively large reverse bias. This suggests that higher device efficiencies may yet be obtainable in these systems after optimising other properties of the copolymer, for example its molecular weight or purity.34,35

### Experimental

**Materials**

PCDT2BT-8,19 PFDT2BT-8,18 9-(heptadecan-9-yl)-2,7-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9H-carbazole and 4,7-bis-(5-bromothieno[3,2-β]thiophen-2-yl)-5,6-bis(octyloxy)-benzo[c][1,2,5]-thiadiazole were prepared according to literature procedures. 9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester was obtained commercially. Toluene was dried and distilled over sodium under an inert argon atmosphere. Acetonitrile (high performance liquid chromatography (HPLC) grade) was dried and distilled over phosphorus pentoxide under an inert argon atmosphere, then stored over molecular sieves (3 Å).

**Poly[9-(heptadecan-9-yl)]9H-carbazole-2,7-diyld-alt-(5,6-bis(octyloxy)-4,7-di(thieno[3,2-β]thiophen-2-yl)benzo[c][1,2,5]thiadiazole-5,5-diyl] PCDTBT8**

To a degassed solution of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (1.2329 g, 1.875 mmol) and 4,7-bis-(5-bromo-thieno[3,2-β]thiophen-2-yl)-5,6-bis-octyloxy-benzo[c][1,2,5]-thiadiazole (1.5502 g, 1.875 mmol)
in toluene (30 cm³) was added to a degassed solution of tetraethylammonium hydroxide (10 cm³ of a 20 wt% aqueous solution, 13.54 mmol). Pd(OAc)₂ (15.0 mg, 0.0673 mmol) and tri(ο-tolyl)phosphine (40.8 mg, 0.134 mmol) were subsequently added, followed by degassing the mixture and heating to 95 °C for 72 hours. The mixture was then cooled to room temperature and bromobenzene (0.15 cm³) was added and the mixture degassed and heated to 90 °C for 1 hour. The mixture was again cooled to room temperature and phenylboronic acid (150 mg) was added and the mixture degassed and heated to 90 °C for 3 hours. After cooling to room temperature, the mixture was dissolved in CHCl₃ (300 cm³) and to this solution was added an ammonium hydroxide solution (28% in H₂O, 200 cm³). The mixture was heated to reflux over 3 hours and then cooled to room temperature and the organic phase separated. Ethylenediaminetetraacetic acid disodium salt dihydrate (0.500 g, 2.58 mmol) was added. Pd(OAc)₂ (8.0 mg, 0.0359 mmol) was added to the organic phase and was le

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Found: C, 71.68; H, 7.44; N, 2.73; Br, 0%.
OPV device fabrication. Pre-patterned glass-ITO substrates (20 Ω □⁻¹) were purchased from Ossila Limited. The substrates were cleaned by sonication in isopropyl alcohol and deionized water and dried with compressed nitrogen. PEDOT:PSS (HC Stark Clevios P VP AI4083, filtered with 0.45 μm PVDF) was spin cast on top of the cleaned substrates to form a 30 nm thick layer in air which was then annealed at 150 °C prior to transferring to a nitrogen filled glovebox. A subsequent thermal anneal at 150 °C was performed inside the glovebox for 1 h. The active layer (blend of copolymer:PC71BM) was dynamically deposited via spin casting on the anode buffer layer from a range of solvents. In all cases, the copolymer was dissolved at 4 mg ml⁻¹ with a total blend concentration of 12–24 mg ml⁻¹ depending on the blend ratio of copolymer to fullerene. The active layer thicknesses were varied by adjusting the spin-coating speed and measured using a surface profiler. The cathode (a bilayer of calcium and aluminium – 5 nm and 100 nm respectively) was thermally evaporated within a vacuum chamber held at a pressure < 10⁻⁶ mbar. Devices were encapsulated using a UV-treated epoxy (Ossila Limited) before testing. Device performance was tested in air using a Newport 92251A-1000 solar simulator (AM1.5) with NREL certified silicon reference cell at 100 mW cm⁻². Here, an aperture mask (0.025 cm²) was placed over each pixel to accurately define the device area.

GIWAXS. Wide-angle X-ray diffraction patterns were obtained for each copolymer:PC71BM blend thin-film in a grazing-incidence geometry at the I07 beamline at the Diamond Light Source (Didcot, UK). Blend thin-films were deposited onto silicon/native oxide substrates for measurement. Samples were measured within a custom-built cell containing a slight over-pressure of helium to minimise background X-ray scatter. For measurement, an 8 keV X-ray beam was incident on the sample surface at a grazing-incidence angle of 0.2°. Data was collected using a Pilatus 2M detector and analysed using the DAWN software package (http://www.dawnscl.org). Silver Behenate powder was used as a calibrant.

Transient absorption spectroscopy. Micro- to milli-second transient absorption spectroscopy was performed on films in a N₂ environment and all data shown is scaled for the fraction of total blend concentration of 12 cast on top of the cleaned substrates to form a 30 nm thick layer of approximately 0.9 V. A detailed study employing a range of complementary techniques probing the structural, optical and electronic properties of the materials have been used to explore the underlying physical differences between the copolymers and provide insight into the device PCEs. We find that thienothiophene substitution is an effective method to modify the optical absorption properties of the copolymers. Optical probes show no discernable differences in the photoexcited state quenching efficiency or charge generation yields between each copolymer:PC71BM blend. Probes of film structure using X-ray scattering reveal that whilst the polymer component is largely amorphous in all cases, the degree of PC71BM crystallinity varies between the different polymer-blends studied. In photovoltaic devices, we find that thienothiophene substitution does not result in improved device efficiency. However we find that improved device efficiency (particularly deriving from improved
fill-factors) is positively correlated with polymer blends in which there is higher hole mobility and more extensive PC71BM crystallisation. These results highlight the complexity in semiconductor design for OPV applications and suggest possible routes for polymer optimisation (for example M\textsubscript{w}). For devices incorporating the copolymer PFDT2BT-8, relatively high photovoltaic efficiencies (maximum of 6.2\%) have been obtained. This result suggests PFDT2BT-8 holds promise as a suitable semiconductor for single junction organic photovoltaic devices, or as a wide band-gap semiconductor for tandem solar cells.

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References