

Poly(thienylenevinylene) prepared by ring-opening metathesis polymerization: Performance as a donor in bulk heterojunction organic photovoltaic devices

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ABSTRACT

Poly(3,4-dioctylthienylenevinylene) (PDOTV) was synthesised by ring-opening metathesis polymerization (ROMP) with controlled molecular weight. PDOTV has been used to fabricate organic photovoltaic devices in combination with phenyl C₆₁-butyric acid methyl ester (PCBM) for the first time. The devices show power conversion efficiency up to 0.18%. Optimal device performance was found at a film thickness of 100 nm and a ratio of PCBM to PTV of 2:1. External quantum efficiency (EQE) measurements, transient absorption spectroscopy and morphology studies were carried out to establish factors governing photovoltaic performance. These results suggest that the efficiency values for the devices were limited by the hole mobility and unexpected phase separation within the blend. Nevertheless, the results show that ROMP is a viable, alternative, synthetic strategy for preparing PTV donors for use in bulk heterojunction OPVs.

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1. Introduction

Conjugated polymers show great promise as the semiconducting layer in devices such as polymer light emitting diodes (PLEDs) [1], organic field effect transistors (OFETs) [2] and organic photovoltaic (OPV) cells [3–7]. One of the key attractions of using these polymeric semiconductors is the ability to fabricate electronic devices using solution based deposition methods, including well-established printing techniques such as ink-jet and gravure. Bulk heterojunction OPV devices have been fabricated by solution processing [3–7], including printing [8]. Slot-die coating [9] and screen printing [10] are also successful application techniques for OPV. In these devices, there is a large contact area between the donor and acceptor phases, leading to efficient exciton dissociation and high power conversion efficiencies (PCE). The conjugated polymers most often used as the donor materials are based on derivatives of polythiophenes [6] or poly(1,4-phenylenevinylene)s (PPV) [7]. These polymers are blended with an electron acceptor such as the functionalized C₆₀ derivative,

1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-C₆₁ (PCBM), to give devices with PCE > 5%. Increased performance can be achieved by a number of factors, including the use of donor polymers that harvest more of the incident solar radiation and that give greater control of the microphase separation in the bulk heterojunction.

Poly(thienylenevinylene)s (PTV)s are an attractive alternative donor polymer for OPVs as these polymer have a lower band gap (1.55–1.8 eV) than polythiophenes and a rigid polymer backbone [11,12]. Previous reports for devices fabricated using PCBM as an acceptor have shown PCE in the range of 0.2–0.7% [11].

PTV polymers are generally prepared by either precursor routes through thermal elimination such as Wessling method [13], or direct polycondensation reactions such as Wittig-Horner [14], Stille [15] and Kumada reaction [16]. Those methods give polymers with broad molar mass distributions and can introduce undesired structural defects, e.g. saturated linkages in the Wessling method, that may decrease the conjugation length of the polymer [17]. We were therefore motivated to investigate alternative synthetic methods for preparing this family of polymers.

Ring-opening metathesis polymerization (ROMP) is a kind of olefin metathesis polymerization and requires strained cyclic olefin monomer [18]. It offers the potential to prepare well-defined conjugated polymers with a lower polydispersity and fewer intrinsic backbone defects [19]. ROMP has been used to prepare

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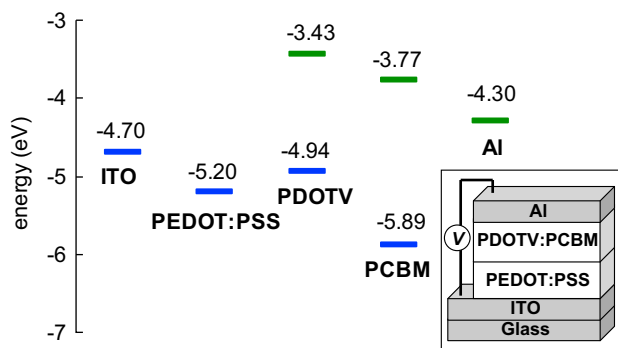


Fig. 3. Energy level diagram for photovoltaic cell shown in inset.

is red shifted from the regioregular poly(3-hexylthiophene) (950–1100 nm) [25], which is consistent with the smaller band gap of PDOTV. The magnitude of the polaron absorption at the shortest time scale visible (here, approximately 1 μ s), when normalized with respect to the film absorption at the excitation wavelength, can be interpreted as a measure of the charge pair generation yield. A larger polaron absorption signal indicates increased charge dissociation and potentially a higher PCE. Kinetic traces of the polaron absorption for different composition blend films are shown in Fig. 4(b). Transient absorption values at 1 μ s are plotted as a function of PCBM wt% in the inset to Fig. 4(b). The blend films

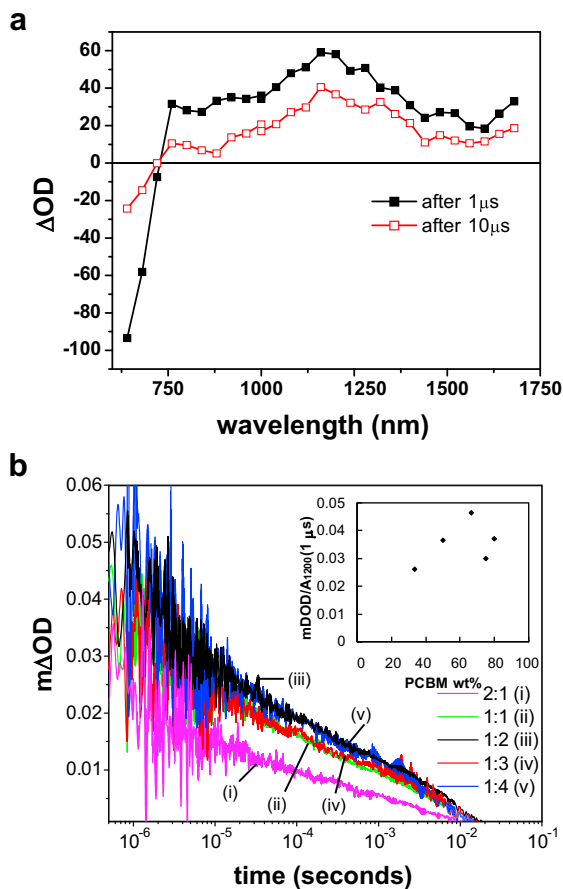


Fig. 4. (a) The transient absorption spectrum of PDOTV:PCBM = 1:1 film excited at 550 nm; (b) The transient absorption decays of PDOTV:PCBM blend film monitored at 1200 nm. The transient absorption intensity plotted as a function of PCBM wt% at 1 μ s is shown.

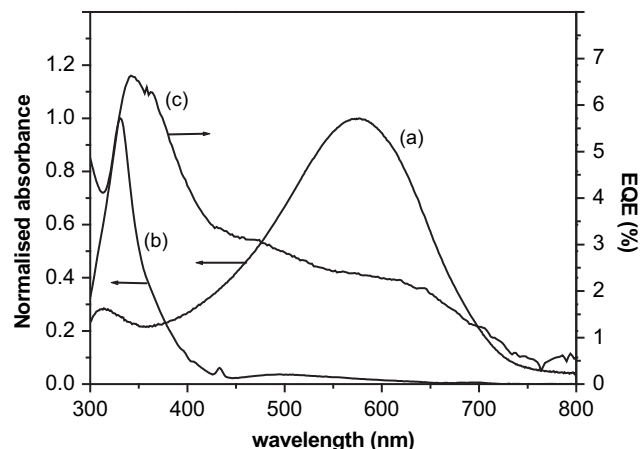


Fig. 5. The absorption spectra of (a) a pristine PDOTV film and (b) a solution of pristine PCBM in chlorobenzene. (c) EQE spectrum of a PV device (PDOTV:PCBM = 1:2).

with composition of 1:2 PDOTV:PCBM (i.e., 66 wt% PCBM) exhibited the highest polaron absorption on the time scales probed. This observation might suggest that this composition would show better PCE in PV devices and this is investigated in detail below.

The external quantum efficiency (EQE) is the percentage of incident photons that are converted to electrons in the external circuit. The absorption spectra of pristine PDOTV **3** and PCBM are shown in Fig. 5(a) and (b) respectively, and indicate that light is absorbed across a wide range of incident energies. The EQE spectrum of the PDOTV:PCBM (1:2) blend PV device, Fig. 5(c), showed

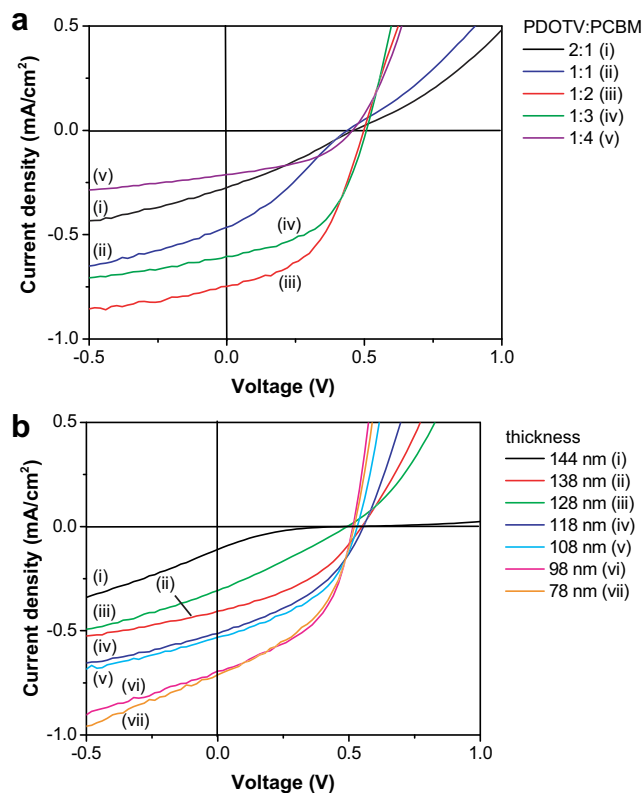


Fig. 6. The J - V characteristics of the PDOTV:PCBM bulk heterojunction PV devices at (a) various blend compositions (100 nm thickness) and (b) different film thickness using the composition ratio of PDOTV:PCBM = 1:2.

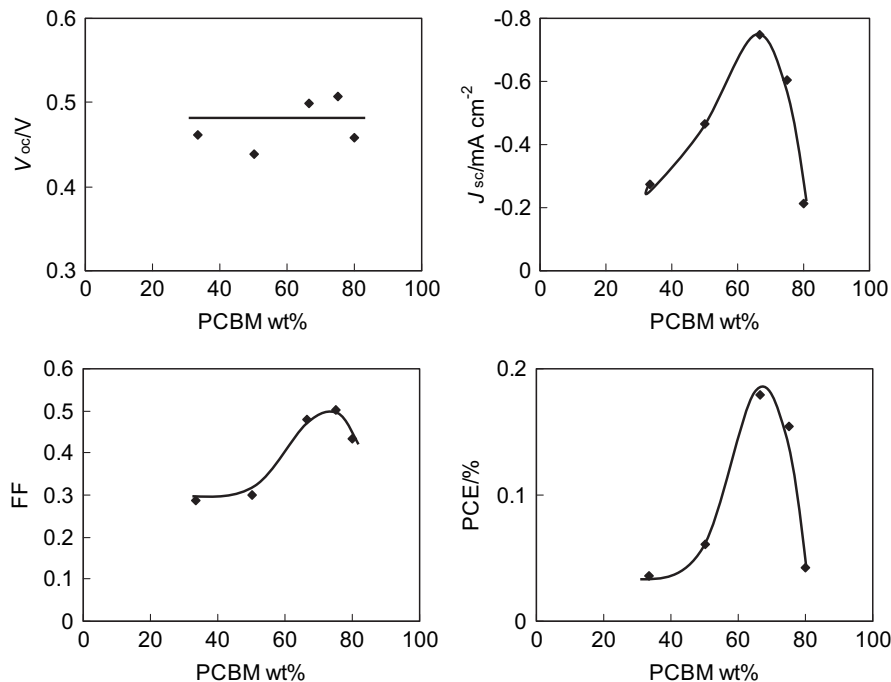


Fig. 7. The influence of blend composition on the PV performance of PDOTV:PCBM blend devices of active layer thickness of 100 nm. The lines are guides to the eye.

a photoinduced current from 300 nm to 750 nm consistent with the overlap of the PDOTV and PCBM absorption spectra. Surprisingly, the EQE values were low (<5%), particularly in the region associated with the PDOTV, which is suggestive of a reduced overall performance for the device.

Current density–voltage (J – V) measurements for the devices were conducted and the data are illustrated in Fig. 6. These measurements gave values for the open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) and PCE (see Figs. 7 and 8 and Table 1 in Supplementary data). A range of blend compositions

for the PDOTV:PCBM active layer were examined at constant film thickness (100 nm) and the influence of active layer thickness investigated for devices with a ratio of PDOTV:PCBM of 1:2. These systematic measurements show that the PCE was strongly affected by both the blend composition (Fig. 7) and the blend film thickness (Fig. 8).

No significant changes in V_{oc} were observed on increasing the proportion of PCBM or the thickness of the active layer (Fig. 7). This is expected as V_{oc} for the photovoltaic device is controlled by the difference between the HOMO of the donor (PDOTV) and the LUMO

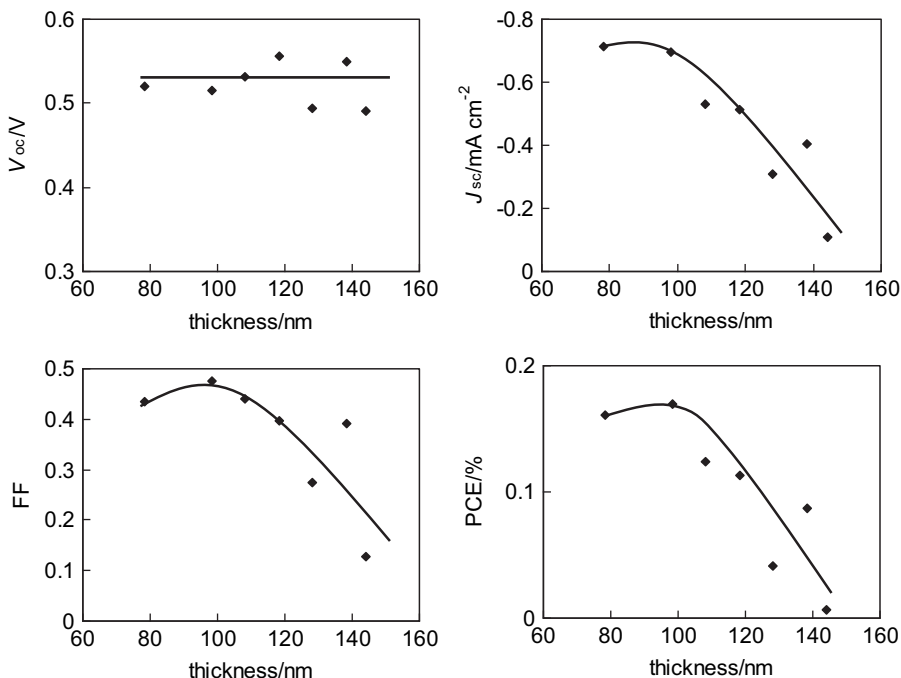


Fig. 8. The influence of thickness on the PV performance of PDOTV:PCBM blend devices (PTV:PCBM = 1:2).

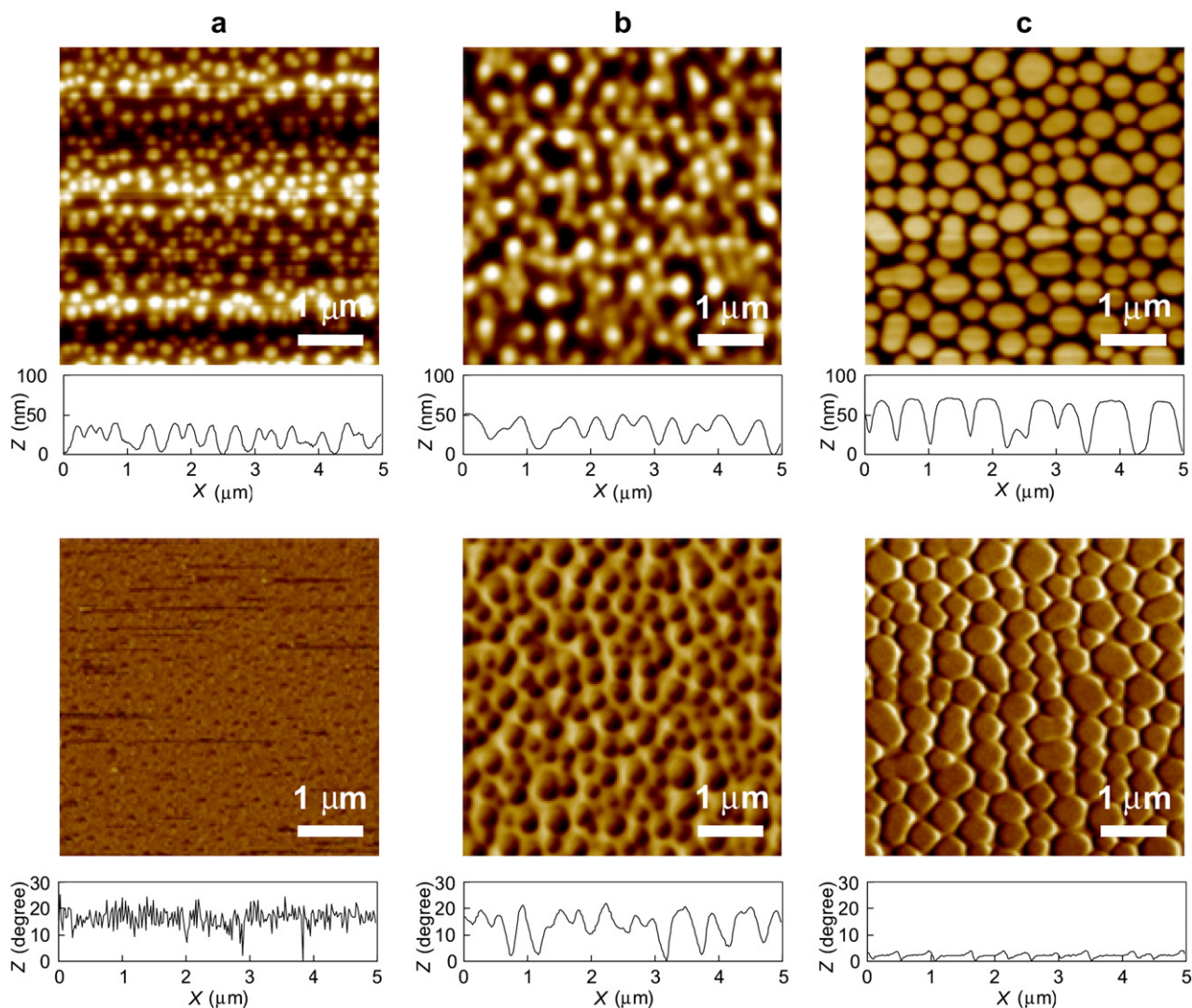


Fig. 9. AFM images for a PDOTV:PCBM (a) 1:1, (b) 1:2, (c) 1:4. Top images are topography and bottom images are phase with corresponding cross section.

of the acceptor (PCBM) (see Fig. 3) [26]. An empirical relationship between these parameters was determined by Scharber et al. from a comprehensive study of 26 different PCBM-polymer photovoltaic devices [26a]. According to that relationship, a V_{OC} of 0.34 V is expected for devices made from PDOTV (HOMO at -4.94 eV) and PCBM. The V_{OC} obtained from the devices prepared for this study range from 0.44 to 0.51 V, which is close to the value calculated from the formula in Ref. [26a].

Interestingly, the J_{SC} values increased significantly as the weight fraction of PCBM in the active layer increased towards around 70 wt% (Fig. 7). It reached the highest value for the composition of PDOTV:PCBM of 1:2. The FF also increased with increasing PCBM content and approached a maximum at a composition of 1:2. The lower FF for devices with a 2:1 and 1:1 composition can be attributed to poor diode quality of the device due to the low mobility of polymer **3** (see below). These features led to the highest PCE of 0.18% being obtained at a blend composition of 1:2.

In light of the previous results a blend composition of 1:2 was chosen to investigate the influence of PDOTV:PCBM film thickness on device performance. The V_{OC} was essentially constant (0.49–0.55 V) regardless of the film thickness (see Figs. 6(b) and 8). For films thicker than 100 nm the J_{SC} decreased linearly with the film

thickness. In theory, thicker films should absorb more light, leading to more photoinduced charge and a larger external current. However, in thicker films not all of the charge carriers may reach the collecting electrode if the mobility is low and this is presumably the origin of the low J_{SC} observed in the thicker film devices reported here [27] (Mobility measurements are performed below). The FF and the PCE show a similar relationship with the blended film thickness (Fig. 8) and show a maximum value when the blend film was 100 nm thick. A PCE of 0.17% was measured for the PDOTV:PCBM (1:2) blend PV device prepared with 100 nm in thickness. This value is similar to that prepared during the optimization of the composition.

In order to test the proposal that the low PCE values were the result of low mobilities, OFET measurements were performed. A rather low hole mobility for PDOTV ($\mu = 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was determined in an OFET. The relatively low mobility value is probably the main cause for the limited PCE values and the observed dependence of FF and PCE on film thickness noted above. An interesting question concerns the origin of the relatively low mobility for the PDOTV films.

The surface morphology of the PDOTV:PCBM films was examined by atomic force microscopy (AFM) and the results are shown in Fig. 9. The morphologies showed domains with diameters in the

size of about 150–500 nm depending on film composition. Increasing PCBM concentration increased the domain size and depth in the phase image. The average domain size and depth are ca. 150 nm and 39 nm (roughness factor, $R_a = 9.8$ nm) for PDOTV:PCBM = 1:1, ca. 250 nm and 52 nm ($R_a = 12.5$ nm) for 1:2 and 500 nm and 72 nm ($R_a = 12.5$ nm) for 1:4, respectively. The present morphologies are new for PDOTV blends. Sariciftci et al. have reported related morphologies of MDMO-PPV (poly[2-methyl,5,3',7''dimethyloctyloxy]-*p*-phenylenevinylene):PCBM (1:4 wt%) blend films [7d,g]. Their films spin-coated using either toluene or chlorobenzene solution show around 500 nm (10 nm height) or 100 nm (1 nm height) of nanoclusters. Changing the solvent from toluene to chlorobenzene increased the efficiency from 0.9 to 2.5% due to these changes in the film morphology [7d]. Similarly morphologies of P3HT:PCBM blend films have also been observed in previous reports and devices having domains in the region of 10–30 nm show the highest PCE (4–5%) [6c,f,g]. There is therefore evidence from the literature that PCE generally decreases with increasing domain size. However, for the present study the best PCE found for the PDOTV:PCBM devices in this study is at a blend composition of 1:2. The domains for these devices are much larger (ca. 250 nm) than the exciton diffusion length (<10 nm) and this presumably contributes to the low PCE value for these devices.

Photovoltaic devices prepared using poly(3-hexylthiophene vinylene) by Vanderzande et al. [11c] and by Li et al. [11b] revealed much higher photoinduced current, $J_{SC} = -4.85$ mA cm⁻² (PCE = 0.76%) and $J_{SC} = -1.30$ mA cm⁻² (PCE = 0.26%), respectively than the devices in this report. It is suggested that the lower J_{SC} in the present case results, in part, from a disordered arrangement of PDOTV chains due to the presence of two alkyl chains on the thiophene ring leading to lower charge mobility.

3. Conclusions

Dialkyl substituted thiophenevinylene polymers prepared by ROMP were investigated for the first time in the context of bulk heterojunction OPVs. The results have shown that they can be used in organic photovoltaic devices when blended with PCBM. Optimal device performance (PCE 0.18%) was found at a film thickness of 100 nm and a ratio of PCBM to PTV of 2:1. Device performance appears to be limited by poor hole mobility in the PTV polymer phase. The morphology of the blends, as studied by AFM, also revealed the presence of large domains which may have contributed to the low PCE and EQE values obtained. Nevertheless, the results presented here show that ROMP is a viable method for preparing PTVs for use OPVs.

4. Experimental

4.1. General methods

The monomer **1** was synthesised by a modification of established procedures [28]. All experiments were performed under an argon atmosphere using standard Schlenk techniques. Polymer molecular weight was determined by GPC in tetrahydrofuran (THF) solution using a Viscotek GPCmax VE2001 and a Viscotek VE3580 RI detector (referenced to polystyrene standards). UV–Vis absorption spectra were recorded on a Varian Cary 5000 UV–Vis–NIR spectrophotometer. CV was performed at 100 mV s⁻¹ in a BASI Epsilon electrochemical workstation with a three-electrode cell, Ag/AgNO₃ as reference electrode, platinum wire as counter electrode and polymer film on a platinum plate as the working electrode in nitrogen-purged anhydrous 0.10 M tetrabutylammonium hexafluorophosphate acetonitrile solution at room temperature.

Onsets of oxidation and reduction peak potentials were used in the calculation of HOMO and LUMO energy levels [19].

4.2. Synthesis of polymer **3**

The polymer **3** was synthesised by a modification of established procedures [21]. An Ace pressure tube was filled with 2,3,8,9,14,15-hexaoctyl[18]annulene-1,4;7,10;13,16-trisulfide (**1**) (45.8 mg, 0.046 mmol), and the tube was purged with vacuum and filled with argon. A dry toluene solution (1.0 mL) of second generation Grubbs catalyst (3.9 mg, 0.0046 mmol) was then injected into the tube containing the monomer. The tube was heated at a temperature of 110 °C for 5 h. After this period the reaction mixture was cooled to room temperature and excess ethyl vinyl ether (2 mL, 20.8 mmol) was injected into the tube to terminate the reaction. After stirring for an additional 2 h at room temperature the reaction mixture was evaporated in vacuo. The crude polymer was then dissolved in the minimum amount of chloroform and transferred to a Celite plug filled with methanol. This resulted in precipitation of the polymer, which was washed with excess methanol and then redissolved in chloroform and collected. The solvent was removed under reduced pressure and the residual solid film was washed with excess hexane. The film was dried under reduced pressure allowing the isolation of polymer **3** as a dark-blue film. Recovered yield of polymer **3** was 15 mg (31%). GPC in THF; $M_n = 10,400$, $M_w/M_n = 1.8$. ¹H NMR (500 MHz, CDCl₃): δ 7.00 (br), 2.80–2.55 (br), 1.18–1.65 (br), 1.60–1.48 (br), 1.47–1.25 (br), 0.72–0.86 (br). UV–vis (THF): λ_{max} = 594, 633 (sh) nm; UV–vis (film): λ_{max} = 632, 696 (sh) nm.

4.3. Photovoltaic device and TAS measurements

Spectrosil B fused-silica substrates (ITO-coated glasses, Kaypul Optics Limited, UK) were cleaned sequentially with acetone and isopropanol using an ultrasonic bath, and dried under nitrogen atmosphere. The cleaned Spectrosil substrates were then spin-coated with poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid, PEDOT:PSS (Baytron P standard grade, HC Stark), from an aqueous solution and annealed at 200 °C for 15 min. The chlorobenzene solutions containing PDOTV and PCBM with various blend composition were spun-cast using different spinning rate on to these PEDOT:PSS coated substrates. The devices were finished by thermal evaporation of an aluminum top electrode in vacuum. *J*–*V* characteristics of these PV devices were measured under white light illumination (AM1.5) using an Oriel Newport solar simulator based on a filtered Xe lamp with output intensity of 100 mW/cm². EQE study was performed under monochromatic light exposure using a system equipped with a Keithley 237 electrometer, an Oriel CVI CM110 monochromator, and a Xe lamp (150 W). The film thickness was measured by surface profilometer, Veeco Stylus Dektak 8 after the *J*–*V* measurement. In TAS measurements, the polaron decay dynamics were obtained by pulsed excitation at 550 nm using a N₂-laser pumped dye laser (GL 3300, PT1, New Jersey, USA) with low pump intensity (ca. 9 μJ/cm²) and the transient absorption decays were monitored at 1200 nm [29].

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Appendix. Supplementary data

The supplementary data associated with this article can be found, in the online version at doi:10.1016/j.polymer.2010.01.049.

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