A novel 2,7-linked carbazole based "double cable" polymer with pendant perylene diimide functional groups: preparation, spectroscopy and photovoltaic properties[†]

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The preparation and chemical analysis of a 'double-cable' conjugated polymer comprising a backbone of alternating 2,7-linked carbazole repeat units with covalently attached perylene diimide (PDI) substituents and dithienyl repeat units is presented. The backbone of the new "double-cable" polymer P1 acts as an electron donor while the pendant PDI substituents act as electron acceptors. In order to investigate the influence of the PDI moieties on the polymer backbone as well as to elucidate their photophysical interaction, three reference-compounds were also prepared and analysed: a polymer with the same backbone as that of P1 but without PDI substituents (P2) and two PDI derivatives with branched alkyl side chains (PDI 2 with 12-tricosanyl substituents and PDI 1 with 3-pentyl substituents). We find that polymer P1 shows pronounced electron transfer from the polymer backbone to the PDI chromophore units covalently bound to it, resulting in highly efficient quenching of excitons and strong suppression of fluorescence in solutions and in thin films. The existence of long-lived polaronic states resulting from exciton dissociation on P1 is confirmed using steady state photo-induced absorption spectroscopy. Despite the improved exciton quenching yield shown by P1 over a blend of P2/PDI, photovoltaic devices fabricated from P1 have a low external quantum efficiency (EQE) of around 0.43% at 410 nm; a value that is smaller than that from a conventional BHJ device of P2/PDI which is found to have a peak external quantum efficiency of 3.7% at 463 nm. We tentatively ascribe the reduced EOE of the double-cable polymer to geminate recombination of charge-carriers as a result of poor charge transport and a complete lack of donor acceptor phase separation.

1. Introduction

There is currently a concerted effort aimed at developing new materials for use in photovoltaic (PV) devices. Organic PVs have been targeted as a potentially promising technology due to the inherently low costs associated with manufacturing and production, and research is actively evolving in this area.¹ Bulk heterojunction PV cells comprising conjugated polymer donors and fullerene acceptors have attracted most interest.² The control of the morphology of blends in these cells is an important component of generating systems in which there is efficient separation of excitons at the donor–acceptor interface and charge collection at electrodes. Indeed, donor and acceptor components should be intimately mixed so that a donor–acceptor interface is within a distance less than the exciton diffusion length whilst maintaining a continuous percolation path to extract charge carriers from the device.

To this end the concept of double-cable polymers was developed.

Double-cable polymers are generally composed of covalently linked acceptors to polymer donors, with two 'cables' existing on a single molecule permitting charge carriers of both signs to be extracted using a single material system. Most studies have so-far targeted polymer donors that are covalently linked to fullerene acceptors.3 The covalent attachment of fullerenes to conjugated polymer donors remains a challenging problem; while many such systems have been described in the literature, there remain issues associated with the processability of these materials as well as their percentage loading with fullerenes. Alternative acceptor systems to fullerenes such as anthraquinone have been explored in this area and it has been shown that covalently bound anthraquinone to conjugated polymers displayed photoinduced electron transfer from the polymer backbone to the covalently attached anthraquinone moieties.⁴ Perylene diimides show strong n-type character and attractive properties such as long exciton diffusion ranges of up to 2.5 µm in vacuum deposited films⁵ and high electron carrier mobilities.⁶ Consequently, they have been used as electron acceptors in bulk heterojunction devices with conjugated polymers^{7a-e} showing external quantum efficiencies (EQEs) as high as 16% and also with discotic liquid crystals⁷ where the EQE was 34% at 490 nm (the perylene absorption peak). However, in view of the difficulty in directing optimal phase separation, these systems have relatively limited power conversion efficiencies. Covalent attachment of perylene diimides to conjugated polymers such as poly(p-phenylene vinylene)s⁸ and alternating poly(fluorene-alt-phenylene)⁹ have

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also been described but to our knowledge, no photovoltaic devices have been reported on these materials.

In this work, we report the preparation of alternating poly-(carbazole-alt-dithienyl) polymers with and without covalently attached perylene diimide (PDI) units. Owing to the relatively deep LUMO level of the PDI moieties, they act as strong electron-acceptors coupled to a carbazole-based backbone-polymer (donor). We present a range of studies on the photophysical properties of these materials as pristine materials as well as in blends with free perylene diimide chromophores. Through functional control of active layer morphology, we show that the quenching of excitons on these materials is particularly efficient a conclusion supported by steady-state photoinduced absorption measurements. But, devices based on this particular double-cable polymer have a lower efficiency than those from blends of a polymer with a similar backbone with free PDI chromophores. We tentatively propose that the efficiency of the double-cable polymer devices we fabricate is limited both by geminate charge recombination, and poor charge extraction.

2. Experimental methods

Experimental details of the monomer and polymer synthesis are provided in the supplementary information. Characterization data are also presented.

2.1. Spectroscopy of solutions and thin-films

Samples of polymer thin films for UV-visible absorption, photoluminescence and photoinduced absorption (PA) spectroscopy measurements were prepared by either spin-coating or dip coating quartz substrates from polymer solutions in chloroform (HPLC grade) or dichloromethane (HPLC grade). Typical thin films had a thickness of ~ 100 to 150 nm unless otherwise specified. Photoluminescence and Absorption spectra were obtained using Hitachi F-4500 Fluorescence Spectrophotometer or a JY Fluoromax 4 Fluorimeter. Solution photoluminescence (PL) measurements were carried out using a quartz fluorescence cuvette (light path length = 10 mm). Absorption and PL measurements were carried out at ambient temperature in air.

PA spectroscopy measurements were performed by measuring the transmission difference caused by photoexcited states of a 100 W tungsten lamp focussed to a \sim 5 mm diameter spot onto the sample, mounted onto the cold finger of an Oxford-Instruments DN type cryostat cooled to 77 K. Films were optically pumped using the 488nm line from an Ar⁺ laser that was chopped using either an opto-acoustic modulator for modulation resolved experiments or a mechanical chopper for the wavelength and intensity dependent measurements. The transmitted light was imaged into a JY SPEX monochromator using a silicon photodiode to detect light from 2.2 eV to 1 eV and thereafter with an InSb detector to 0.5 eV. Photodiode signals were amplified by an EG&G current voltage amplifier which separates the DC and AC signal components and provides some preamplification. A Stanford Research Systems SR830 Lockin-amplifier was used to collect the phase information from the AC component. Zero phase is defined as the laser modulation. Both the in-phase and out-phase signals were recorded.

2.2. Fabrication of OPV devices

Photovoltaic devices were fabricated using the basic architecture ITO(50 nm)/PEDOT:PSS(30 nm)/Active Layer(100-150 nm)/ Al(100 nm) where the active layer was a thin-film of the doublecable polymer P1 or a blend of the model polymer P2 and acceptor moieties in a variety of blend ratios. For benchmarking purposes, we also explored blends of polymer P2 with the fullerene acceptor PCBM to assess the relative suitability of the polymer as an electron donor and charge transporting material in a comparative BHJ device. 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 N₂ atmosphere maintained in a glove box. Solutions were prepared at 20 g/l concentration in a variety of solvents (vide infra) then heated overnight at 60 °C. To ensure that each material was dissolved, they were passed through a 0.45 µm PTFE syringe mounted filter. All films were spin cast in a glove box prior to the deposition of the Al cathode. Devices were encapsulated in nitrogen using a UV curable epoxy that was used to stick a glass slide to the device surface. Devices were then thermally annealed by heating to 120 °C for 10 min.

AFM images were obtained with a *Veeco Dimension 3100* atomic force microscope in tapping mode using TAP300AL cantilevers supplied by Budget Sensors Ltd. Thickness measurements were taken with a Veeco Dektak 150 profilometer.

2.3. Material synthesis and characterization

Synthesis of 2 was performed via a condensation reaction (Scheme 1) of perylene-3,4,9,10-tetracarboxylic dianhydride with 1-undecyldodecylamine in imidazole. Partial hydrolysis of bisalkylated 2 with potassium hydroxide in *tert*-butanol followed by treatment with hydrochloric acid provided 3 in moderate yields. Reaction of 3 with 6-aminohexanol in the presence of zinc acetate in N,N-dimethylacetamide afforded 4. Compound 5 was obtained via tosylation of 4 using p-toluenesulfonyl chloride in the presence of triethylamine and catalytic amounts of trimethylamine hydrochloride. The compound was purified by recrystallisation of the crude product from diethyl ether and methanol. Carbazole compound 6 was obtained in moderate yields on reacting 5 with 2,7-dibromo-3,6-dimethyl-9H-carbazole and potassium hydroxide. The NMR spectra of 6 are concentration dependant and while intermolecular interactions affecting perylene diimide units are well documented in the literature, the chemical shifts of signals from the carbazole units on 6 do also change significantly with concentration. At a concentration of 9 mg/ml in $CDCl_3$, the carbazole moiety on 6 can be easily identified from the ¹H-NMR spectrum, (Fig. S1, ESI[†]) with two singlet peaks with an integral intensity of two protons at 7.788 ppm and 7.516 ppm (aromatic protons) and one singlet peak with an integral intensity of six protons at 2.583 ppm (protons of the methyl groups attached to the carbazole) while the aromatic protons of the perylene ring are observed as one multiplet at 8.602 ppm. At a higher concentration of 6 in CDCl₃, (37 mg/ml), the signals of the carbazole moieties on the compound are shifted upfield to 7.630 and 7.391 ppm for the aromatic protons and at 2.450 ppm for the methyl substituents



Scheme 1 (i) NH₂(CH(C₂H₅)₂), Zn(OAc)₂, pyridine, 80 °C for 4 h then reflux overnight; (ii) NH₂(CH(C₁₁H₂₃)₂), imidazole, 140 °C; (iii) (a) KOH, *t*-BuOH, reflux, (b) HCl; (iv) NH₂(C₆H₁₂)OH, Zn(OAc)₂, DMAC, 110 °C then 160 °C; (v) *p*-CH₃C₆H₄SO₂Cl, NEt₃, NH(CH₃)₃Cl, 0-5 °C; (vi) 2,7-dibromo-3,6-dimethyl-9*H*-carbazole, KOH, DMSO/THF, RT.

on the carbazole rings. The signals of the aromatic protons of the perylene ring are split into a multiplet and three doublets at respectively 8.593, 8.4817, 8.416 and 8.335 ppm. The concentration related changes point to the fact that these must be due to intermolecular interactions. We believe that these changes are due to donor/acceptor intermolecular interactions since the changes in chemical shifts affect both the carbazole donor moieties and the PDI acceptor moieties on monomer **6**.

The preparation of polymer P1 is outlined in Scheme 2. The polymer was obtained in good yields upon reaction of 5,5'-bis-(tri-n-butylstannyl)-2,2'-bithiophene with 6 and using a Stille type cross coupling condensation polymerization reaction. The Stille coupling was chosen in preference to the Suzuki coupling for this polymerization reaction in order to avoid any side reactions as a consequence of alkaline conditions that might involve partial hydrolysis of the perylene diimide substituents on P1 during its preparation. P1 was purified by Soxhlet extraction with methanol, acetone, toluene then chloroform and the chloroform extracts afforded the first fraction of the polymer which has a weight average molecular weight Mw of 28,800 Da and a polydispersity (PD) of 2.2. The residues left in the thimble after extraction with chloroform were refluxed with chloroform and afforded a second fraction of the polymer after precipitation in methanol with a weight average molecular weight Mw of 46,900 Da and a polydispersity PD of 1.8. It is notable that the second fraction of the polymer is soluble in chloroform at room



Scheme 2 (i) Pd₂(dba)₃, P(o-totyl)₃, toluene, 95 °C.

temperature to some extent even though this portion of the polymer was not extracted by warm chloroform during the Soxhlet extraction of the first fraction of the polymer. We believe that this is due to aggregation of polymer chains during the Soxhlet extraction process.

Polymer **P2** was prepared so as to provide a basis of comparison to that of the backbone of polymer **P1**. Stille cross coupling of 5,5'-bis(tri-*n*-butylstannyl)-2,2'-bithiophene and 2,7-dibromo-3,6-dimethyl-9-(2-hexyldecyl)-9*H*-carbazole provided **P2** (Scheme 2) which has a weight average molecular weight Mw of 59,800 Da and a polydispersity PD of 2.2.

¹H-NMR spectra of P1 in deuterated chloroform provides broad signals especially for the protons in the aromatic region. ¹H-NMR studies of P1 in deuterated 1,1,2,2-tetrachloroethane at room temperature provided better spectra but still broad signals in the aromatic region, however, upon heating to 100 °C, the signals were better defined with a multiplet between 8.54-8.08 ppm corresponding to four protons and four broad singlets corresponding to two protons each at respectively 7.790, 7.399, 7.192 and 7.039 (Fig. S2, ESI[†]). We believe that this behaviour is due to aggregation of pendant PDI units on P1. Similar effects have been previously observed for donor-acceptor molecules such as those incorporating zinc tetraphenyl-porphyrin with PDI substituents.¹⁰ Broadening of the peaks in the¹H-NMR spectra of P1 is persistent even at high dilution which could point to intramolecular aggregation of the pending PDI units on polymer chains and that aggregates are reduced at higher temperature. However, intermolecular aggregates associating different polymer chains could not be ruled out given the changes observed in the solubility of **P1** during the separation of its second fraction.

Thermal gravimetric analysis of **P1** and **P2** indicated a good thermal stability for both polymers with an onset of the first degradation at 399 °C for **P1** and at 428 °C for **P2**. The residual mass at 800 °C for polymer **P1** (59.3%) corresponds well to the sum of the bare polymer backbone and the aromatic core structure of its PDI-units. Polymer **P2** shows a mass loss after the first thermal degradation of 29.6%, which is consistent with the loss of the alkyl chains. Differential scanning calorimetry studies on **P1** did not reveal any clear glass transition while studies on polymer **P2** indicate a glass transition around 95 °C which is higher than that of the equivalent polymer without methyl groups on carbazole repeat units reported in the literature.¹¹

3. Results and discussion

3.1. Absorption and PL emission in solution and thin-film

The absorption spectra of perylene diimides in solutions generally display three distinct vibronic transitions; (0,0); (0,1); (0,2)and one shoulder indicating a fourth transition, (0,4). These are separated by 200 meV corresponding to the C=C stretching mode. This is indeed observed for PDI 2 as shown in Fig. 1(a). The ratio between the (0,0) transition and the (0,1) transition is an indication of the degree of self-assembly of pervlene diimides and can be calculated as 1.66 in both THF and toluene solution for PDI 2 (only absorption in toluene is shown in Fig. 1(a)). This suggests that the PDI-units are not affected by aggregation at the concentrations investigated.9a However, in films of PDI 2, aggregation becomes predominant, resulting in a red-shift of the peak maxima and an increase of the (0,1) vibronic transition relative to the (0,0) transition leading to a lower (0,0)/(0,1) ratio. These spectral changes derive from a π - π stacking of the PDI chromophores as observed for similar perylene diimides with only hydrogen substituents at the core. This stacking has the form of a face-to-face assembly (H-type aggregation).¹² Due to this aggregation the onset of absorption in thin films is shifted to higher wavelengths, resulting in an optical band gap of 2.16 eV for PDI 2 as determined from the onset of its absorption band in the solid state.



Fig. 1 (a) UV/Vis absorption spectra of polymer P2 in toluene (dashed line), P2 as a film (solid line), PDI 2 in toluene (dash dotted line) and PDI 2 as a film (dotted line). (b) UV/Vis absorption spectra of polymer P1 in THF (dotted line), toluene (dashed line), chloroform (solid line) and as a film (dash dotted line).

The absorption spectra of **P2** in toluene solutions and as a thin film are shown in Fig. 1(a) and display absorption maxima at 394 nm in toluene solutions and at 419 nm as a thin film. The optical band gap of **P2**, as determined from the onset of its absorption band in the solid state, is 2.48 eV. This is slightly higher than that reported for the equivalent polymer without methyl groups on carbazole repeat units reported in the literature (2.36 eV).¹¹ This difference can be explained by the additional 3,6-dimethyl groups on **P2** which induce a higher degree of twisting between the carbazole and the bithiophene repeat units along the polymer chains, resulting in a reduction of the electronic conjugation and a small increase in the band gap.

The absorption spectra of the P1 double-cable-polymer in THF and toluene solutions and as thin films are shown in Fig. 1(b). Table 1 summarises the measured absorption maxima and associated extinction coefficients. It can be seen from the figure that the absorption spectrum of P1 in toluene consists to some extent a superimposition of the absorption spectra of PD1 2 and P2 (compare with Fig. 1(a)). We assign the strong absorption band at 392 nm to absorption from the carbazolebithiophene backbone of the polymer while the bands at 494 nm and 527 nm arise from the absorption of the PDI substituents on **P1**. However, the absorption bands of the PDI substituents on P1 bear more of a resemblance to those of compound 2 in a thin film rather than in solution, indicating a likely aggregation of the PDI chromophores of P1 in solutions of THF and toluene. It is tempting to assume that this stacking occurs mainly within the polymer chain itself rather than between PDI units of different chains as a result of intramolecular aggregation. Aggregation of PDI units on a single molecule is distinctly possible; as such moieties of P1 are covalently bound to the polymer backbone which leads to high local concentrations and in turn to aggregation. However, we cannot exclude intermolecular interactions of PDI units from different polymer chains at this stage.

The comparison of the absorption spectra of **P1** in solutions and as thin film (Fig. 1(b)), shows that the absorption band of the carbazole-bithiophene backbone of the polymer displays a redshift (15 nm) in the solid state compared to that in solution indicating better electronic delocalisation and a more planar polymer backbone in films of **P1**. In contrast, the absorption bands corresponding to the PDI-units show only minor changes in the position of their absorption bands in THF, toluene and in films. It appears however that the degree of aggregation of PDI substituents on **P1** depends on the solvent used, as the (0,0)/(0,1)absorption band ratio changes in different solvents. These ratios in THF, toluene and CHCl₃ are respectively 0.76, 0.82 and 1.04 while that in thin films is 1.02. Interestingly the PDI moieties on

 $\label{eq:table_$

Transition	THF solution		Toluene s		
	λ _{abs max} / nm	ϵ/M^{-1} cm^{-1}	λ _{abs max} / nm	ϵ/M^{-1} cm^{-1}	Thin film λ _{abs max} / nm
PDI-unit (0,0) PDI-unit (0,1) Polymer backbone	527 494 392	17700 22800 39400	530 495 393	18200 22000 35600	532 495 407

P1 appear to be more aggregated in solutions of toluene and THF than in the solid state. Despite such apparent changes in the PDI absorption, it is clear that the absorption of **P1** is an approximate superposition of that of **P2** and PDI suggesting that there is no ground state charge transfer in the double-cable-polymer system.

The emission spectra of P1, P2 and PDI 1 in dilute solutions (10^{-6} M) are shown in Fig. 2(a). They are corrected for relative absorbance and excitation fluence, and thus can be used as an approximate measure for fluorescence quantum yield. We find that PDI compound 1 emits intense fluorescence (as is the case for a large number of such compounds) with polymer P2 emitting relatively modest fluorescence in comparison. Upon excitation at 480 nm, we find that emission from polymer P1 closely resembles that of PDI 1, however its emission intensity is over 5 orders of magnitude weaker indicating almost complete exciton quenching and concomitant suppression of PL. A very similar result is also obtained when P1 is excited using shorter wavelength radiation that is principally absorbed by the backbone polymer. This is consistent with the results published for a PDI functionalised alternating fluorene-phenylene polymer,9a which also showed residual fluorescence from both the PFP and PDI moieties. We can understand such quenching on the basis of rapid charge transfer from the backbone of P1 to its PDI substituents. We show in section 3.5 that charge transfer from the

····· P1

P2

PDI 1



(a) Solutions 10⁻⁶ mol dm⁻³

10⁰

10-2

PI excited at 480 nm (dotted line), **P2** excited at 360 nm (dashed line) and PDI **1** excited at 480 nm (solid line). (b) Thin film PL spectra as cast from chloroform solution: **P1** (dotted line) excited at 480 nm, **P2** (dashed line) excited at 410 nm scaled by 1/100, PMMA/PDI **1** (1 : 1 b.w.) blend (solid line) excited at 480 nm. All spectra are corrected for sample absorption and excitation fluence.

backbone of **P1** to its PDI substituents leads to the formation of long-lived metastable charge states.

3.2. Spectroscopy of thin-film blends of P1 and PDI

In Fig. 2(b), we plot PL emission spectra from thin films of polymer **P1**, **P2**, PDI **1** dispersed in **P2** (at 1 : 1 by weight) and for comparison PDI **1** dispersed in the electronically inert polymer poly(methyl methacrylate) (PMMA) at the same concentration. Notably, the vibronic structure evident in the solution spectra of PDI **1** (shown in Fig. 2(a)) is absent in the thin film. Instead we observe a broad emission band that peaks at 624 nm. Such emission is relatively red-shifted and broadened compared to that from PDI **1** in solution phase (see Fig. 2(a)), and suggests that intermolecular interactions may well be present. Indeed, previous studies have identified excimer emission in perylene-based materials.¹³

The data in Fig. 2(b) is again corrected for relative absorbance and excitation fluence, and thus can be used as an approximate measure for fluorescence quantum yield. As was found in solution measurements (see Fig. 2(a)), it is apparent that the emission from the P1 double-cable polymer is strongly quenched compared to either P2 or PDI 1. Critically however, we find that the emission from the P1 double-cable polymer is weaker than that emitted by the P2/PDI 1 blend. As we argue section 4, this result is consistent with phase-separation and crystallization in the polymer/perylene blend. It can be seen that the P1 polymer PL emission spectrum resembles that of the PDI monomer, having characteristic sharp vibronic peaks at 526 and 567 nm (although these are blue-shifted by 10 nm compared to PDI in solution, see Fig. 2(a)). Interestingly, we observe a broad emission band in the as cast P2/PDI 1 blend centred at 736 nm. We believe that this emission may result from exciplex states; our assignment is based on the fact that this feature appears only in the emission of the donor-acceptor systems and does not correspond to the fluorescence of either moiety. It is also only accessible from the excited state. Similar exciplex emission has also been observed in perylene/pthalocyanine thin-film blends.14 Note that the emission from such red-shifted exciplex-like states is strongly quenched in P2/PDI 1 blends on annealing and thus we assume, in this case, that they play only a minor role in device physics. The contribution of excimer and exciplex-like states in the P1 polymer emission is an area of ongoing research.

In Fig. 3(a), we plot the absorption coefficient of **P1** and a 1 : 1 **P2**/PDI **1** blend. We find that the absorbance of **P1** can be approximately described by a linear superposition of PDI **1** and **P2** absorption spectra confirming that there is no ground state charge transfer and little electronic hybridization between the donor and acceptor. The PDI **1** and **P2** blend have however an absorption tail that extends to red-wavelengths which is most probably accounted for by increased optical scattering within the blend thin films resulting from phase-separation (*vide infra*).

In Fig. 3(b) we plot the emission from a 1 : 4 **P2**/PDI **1** blend film excited at 490 nm before and after heat treatment on the same intensity scale. It is apparent that the heat treated film shows enhanced fluorescence which suggests reduced exciton quenching due to coarsened phase-separation. This, as we later demonstrate, is associated with improved OPV device performance.



Fig. 3 (a) Absorption of **P1** film (dotted line) and 1 : 1 **P2**/PDI **1** blend (dot dashed line). (b) PL from a 1 : 4 **P2**/PDI **1** blend film before and after thermal treatment (solid and dashed lines respectively) excited at 490 nm.

3.3. Electrochemical studies

Cyclic voltammetry measurements on drop-cast **P1** and **P2** polymer films were conducted in acetonitrile with tetrabutylammonium hexafluorophosphate as an electrolyte. The cyclic voltammograms of these materials are shown in Fig. 4.

The cyclic voltammogram of **P1** (Fig. 4(a)) displays an oxidation wave at +0.67 V and an associated reduction wave at +0.49 V that corresponds to the oxidation of the backbone of the



Fig. 4 CV curves of thin films of (a) polymer **P1** and (b) polymer **P2** on platinum disc electrodes (area 0.031 cm^2) at a scan rate of 100 mV s^{-1} in acetonitrile/tetrabutylammonium hexafluorophosphate (0.1 mol dm⁻³).

polymer. It also displays a reduction wave at -2.42 V with an associated oxidation wave at -2.37 V that corresponds to the reduction of the polymer backbone of the polymer. The PDI moieties on **P1** can be clearly identified on its cyclic voltammogram by the reduction waves at -1.29 V and -1.47 V and two associated oxidation waves that show up as one broad peak at -1.15 V.

From the onset of oxidation (+0.58 V) and that of the reduction (-2.32 V) of the polymer backbone of P1, the ionisation potential, I_P , and the electron affinity, E_A , for the polymer backbone can be derived as -5.38 eV and -2.48 eV respectively (on the basis that ferrocene/ferrrocenium is 4.8 eV below the vacuum level⁹). Therefore the electrochemical band gap can be calculated as 2.9 eV. It is not possible to calculate the optical band gap of polymer P1 directly from its absorption spectrum in films since the edge of the absorption from the polymer backbone is masked by the absorption of the PDI substituents, however, we can safely say that the band gap of the backbone of the polymer should be slightly higher than that of polymer P2 since the absorption maxima for the backbone of the polymers are respectively at 407 nm for P1 and 419 nm for P2. The optical band gap of P1 should be around 2.6 eV (optical band gap of P2 is 2.48 eV). This value of 2.6 eV is lower than that deduced from the electrochemical measurements (2.9 eV), however, it is not uncommon to observe slight variations between the optical and electrochemical band gaps. The LUMO level of the PDI moieties attached to P1 as determined from their onset of reduction (-1.06 V) in Fig. 4(a) is -3.74 eV. On the basis of these measurements, we present the energy band diagram for P1 in Fig. 5 and compare it with the known HOMO and LUMO levels of PDI. It is clear that efficient chatge transfer is expected in P1 since PDI has a large electron affinity with its LUMO level lying some 1.26eV deeper than the LUMO level of P1.

The cyclic voltammogram of **P2** is very much similar to that of **P1** (Fig. 4(b) apart from the absence of the features resulting from the PDI units. The ionisation potential, I_P , and the electron affinity, E_A , for polymer **P2** can be derived as -5.38 eV and -2.34 eV respectively.



Fig. 5 Energy level diagram of the polymer backbone and PDI moieties on polymer P1.

3.4. Thin-film morphology

We have used tapping mode Atomic Force Microscopy (AFM) to study thin-films of **P1**, PDI **1**, **P2** and blends of **P2** and PDI **1**. The results of our studies are shown in Fig. 6, where we plot AFM images of thin-films of thermally annealed (120 °C for 10 min) **P1** (part (a)), as spun PDI **1** (part (b)), as spun **P2** (part (c)), a thermally annealed 4 : 1 **P2**/PDI **1** blend (part (d)), an as spun 1 : 4 **P2**/PDI **1** blend (part (e)) and a heat treated 1 : 4 **P2**/PDI **1** (part (f)). It is evident that there is a degree of



Fig. 6 Tapping mode AFM height images. Part (a): **P1** after thermal treatment 10 min at 120 °C, part (b): pristine PDI **1**, part (c): pristine **P2**, part (d): heat treated 4 : 1 **P2**/PDI **1** blend, part (e): pristine 1 : 4 **P2**/PDI **1** blend, part (f): heat treated 1 : 4 **P2**/PDI **1** and part (g): height distribution of image (e) and (f) in the left and right panel respectively with fits. Note that all images have the same lateral scale but the height scaling varies between images.

self-organization in all films, even those cast from a single material. For example, characteristic elongated crystals of PDI are seen in Fig. 6(b) and also in a matrix of P2 as shown in Fig. 6(d) and (e).77,15,16 Thermally assisted diffusion of PDI leads to the growth of PDI crystals and the formation of smaller surface crystallites as is seen in Fig. 6(f). A clear comparison is made in Fig. 6(g) where we plot the deviation of the height from the mean for the 1 : 4 P2/PDI 1 blend before and after thermal treatment (left and right panels respectively). We find that the as spun film shows a bimodal height distribution, and is fitted by two Gaussians. The primary peak is offset from the mean by -2.3 nm with a FWHM of 6.6 nm and a secondary peak centred around +14.1 nm from the mean which we assign to the elongated crystals appearing on the surface. After thermal treatment, the height distribution broadens (FWHM increases to 9.4 nm) and loses its bimodal character. We tentatively attribute this to the breakup of the large PDI crystals and an increase in submicron length-scale roughness owing to further PDI crystallisation and associated P2 enrichment.

The coarse morphology resulting from crystallization that is evident in PDI 1 and the P2/PDI 1 blend thin-films is suppressed in films of the P1 double-cable polymer as seen in Fig. 6(a). Furthermore, thin films of P1 have an RMS roughness of 0.64 nm in contrast to a value of 18.9 nm determined from the thermally annealed thin films of the 1 : 4 P2/PDI 1 blend. This relative flatness in the double-cable polymer is indicative of a lack of coarse phase-separation that results from the covalent linkages between PDI substituents and the backbone of P1 that prohibit their demixing and demonstrates the potential of the double-cable concept to affect film morphology.

3.5. Photoinduced absorption spectroscopy

We have used photoinduced absorption (PA) spectroscopy to study the various excited charged states of P1 double-cable polymer and its constituent components. The PA signatures of P1, a 4 : 1 P2/PDI 1 blend, P2 and a 1 : 4 blend of P2 with PCBM are shown in Fig. 7(a), (b), (c) and (d) respectively. In parts (a) and (b), we detect prominent features that arise from the PDI⁻ radical anion which are located at 1.28, 1.54 and 1.72 eV in the P2/PDI blend and in the P1 double-cable polymer.^{8,17} We can gain further insight into these spectra on the basis of the PA spectrum of the 1 : 4 P2/PCBM blend (shown in Fig. 7(d)). Here, correlated P2⁺ bands are seen at 0.56 and 1.83 eV that we assign to the P_1 and P_2 transitions respectively. A feature at 1.25 eV is also observed and we assign this to the $C_{60}^{-.18}$ On the basis of measurements on the 1:4 P2/PCBM blend, we are able to identify the low energy P_1 transition of **P2**⁺ radical cation which is evident in the PA spectra of both P1 and the 4 : 1 P2/PDI 1 blend (see parts (a) and (b)). Note that the high energy P_2 transition of the P2⁺ radical is likely to be superimposed on the PDI⁻ transition that is located at around 1.8 eV.

Further support for the polaron assignment made here derives from the FBC model that predicts the intragap polaron levels.¹⁹ In the model, if the π - π * energy gap is equivalent to 2Δ and ω is half the energy separation of the two polaron levels, then the following ratio $\omega/\Delta \ge 1/\sqrt{2}$ is expected. From the absorption spectrum of **P2** shown in Fig. 1(a) we determine a π - π * energy gap of 2.48 eV. From the PA spectrum shown in Fig. 7(d), we



Fig. 7 Steady state PA spectra. Part (a) shows the PA spectrum from **P1** (f = 135 Hz), part (b): a **P2**/PDI **1** 4 : 1 blend (f = 400 Hz), part (c): unblended **P2** (f = 135 Hz) and part (d): **P2** (f = 135 Hz) blended with PCBM in a 1 : 1 ratio. All samples are held at 77 K, pumped at 488nm with a photon density of 1.2×10^{17} cm⁻² s⁻¹.

deduce that the **P2** intragap polaron levels are spaced in energy by 1.83 eV from which we calculate a ratio of $\omega/\Delta = 1.36$ and the FBC criterion is satisfied. Note that bipolaron levels would be found much deeper in the energy gap.

We have also performed PA on a pure film of **P2** as shown in Fig. 7(c). Here, the spectrum is dominated by a single feature at 1.64 eV that we assign to the triplet-triplet exciton transition (T_1) of **P2**. This assignment is made on the basis that it appears without an accompanying transition. Some support for this particular assignment is found in the literature since this feature bears a resemblance to the triplet transition in polyvinyl

carbazole.²⁰ Note that without access to LESR or PADMR spin resolved measurements, any excited state assignment must still be considered tentative at this stage.

We can relate the PA signal to the density of photoexcited states using $-\Delta T/T \approx nd\sigma$ as described by Lanzani *et al.*²¹ Here, *n* is the density of excited states, σ is their absorption crosssection and *d* is the thickness of sample. It is more appropriate to use the penetration depth of the pump laser, or $1/\alpha_L$, as this is the effective thickness in which most of the laser is absorbed. As the absorption coefficient of all the films studied are roughly comparable, we can relate $\Delta T/T$ measured for the different samples to the polaron yield. Comparing the peak values of $\Delta T/T$ in Fig. 7 parts (a), (b) and (d), it appears that that there is a larger photoexcitation density in **P1** in comparison with both the **P2**/ PDI and **P2**/PCBM blends.

Using our measured parameters, we determine a singletexciton to polaron yield of $\eta_p = 6\%$ (see ESI†). Although this value is smaller than expected from the efficient exciton quenching that we observe in **P1**, we associate this yield with a long-lived ($\tau = 0.56$ ms – see ESI†) population of trapped charge carriers that we discuss later. We note that this value is relatively large in comparison with other studies by List *et al.*²² where a yield of 0.08% was measured in a fluorescent conjugated ladder-type polymer, however in such materials the direct dissociation of excitons into polarons is anticipated to be a relatively inefficient process.

3.6. Device fabrication and characterization

We have made a series of OPV devices based on P1 double-cable polymer together with devices based on a number of different weight blends (4:1, 1:1 and 1:4) of P2 and PDI 1 donor and acceptor materials. As a bench-mark, devices were also fabricated from P2 in a 1:4 blend with the fullerene acceptor [6,6]phenyl-C₆₁-butyric acid methyl ester (PCBM). The effect of casting solvent and the use of thermal annealing protocols were in all cases explored in order to optimize device efficiency (see Table 2 for details). The performance metrics for the various devices studied (J_{SC} , V_{OC} , FF, PCE and peak EQE) are listed in Table 2. In all cases, we report the metrics of the *highest efficiency* devices fabricated, along with the conditions (casting-solvent, film-thickness and thermal-annealing protocol) used to create such a device. It can be seen that devices based on the doublecable polymer P1 are less efficient than those of the optimised 1:4,1:2 and 1:1 P2/PDI 1 blends. Specifically, we find that the 1 : 4 P2/PDI 1 blend has a maximum power conversion efficiency (PCE) of 0.15% compared with devices based on double-cable polymer P1 that have a PCE of 0.011%. A clear trend also emerges in the efficiency of the blend devices as a function of relative blend composition, with devices having increased PDI concentrations having improved efficiencies.

The relative superiority of the blend films compared with the double-cable material is also reflected in the external quantum efficiency (*EQE*) spectra presented in Fig. 8. Specifically, parts (a) and (b) are measurements made on fully optimized devices composed of a 1:4 **P2**/PDI **1** blend before and after thermal treatment respectively. Part (c) shows an *EQE* spectrum of an optimized device based on **P1**. It can be seen that the **P1** device reaches a maximum *EOE* of 0.43% at 405 nm, whilst the

Table 2 Performance metrics from the P1 and P2/PDI 1 blend devices

Material	Preparation	Thickness/nm	$J_{SC}/\mathrm{mA~cm^{-2}}$	V_{OC} /V	FF (%)	PCE (%)	EQE (%)
P1	Spun from DCB, 10 min 120C	53	0.070	0.72	21	0.011	0.43
1 : 4 P2 /PDI 1	Chloroform cast 10 min 120 °C	156	0.71	0.71	30	0.15	3.7
1 : 2 P2/PDI 1	Chloroform cast 10 min 120 °C	52	1.02	0.62	24	0.15	5.0
1 : 1 P2 /PDI 1	Chloroform cast 10 min 120 °C	57	0.67	0.60	24	0.094	3.1
4 : 1 P2 /PDI 1	Chloroform cast 10 min 120 °C	66	5.5×10^{-3}	0.40	27	5.5×10^{-3}	0.038
P2	Spun from chloroform, no treatment	133	$9.1 imes 10^{-4}$	0.58	25	$1.3 imes10^{-4}$	a
1:4 P2/PCBM	Slow spun from TCB, 10 min 120 °C.	Not determined	7.34	0.63	32	1.49	48
^{<i>a</i>} Beyond instrum	ent sensitivity						

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Fig. 8 Comparison of EQE spectra and active layer absorbance. Part (a): the most efficient 1 : 4 P2/PDI 1 device prior to annealing, part (b): the same device after annealing and part (c): the most efficient P1 device.

thermally annealed 1 : 4 **P2**/PDI **1** blend has a maximum EQE of 3.7% at 462 nm. Thus the optimized blend device is at least six times more efficient than the cable polymer based device. Interestingly, the spectral shape of the absorbance and the EQE spectra of the annealed and un-annealed blend devices are different, with (0,0) electronic transition in the annealed device being relatively suppressed compared to the (0,1) transition. As discussed above, this observation suggests increased

optimum performance from **P2**/PDI 1 blend-based devices is achieved when a much more volatile solvent (chloroform) is used to cast thin films. This observation suggests that allowing the **P1**

thermally annealed blend.

to cast thin films. This observation suggests that allowing the **P1** double-cable polymer to undergo self-organization enhances the disassociation and extraction of charge, whereas this is not the case for the blend. Rather, it appears that a thermal annealing step in conjunction with a fast drying solvent encourages the formation of **PDI** crystals which we presume are dispersed in a matrix of **P2**. It is possible that the use of slow-drying solvents to cast blend films results in the formation of domains that are so large that exciton dissociation is suppressed resulting from the low density of interfaces between donor and acceptor components.

intermolecular interaction resulting from crystallization in the

double-cable polymer based devices results from using thin-films

cast from a slow-drying solvent (dichlorobenzene). In contrast,

In general, we find that optimum performance from P1

As anticipated, the lowest efficiency devices $(1.3 \times 10^{-4} \%)$ PCE) were produced from a 'pristine' film of polymer P2. Clearly, the lack of a donor-acceptor couple in this co-polymer system results in a very low degree of charge separation and thus very poor device efficiency. When polymer P2 is blended with PCBM and cast from TCB, devices created had a PCE of 1.5%. On the basis of the model by Scharber et al.,²³ we can expect a maximum power efficiency of PCBM/P2 blends of $\sim 2\%$, suggesting that our devices are relatively well optimized.²⁴ In contrast to what is observed in P1 or the P2/PDI 1 blends, it appears therefore that the devices based on a blend of P2 and PCBM are significantly more efficient than those utilizing PDI, as an acceptor material. As we argue below, we believe that P2/ PDI 1 and P1 devices are dominated by geminate or non-geminate recombination; an effect that is presumably suppressed in the P2/PCBM devices.

In Fig. 9(a) and (b), we plot current–voltage (J–V) spectra from a **P1** and a 1 : 4 **P2**/PDI **1** OPV device respectively recorded under illuminated and dark conditions plotted on a semilog scale. The inset shows the same J–V traces over a -1 V to +1.5 V range on a linear scale. It can be seen that the **P1** based device exhibits an approximately linear J–V trace up to V_{OC} with low fill factors indicative of high series and low shunt resistances²⁵ that most likely arises from poor charge transport. An improved Fill Factor is evident in the 1 : 4 **P2**/PDI **1** device. We can quantify charge transport in the devices we have studied by estimating the active region charge carrier mobility by fitting to the quadratic,



Fig. 9 Current–voltage spectra under simulated AM1.5G irradiation at 1 Sun and in the dark with space charge limited current fits, part (a): the most efficient **P1** device after annealing, part (b): the most efficient 1 : 4 **P2**/PDI **1** device after annealing. The same data is plotted on a linear scale inset. Part (c): J_{SC} vs. 488 nm laser illumination intensity with fits for **P1** (closed squares), 1 : 4 **P2**/PDI **1** (open squares) and 4 : 1 **P2**/PDI **1** (open circles) devices.

space charge limited region of the dark J–V curves presented in Fig. 9(a) and (b). Specifically at high applied-bias, we fit the following space-charge limited expression²⁶ that includes a Pool–Frenkel mobility term

$$J_{e(h)} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_{e(h)} \exp\left(0.891 \gamma_{e(h)} \sqrt{\frac{V}{L}}\right) \frac{V^2}{L^3}$$
(1)

Using a value of 3 for ε_r , together with the device thickness (*L*) listed in Table 2, we obtain values of charge carrier mobility of 4.0×10^{-7} cm² V⁻¹ s⁻¹ and 3.8×10^{-6} cm² V⁻¹ s⁻¹ for the **P1** and 1 : 4 **P2**/PDI **1** devices respectively. The fits used to derive these values are also shown in Fig. 9(a) and (b) along with the experimentally determined J–V spectra. Note that should transport be imbalanced between donor and acceptor, the values calculated here are representative of *highest mobility* carrier. These

estimates are subject to an uncertainty of *ca.* 20% arising from errors in measuring device thickness and fitting, however it appears that carriers in the **P2**/PDI **1** blends have a mobility that is approximately 10 times larger than that in the **P1** device.

As summarized in Table 2, devices based on polymer P1 are characterized by an open circuit voltage (V_{OC}) of 0.72 V. The V_{OC} of the P2/PDI 1 blend ranges from 0.4 V to 0.71 V as the blend composition is varied between 4:1 and 1:4 P2/PDI 1 respectively. Empirically, Scharber et al.23 have shown that $V_{OC} = (1/e)(LUMO_A - HOMO_D) - 0.3$ V where e is the elementary charge. Using the same reasoning, we should expect a value of $V_{OC} = 1.34$ V in devices based on double-cable polymer P1. This is however not observed in practice, with V_{OC} in all devices being much lower than ideality. Even in state of the art P3HT/PCBM devices, there is some voltage loss (ca. 0.3 V) owing to the nonideal nature of the current-voltage characteristic.²⁷ Because V_{OC} is the voltage at which the injected current compensates the photocurrent, any dark-injection will act to reduce V_{OC} from the idealized limit of V_{bi} which here is anticipated to be 1.64 V determined from the difference between acceptor LUMO and donor HOMO levels. The most likely explanation for the discrepancy is that photocurrent is largely field driven with the reduced charge carrier mobility responsible for a reduced V_{OC} .

An insight into loss mechanisms in the devices studied can be gained by studying the dependence of the short-circuit current (J_{SC}) against incident flux as presented in Fig. 9(c). We find that for the double-cable polymer based device, J_{SC} is to a good approximation linear with optical power (fitted by an exponent of 0.92). This suggests that the dominant charge-carrier recombination mechanism within P1 based devices is likely to be via geminate recombination of charge carriers rather than a bimolecular process involving non-geminate recombination. Bimolecular recombination would instead have a sub-linear J_{SC} vs. incident flux following a $J_{SC} \sim P^{3/4}$ law.²⁸ In the blend devices however, the situation is more complicated, with J_{SC} being fitted by an exponent that varies between 0.87 in a 4 : 1 P2/PDI 1 blend to 0.96 in a 1:4 P2/PDI 1 blend. This result suggests that in devices with a low PDI fraction, recombination is predominantly bi-molecular. As the PDI concentration increases however, the device efficiency improves with recombination becoming significantly more monomolecular in character. This finding is in qualitative accord with those of Howard et al.,29 who also identified bimolecular recombination as a dominant loss mechanism in blends of PDI and a conjugated polymer, where the PDI and polymer had relative mass fractions of 3 : 2 respectively.

4. Discussion

We find that photovoltaic devices based on a double-cable polymer-type material in which donor and acceptor moieties are covalently linked are less efficient than those of an optimised blend of donor and acceptor materials. It is interesting to explore the reasons for the reduced efficiency of the double-cable polymer. We found that the J–V traces of the **P1**-based devices are almost linear, (symmetric around V_{OC}) suggesting that charge transport is poor. This conclusion is supported by the fact that the short circuit currents and fill-factors measured are low resulting from poor charge transport and resistive losses within the device.²⁵ It is clear however that excitons are quenched efficiently in **P1**, as seen from the suppresion of PL evidenced in Fig. 2(b). However, the low values of *EQE* and J_{SC} measured demonstrate that charge is not being efficiently collected. On the basis of previous work,^{30,31} we assume that the long-lived polarons detected in PA are associated with charge stored in deep traps whereas photocurrent measurements on devices sample a different population of mobile polarons. This suggests therefore that there is a large population of charge carriers that undergo recombination on a timescale that is faster than the resolution of our PA measurement. Our measurements of photocurrent *vs.* optical pump-power on **P1** devices suggest that this recombination mainly occurs *via* geminate recombination.

Given the lack of significant observable structure in AFM height images of P1, we conclude that the donor and acceptor components are intimately mixed at least at a length-scale below the resolution of our microscope (~ 10 nm corresponding to the tip radius), suggesting a lack of the mesoscale order of donor and acceptor domains essential for a bicontinuous charge transporting network. It is likely that the resultant morphology in the double-cable polymer also prevents complete exciton separation into free carriers and results in rapid geminate recombination. Indeed work on polymer-polymer blends³² has argued that the spatially-confined geometry present in an intimately mixed polymer blend suppresses charge-separation and results in geminate recombination. It is also possible that the relatively high 'steady-state' trapped-charge population detected in P1 also directly results from charges stabilized on PDI molecules that are effectively "isolated" from the polymer backbone by the saturated linker group.

AFM measurements on P2/PDI 1 blends suggest that phaseseparation occurs over significantly larger length-scales than in the double-cable polymer - an effect that results in a reduced exciton quenching efficiency. On thermal annealing, we find that the PL intensity emitted by the blends increases, a result consistent with the increased phase-separation, domain nucleation and crystallization of the PDI (as evidenced by AFM and modified device absorbance). Despite the reduced exciton quenching efficiency in annealed P2/PDI 1 blends, it appears that a coarsening of phases in an excess of PDI is necessary for efficient device operation. However, in P1 devices, neither of these criteria is met since the weight concentrations of donor and acceptor are roughly equal and phase separation is arrested by their covalent-linkage. Consequently, we see an increased EQE in P2/PDI 1 in comparison with the double-cable polymer based devices as shown in Fig. 8. Although exciton quenching is very efficient in P1, it is likely that device efficiency is limited by either poor extraction of carriers or incomplete separation of geminately bound electron-hole pairs. The observation of a large polaron yield with monomolecular recombination kinetics would suggest that it is the latter. By contrast, we find a reduced polaron yield in a 4 : 1 P2/PDI 1 blend, illustrating that fewer polarons become trapped - presumably as a result of an improved nanoscale-morphology.

We have found that the recombination kinetics of the **P2**/PDI **1** blend apparently change as the composition of the material is varied. In blend materials that make the worst performing devices (having a low PDI fraction), the photocurrent dependence against pump-power is sub-linear, suggestive of

bimolecular recombination. This apparently switches over to monomolecular recombination in more efficient devices in which PDI is in excess. Bimolecular recombination has previously been observed in PDI/conjugated polymer based devices.29 We therefore suggest that there is a competition between geminate and non-geminate recombination dynamics in P2/PDI blends. At high PDI fractions, separate percolation pathways exist for electrons and holes, formed as a result of phase-separation.³³ This spatial-separation of electron and hole currents, together with a general increase in carrier mobility in the blends results in a reduced bimolecular recombination rate, with a consequence being that monomolecular recombination effectively dominates. However as the PDI fraction is reduced, self-organization of the PDI is suppressed, resulting in a lack of percolation paths for electrons and a general reduction in the bulk mobility of charge carriers. The consequence of this is that the bimolecular recombination rate apparently increases and 'overtakes' the monomolecular recombination channel. Clearly, time-resolved spectroscopy would be useful in confirming this hypothesis.

5. Conclusion

We have synthesized and characterized a double-cable polymer composed of perylene diimide acceptor groups that are covalently linked to 2,7-linked carbazole bi-thiophene polymer chains. Excitons created on this polymer following optical excitation are very efficiently dissociated as fluorescence from the polymer is strongly quenched both in solution and in thin film. Photoinduced absorption measurements indicate that polarons are generated on the double-cable polymer with high yields. Photovoltaic devices utilizing the double-cable polymer generate a symbatic photoresponse, demonstrating charge transport arising from photoexcitations. However such devices have low peak quantum efficiency resulting from poor charge transport and resistive losses within the device. Comparative studies on devices based on thin-film blends of perylene diimide moieties and a carbazole bi-thiophene polymer without PDI substituents had a higher efficiency than those based on the double-cable polymer. AFM studies on thin films of the double-cable polymer suggest that phase-separation is almost completely suppressed, whereas a coarser grained structure is observed in the thin-film blend. Herein lies the explanation for reduced device efficiency of the double-cable polymer; such fine-scale phase separation results in geminate recombination since the absence of phase separated domains prevent the separation of electron-hole pairs into free carriers. This latter effect is consistent with the emergence of charge-traps that are evidenced by a large and long-lived polaron population (see Fig. S3, ESI[†]). Optimized blend devices based on an excess of PDI acceptor molecules however are characterized by a reduced trapped polaron population and superior operational efficiency. We propose that this results from the formation of improved charge extraction pathways resulting from phase-separation and crystallization of the PDI acceptor molecules.

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