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1 Introduction

Solution-processable organic photovoltaic (OPV) cells have attracted considerable attention in the past decades, owing to their potential of providing environmentally safe, flexible, lightweight, inexpensive solar cells.1 The most studied and successful OPV devices employ a bulk heterojunction (BHJ) architecture, often made upon blending an electron-donor conjugated polymer to an electron-acceptor fullerene derivative.2 OPV performance has significantly advanced in the last few years through successive implementations of material design,³ morphology control⁴ and device engineering.⁵ In recent years, the power conversion efficiencies (PCEs) of polymer/ fullerene BHJs have risen rapidly,6 with best reported PCEs in 2012 around 9%.7 Nevertheless, despite this rapid PCEs improvement, OPV performance is still significantly below that of their inorganic counterparts,8 and more intensive research will be needed to further enhance the device performance.

Double acceptor D–A copolymers containing benzotriazole and benzothiadiazole units: chemical tailoring towards efficient photovoltaic properties†

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This study reports the design and synthesis of a series of D–A copolymers alternating benzothiadiazole and benzotriazole acceptors to a donor co-unit, and investigates their photovoltaic properties in bulk heterojunction solar cells with PC₇₁BM. Successive modifications to the copolymers are carried out, passing from thiophene to benzodithiophene (BDT) donor co-units and from regular to random alternation of the accepting units. A copolymer containing a thiophene co-unit has reached a power conversion efficiency (PCE) of 1.88% in optimised devices. Moving from thiophene to BDT leads to some advantages, such as a lower optical energy gap and a lower confinement of the photo-generated charges, that positively affect the spectral coverage to solar radiation and the fill factor (FF) parameter in the devices. Passing from regular to random distribution of the accepting units, the BDT copolymer solar cells have reached a PCE of 5%. Such encouraging photovoltaic performances are combined with high solubility, high molecular weight and with an easy preparation procedure. These characteristics are necessary requirements to envisage the scale-up to industrial applications.

The design of more effective conjugated polymers to be applied in polymer/fullerene BHJ solar cells remains a challenge for the development of OPV solar cells. In order to achieve high efficiency, the optoelectronic properties of the donor polymer should be tailored to combine: (i) broad absorption spectra and relatively low optical absorption band gaps with suitable energy level offsets to a fullerene acceptor⁹ and (ii) extended π -electron delocalization and backbone planarity,^{10a} low charge carrier confinement.10b Besides the optoelectronic properties, also some other polymer characteristics need to be tailored for good device operation. Suitable molecular weight, solubility and processability are also needed for effective mixing to fullerene acceptors to form a bicontinuous nanoscale morphology.^{2,4} Moreover, when designing novel polymers for OPVs, the ease of synthesis is an important aspect that should be also considered to envisage the scale-up to industrial applications.11

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An important approach used for the design of conjugated polymers with tailored properties for solar cells is the donor-acceptor (D–A) copolymerisation.^{3a,12} The D–A strategy allows an effective tuning of both band gaps and energy levels of conjugated polymers.¹³ To date, there are several donor and acceptor units found to be suitable for developing high performance D–A copolymers for solar cells.^{3,12} However, there remains a need to further investigate new D–A combinations to optimize materials for OPVs.

An interesting design approach, so far rarely used to exploit the modular nature of the D–A copolymer architecture, consists in alternating a donor co-unit to two different acceptors in the

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polymer backbone. This type of strategy has been recently used to design polymers with ambipolar carrier transport properties for field effect transistors,¹⁴ and acceptor or donor polymers for BHJ solar cells.¹⁵

Among these few examples, we have been attracted by the copolymers containing benzothiadiazole (BT) and benzotriazole (BTz) as electron-accepting units.^{15a,b} BT has been the first and one of the most widely used accepting moieties in D-A copolymers for OPVs, due to its suitable electron withdrawing ability that allows lowering of the polymer energy band gap while preserving deep HOMO levels, which favors relatively high Voc.16 In the past few years, there has been growing interest in using BTz derivatives to design D-A copolymers for OPVs.3c,17 BTz, which is a weaker acceptor compared to BT, can readily incorporate a convenient alkyl substituent for solution processability.18 When BT and BTz accepting units are combined in the same polymer backbone, it is possible to tune the D-A interaction and, equally importantly, the number and distribution of alkyl side chains can be easily tailored to control the polymer backbone planarity and interchain π - π interaction, as well as its processability and mixing morphology to fullerene. For these reasons, studies on the photovoltaic characteristics of copolymers that alternate BT and BTz acceptors to a thiophene donor co-unit have recently appeared in the literature.^{15a,b}

The intrinsic potentialities of double acceptor D-A copolymers containing BT and BTZ, to design novel materials for OPVs, could be further exploited. The substitution of the thiophene with a benzodithiophene (BDT) donor co-unit may bring some advantages. BDT derivatives provide an effective tuning of the band gap and energy levels when combined with several accepting co-units in D-A copolymers for OPVs.12c,16a,19 BDT combines the advantage of an extended π -conjugated structure, regioregularity, low steric hindrance to neighbouring units, with easy modification, with proper side chains, for enhanced solubility.19 The monomer units sequence design can also bring additional features. Pseudorandom copolymers, where the donor units are alternated to the two acceptor units, which are randomly distributed, exhibit the additional benefits of a better solubility and of a quite easy preparation, when compared to their regular counterpart.20 This approach can be used to further exploit the chemical versatility of D-A copolymers containing BTz and BT units to improve the photovoltaic performance.

In this paper, we report the design and synthesis of a series of D–A copolymers containing benzothiadiazole and benzotriazole as accepting units and we investigate their use as donor polymers in BHJ OPV devices, with PC₇₁BM as acceptor.

2 Results and discussion

We have prepared a series of copolymers containing benzothiadiazole and benzotriazole as accepting units, **P1–P4** (see Scheme 1). Three of them (**P1**, **P3** and **P4**) are reported in this study for the first time. In polymers **P1** and **P2** we have used a thiophene donor unit alternating to BT and BTz. In **P1**, the thiophene unit bears an alkyl substituent to increase solubility; the thiophene alkyl side chain is close to BTz, thus differing from the previously reported polymers, where the alkyl side chain was close to BT.^{15*a,b*} An un-substituted thiophene has been used in **P2**, similar to a previously reported study.^{15*b*} In polymers **P3** and **P4**, benzodithiophene (BDT) has been chosen as a donor co-unit. Finally, **P3** has been prepared with a regular sequence of the co-units, while **P4** is its analogue random copolymer, where the donor units are alternated to the two acceptor units which are randomly distributed. A chart containing the structures of the published copolymers mentioned through the discussion of the results has been added to the ESI.[†]

2.1 Synthesis and characterisation

The structure of polymers **P1–P4** and the synthetic routes to the polymers are shown in Scheme 1.

The Mws, listed in Table 1, have been measured in TCB by high-temperature SEC, a technique that prevents aggregation phenomena and affords molecular weight values that are more reliable than low-temperature SEC in THF.²¹

P1 and **P2** were prepared by Suzuki cross-coupling polymerization. Because of an extremely low solubility, it was found that **P2** started to precipitate in the early stages of polymerization, thus limiting its molecular weight.

The same approach was attempted for the preparation of **P3**, but the selective bromination of 4,7-bis-(4,8-di(2-ethylhexyloxy)-benzo[1,2-b:4,5-b']dithiophen-2-yl)-2-(2-octylnonyl)benzotriazole (9) and the subsequent purification were unsuccessful.

Therefore, **P3** was prepared by direct arylation polycondensation. This polymerization method is more environmentally friendly than other techniques and does not require pre-functionalization of the monomers,²² but it needs a more careful optimization and with some substrates it leads to lowmolecular weight polymers.²³ This is indeed the case of **P3**, which exhibited a Mw of about 7000.

P4 was obtained by Stille polymerization from the distannyl derivative of benzodithiophene and the dibromides of benzothiadiazole and benzotriazole in equimolar amounts. The ratio of BT/BTz monomer units in the resulting copolymer was 1 : 1, as confirmed by NMR. **P4**, similar to **P3**, was soluble in several organic solvents but showed a higher molecular weight, see Table 1. The solubility of **P4**, >80 g l⁻¹ in chlorobenzene (CB) at room temperature, makes it possible to prepare high-viscosity inks, which are suitable for gravure printing or slot-die coating.¹¹

2.2 Optical and electrochemical properties

The UV-Vis absorption spectra of polymers **P1–P4** dissolved in *o*-dichlorobenzene and in thin films are displayed in Fig. 1. The optical energy gaps (E_g), measured at the onset of the absorption, are comprised between 1.93 eV and 1.61 eV and are collected in Table 1. The spectra contain multiple absorption peaks, which are typical for D–A based conjugated polymers and are related to donor–acceptor orbital hybridisation. In analogy to other D–A copolymer systems, these peaks should result from π – π * transitions and/or intramolecular charge transfer transitions.²⁴

Copolymers **P1** and **P2** are made with similar building blocks but differ by the presence of an alkyl side chain substitution



Scheme 1 Synthesis of P1–P4 copolymers (R1 = 2-hexyldecyl; R2 = 2-octyldecyl; R3 = 1-octylnonyl; R4 = 2-ethylhexyl). *Reagents and conditions*: (i) 2-hexyldecyl bromide, Bu^tOK, methanol, 60 °C, 5 h; (ii) Br₂/HBr aq., 100 °C, 60 h; (iii) 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-hexylthiophene, DMF, K₂CO₃ aq., Pd(PPh₃)₄, 100 °C, 9 h; (iv) NBS, THF, r.t., 24 h; (v) 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole, toluene, *n*-propanol, K₂CO₃ aq., Aliquat 336, Pd(PPh₃)₄, reflux, 40 h; (vi) 2-octyldecan-1-ol, THF, PPh₃, diisopropylazadicarboxylate, 0–20 °C, 12 h; (vii) 2-(tributylstannyl)thiophene, DMF, Pd(PPh₃)₂Cl₂, 80 °C, 10 h; (viii) 9-heptadecanol, THF, PPh₃, diisopropylazadicarboxylate, 0–20 °C, 12 h; (ix) 2-(trimethylstannyl)-4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene, DMF, Pd(PPh₃)₂Cl₂, 80 °C, 6 h; (x) 4,7-dibromo-2,1,3-benzothiadiazole, 2,6-bis-(trimethylstannyl)-4,8-di(2'-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene, toluene, Pd(PPh₃)₄, 70 °C, 50 h.

 Table 1
 Molecular weights, optical properties, HOMO and LUMO energy levels of the polymers

	Mw^a (g mol ⁻¹)	PDI (Mw/Mn)	$E_{ m g}^{ m sol}$ (eV)	$E_{ m g}^{ m film}$ (eV)	HOMO ^b (eV)	LUMO ^b (eV)
D1	13 800	1.8/	2.02	1 03	-5.30	_3 15
	13 000	1.04	2.02	1.95	-3.39	-3.13
P2	7000	1.46	1.79	1.61	-5.11	-3.11
P3	7200	1.20	1.90	1.80	-5.31	-3.09
P4	61 300	3.21	1.79	1.75	-5.17	-3.19

 a From GPC, see ESI. b Evaluated from the $E_{\rm ox}$ and $E_{\rm red}$ onsets (see the text and ESI).

into the thiophene unit. It can be seen that this difference has a relevant impact on the copolymers optical absorption spectra. The spectral pattern of **P1** consists of three bands at shorter and longer wavelengths, peaked in solution at 313, 390 and 530 nm. For **P2**, these bands shift to 316, 425 and 579 nm. The peaks shift can be ascribed to changes in the backbone conformation that induce some changes in the extent of π electron delocalisation. The steric hindrance of the alkyl side chain is reasonably altering the backbone coplanarity, thus reducing the effective conjugation length of **P1**. In **P2**, the steric twisting is released so



Fig. 1 Optical absorption spectra of polymers **P1**, **P2**, **P3**, and **P4** in *ortho*dichlorobenzene solutions (dotted lines) and thin films (continuous lines with open circles, triangles, diamonds, squares, respectively).

that the backbone conformation is more planar and the extent of π electron delocalisation is enhanced, explaining the red shift of the absorption bands. In addition, a more planar backbone conformation facilitates the interchain π - π interactions in films. This explains the appearance in P2 films of a shoulder at longer wavelengths due to aggregation. Note that even in solution, P2 shows a weak spectral feature due to aggregates formation. As will be discussed in the following, such strong tendency of P2 to aggregate is detrimental to the film forming properties of the composite active layers. For this reason, even if P1 has a higher E_g compared to P2, which is a disadvantage for PV applications, the good solubility imparted by the thiophene alkyl side chains makes P1 a better candidate than P2 to be used in BHJ solar cells. However, P1 has an E_{g} , both in solution and in the solid state, of about 0.2 eV smaller than the already published polymer, with an analogous structure but with alkyl side chains positioned close to the BT unit.^{15a,b} This suggests that, in **P1**, there is some increase of the D-A interaction, and thus a lowering of the E_{g} , because of a release of steric twisting between thiophene and accepting unit BT, which is a stronger acceptor compared to BTz.

By introducing the BDT donor unit we have synthesised two D–A copolymers, **P3** and **P4**, which have good solubility and processing properties. As shown in Fig. 1, these copolymers show broader absorption spectra in the visible region and lower optical band gaps compared to polymer **P1**. Therefore, polymers **P3** and **P4** are expected to have better potential for OPV devices,



Fig. 2 FTIR-PIA spectra of (a) pristine polymers **P1–P4** and (b) **P1/P3/P4**:PC₇₁BM blends (1 : 3 w/w) (continuous line) and pristine polymer films (dotted lines). Each spectrum is arbitrarily shifted and plotted in the same scale (1.3×10^{-3} in (a) and 2×10^{-3} in (b)). Temperature: 80 K, exc. wavelength: 514 nm, 10 mW cm⁻².

due to improved solar light harvesting. Polymer P3 solution has three distinct peaks at 322, 449 and 568 nm. Passing from solution to film, P3 exhibits a broader absorption that suggests the occurrence of π - π interchain interactions of some relevance. The observed redistribution of the peaks' intensity is probably related to some backbone planarization in the solid state. Note that BDT has an extended π -conjugated structure that combines with a release of steric twisting along the chain, due to the side chain substituent positions. This should indeed favour π - π inter-chain interactions in the solid state. The absorption spectral pattern of P4 is not resolved in distinct peaks, likely because of the random nature of the alternation of BT and BTz units along the chain. The random copolymerisation of P4 is likely reducing the interchain interactions in the solid state and this may account for the weaker changes in the absorption spectrum of P4 from solution to film.

Note that the above spectral features indicate a general tendency towards a better coverage to solar radiation in copolymers containing both BT and BTz, as compared to parent-like published D–A copolymers, where a BDT or thiophene co-unit alternates either to BT or to BTz.

To estimate the HOMO and LUMO energy levels of the polymers, we studied the electrochemical properties through cyclic voltammetry of the films (see ESI† for details). The HOMO and LUMO energies were evaluated from the onset potential of the first peak of oxidation and reduction, following the literature.²⁵ The HOMO and LUMO levels, listed in Table 1, exhibit the right energy off-sets to fullerene (PC₇₁BM E_{HOMO} : -5.91 eV, E_{LUMO} : -3.86 eV), to make such copolymer series suitable materials to apply as donors to fullerene as the acceptor.

It can be seen that the LUMO levels of the copolymer series are not varying much along the copolymer series. This is consistent with the fact that in D–A copolymers, the LUMO energy levels are primarily correlated with the electron affinities of the electron withdrawing units²⁶ and that in the copolymer series here under study the electron withdrawing moieties are not varying.

Moreover, theoretical studies demonstrated that the frontier orbital's energy and their electron density distribution are localized in the electron-poor region of the structures, while the HOMO are generally delocalized over a large part of the structure and, similar to other conjugated chains, the HOMO energy level is reduced by increasing the effective conjugation length.²⁷

Table 1 shows that the HOMO level is shifting to higher energies when passing from **P1** to **P2**. This feature brings support to the previously discussed increase of conjugation length, passing from **P1** to **P2**, due to the planarization of the structure. Both the oxidation and reduction of polymers in the series are chemically reversible, except for the oxidation of **P3** (see the figure in the ESI[†]). This difference could be probably attributed to the low molecular weight and consequently to the partial solubility of oxidised species in the acetonitrile electrolyte.

2.3 Photophysical characterisations

Steady state FTIR photoinduced absorption (PIA) spectroscopy is a useful tool to detect the formation of long lived metastable charged species in conjugated polymers.²⁸ This characterisation provides a viable technique for the assessment of the photoinduced charge transfer process in polymer/fullerene blends²⁹ and can bring useful information about the electronic structure of the conjugated polymers, in particular on the delocalisation of photo-generated charges into polarons.

The PIA spectra of pristine copolymer films are displayed in Fig. 2a. Polymers P2, P3, and P4 show a series of vibrational bands (IRAV bands) and a broad electronic absorption band in the MIR region, which are the typical spectral signatures of polaron cations.³⁰ Polymer P1 does not show any PIA activity. In pristine polymers, the long lived metastable charged species are few, and their appearance in the PIA spectrum relies on the high oscillator strength of the transitions associated with polarons. These absorption bands are quite intense when charges delocalise along the chain, but decrease heavily in oscillator strength for π -electron confinement. Therefore the absence in Fig. 2a of detectable polaronic features in P1 pristine films is consistent with the twisted conformation and low effective conjugation of P1 that induces charge confinement and thus heavily reduces the intensity of the PIA bands. Moreover, the PIA spectra of P3 and P4 differ from P2, showing IRAV bands superimposed on a broad electronic transition background, which is a typical signature of charged species with extended delocalisation.³¹ Note that, in terms of the photovoltaic process, the improvement of the degree of charge delocalisation in polymers containing the BDT unit should then favour the electrone-hole pair separation at the polymer:fullerene interface.^{10a}

The PIA spectra of polymers/PC₇₁BM blends are shown in Fig. 2b, and compared to pristine polymer films. The PIA spectrum of the blend based on P2 is not shown because it was heavily distorted by a very large scattering background due to micrometer scale segregation between the blend components. While pristine polymer P1 does not show any PIA signal, the formation of polaron cations is clearly detected in the blend with $PC_{71}BM$. This is evidence for efficient photoinduced charge transfer between P1 and $PC_{71}BM$, which enhances significantly the population of long lived metastable charges detected in the blend. Moreover, the PIA spectrum shows a spectral pattern, which is indeed consistent with stronger charge confinement in P1 than in the other copolymers. It can be seen from Fig. 2b that there is a decrease of the relative enhancement of the PIA intensity from pristine films to the blends, passing from P1 to P4 and then to P3.

Even though it is a complicated issue to exactly assess the number of photogenerated charges from the PIA intensity,³² the observed features in Fig. 2a indicate that the effectiveness of charge generation is reduced, passing from **P1** to **P4** and then to **P3** blends. This trend is related to differences in phase segregation that influences the number of charges that are formed in the blends. For example, the low molecular weight and the strong inter-chain interactions of **P3** could favour phase segregation, especially in slow drying drop cast films, as deposited for the PIA measurements. It will be clear from the following that there is a rough correlation between the effectiveness of charge photogeneration, as probed by the PIA measurements, and the incident photon to current efficiency (IPCE) measured in the solar cells.

Photoluminescence (PL) spectroscopy has been used to probe the excitons dissociation efficiency and the mixing nanomorphology in the device active layers. Fig. 3 displays the PL spectra of the device active blend films and of the pristine polymers. The active layers, at 1:3 (w/w) polymer : fullerene composition, are deposited and processed similar to the optimised solar cells reported in the next paragraph.

It can be seen that in the blends the photoluminescence is significantly quenched. This indicates that the excitons generated in the bulk have a high probability to reach an interface between the donor polymer and the acceptor fullerene to dissociate. As the characteristic exciton diffusion length in conjugated polymers is around 10 nm, the PL quenching observed in the blends implies a nano-scale phase segregation between the polymers and fullerene.

The PL peak intensities of the pristine polymers are reduced respectively by 99.9% in **P1**, 98% in **P4** and 97% in **P3** blends. Such a trend of the PL quenching indicates that the probability for an exciton to reach the polymer–fullerene interfaces, where the charge generation processes take place, decreases passing from **P1** to **P4** and then to **P3** based active blends. This behaviour correlates with the changes of the IPCEs and J_{sc} device characteristics, reported in Fig. 4. Moreover, the PL quenching in **P1** based blends indicates that phase segregation is severely hindered in **P1** while increases passing to **P4** and **P3** blends. Such changes in blend nanomorphology are also affecting the FF parameter device characteristics.

The PL spectra of the blends made with **P3** and **P4** show a spectral pattern ascribable to $PC_{71}BM$. This evidences the presence of relatively large PCBM domains in **P3** and **P4** active layers. A method proposed to obtain smaller domains of $PC_{71}BM$ in blends deposited from chlorobenzene consists in adding a small amount of 1-chloronaphthalene (CN) to the solutions.³³ In the inset of Fig. 3, the effect of the CN additive on the PL spectra of the active layers based on **P3** and **P4** is



Fig. 3 Photoluminescence spectra of the P1, P3, and P4 blend films (continuous lines) and pristine films (dotted lines). P1: circles, P3: diamonds, and P4: squares. Spectra are normalised to the fraction of incident photons at 490 nm. The PL intensity of each blend and polymer is normalised to the corresponding polymer peak intensity; the PL intensities of the blends are multiplied by ten. Inset: PL spectra of blends based on P3 and P4 without (upper lines) and with CN additive (bottom lines).



Fig. 4 (a) EQE spectra and (b) J-V curves, recorded under 100 mW cm⁻² solar simulation, of solar cell devices based on **P1**, **P3**, and **P4** blended with PC₇₁BM at 1 : 3 w/w ratio. (a) Inset: absorption spectra of the corresponding blends, normalised to their max value.

displayed. The observed reduction of the PL intensity for the layers prepared with the CN additive evidences the formation of smaller fullerene domains. It will be clear from the following section that the observed reduction of phase segregation with the CN additive increases effectively the J_{sc} and IPCE of the solar cell devices.

To complete the copolymers characterisation we have attempted to measure the SCLC hole mobilities. As shown in the ESI,[†] there are some difficulties in making the measurements with the standard hole only diode architecture proposed in the literature. One of the problems we have encountered was to obtain relatively thick homogeneous films, at least for **P1** and partially for **P3**. This convinced us that it is not possible to provide a reliable comparison of the copolymers hole mobilities in this study.

2.4 Photovoltaic properties

To explore the potentialities for solar cells, the photovoltaic properties of the copolymer series were investigated in blends with $PC_{71}BM$. The device assembling procedure was optimised for each copolymer blend, as described in the ESI.† The photovoltaic parameters obtained after optimisation are summarised in Table 2. Cells were first investigated using

Table 2 Photovoltaic parameters for P1, P3 and P4:PC71BM solar cells^a

Polymer : $PC_{71}BM$ 1 : 3 (w/w)	$V_{ m oc}$ [V]	$J_{ m sc}$ [mA cm ⁻²]	FF	PCE [%]	$J_{ m scEQE}{}^c$ [mA cm ⁻²]
P1	0.91	5.90	0.35	1.88	5.98
P3	0.80	3.11	0.47	1.17	3.28
P4	0.87	4.95	0.61	2.63	4.96
$\mathbf{P3}^{b}$	0.82	3.79	0.46	1.48	4.71
$\mathbf{P4}^{b}$	0.81	10.30	0.60	5.01	9.70
P2	0.46	1.76	0.32	0.26	2.28

^{*a*} Under 100 mW cm⁻² solar simulation. ^{*b*} Deposited from CB:CN (98%:2% v/v) + post-deposition surface treatment with EtOH (see ESI). ^{*c*} From the convolution of the EQE and AM1.5G solar spectra.

chlorobenzene as a processing solvent. For optimized devices, shown in Fig. 4, the polymer:fullerene composition was 1 : 3 weight ratio and the active layer thickness was around 70–80 nm. The solar cells made with **P3** and **P4** were further optimised by additive processing³³ and post-deposition surface treatment³⁴ (see Fig. 5 and ESI†). The photovoltaic performances of the solar cell based on **P2** are rather poor compared to the other blends, see ESI† for details, due to the previously mentioned bad film forming properties of the composite layer, arising from the strong tendency of **P2** to aggregate. For this



Fig. 5 (a) EQE spectra and (b) J-V curves, recorded under 100 mWcm⁻² solar simulation, of solar cell devices based on **P3** and **P4** blended with PC₇₁BM, at 1 : 3 w/w ratio, deposited from CB (dotted lines) and deposited from 98% CB and 2% CN + post-deposition surface treatment with EtOH (continuous lines).

reason, herein we avoid to discuss the PV characteristics of **P2** based solar cells. For a better evaluation of the copolymers as active donor materials for solar cells, the copolymer series were also tested in BHJ with $PC_{61}BM$, see ESI.[†]

It can be seen from Table 2 that the PCE obtained with the devices made with **P1** reaches 1.88%. This feature is more encouraging when compared with reported studies on $PC_{71}BM$ blend devices using parent-like donor polymers, made with a thiophene co-unit alternating either to BT^{35} or to BTz.^{17b} When $PC_{61}BM$ is used, instead of $PC_{71}BM$, the PCE of **P1** lowers to 0.8%, see ESI.[†] Note that in a previously reported study on donor copolymers based on thiophenes alternating to BT and BTz, a PCE of 0.45% was reported in BHJs with $PC_{61}BM$.^{15b}

The copolymer P3, made with a BDT donor co-unit instead of thiophene, shows lower PV performances. Such behaviour can be explained by the low molecular weight of P3, not reaching the threshold necessary for the application of D–A copolymers in BHJ solar cells.³⁶ On the other hand, P4 exhibits much promising results, with PCEs up to 5%. When PC₆₁BM is used, instead of PC₇₁BM, the PCE of P4 solar cells reaches 2.9%, see ESI.[†] Note that the PV studies in the literature of parent-like D–A copolymers, where BDT alternates either to BT (with PC₆₁BM blends)^{16a} or to BTz (in PC₇₁BM),^{17c,d} are reporting significantly lower performances. These features bring support to the general validity of the double acceptor approach to design novel polymer materials for OPVs.

On the basis of the characterisations discussed in the previous paragraphs, it is possible to draw a correlation between the chemical tailoring imparted to these D–A copolymer series and their photovoltaic characteristics.

The EQE spectra, depicted in Fig. 4a, show that the spectral response of the devices has an improved coverage of the 600-700 nm region, when passing from P1 to P3 and then to the P4 active blends. This is leading to better solar light harvesting, so that, passing from P1 to P4 device, the EQE max decreases by about 25%, while the J_{sc}, calculated from the EQE and AM1.5 G spectra, decreases by about 17%. The increased solar light harvesting, passing from P1 to P4 devices, is reasonably related to the changes of the copolymers optical absorption characteristics. We have shown that the optical energy gap lowers from P1 to P3 and then to P4. As shown in the inset of Fig. 4, the active layers absorption spectra are indeed affected by the changes of the copolymers energy gap, showing a spectral coverage to solar radiation that increases consequently passing from P1 to P3 and P4 blends. Fig. 4a shows that the IPCE max value is higher for P1, lowering for P4, and then for P3 solar cells. This feature is unlikely ascribable to variations of the absorption cross-section since the OD max value of the active layers absorption spectra is respectively 0.35 for P1 and 0.42 for P3 and P4. Therefore the changes in the IPCEs correlate with the variations of the IQE. As discussed in the previous paragraph, the PL quenching has evidenced a decrease in the exciton dissociation yield from P1 to P4 and then to P3 blends. Moreover, the effectiveness of the charge generation process, as probed by PIA spectroscopy, has shown a similar variation. As a consequence, it is expected that the charge photogeneration yield, and thus the IPCE, should indeed follow the trend observed in Fig. 4a.

The high degree of intermixing between polymer P1 and $PC_{71}BM$ leads to the relatively high IPCE and J_{sc} found in the solar cells. Moreover, solar cells made with P1 have a low FF. In accordance with the literature, a highly intermixed blend morphology limits the FF parameter in BHJ solar cells.37 In principle, if the high degree of intermixing of P1 and PC71BM could be reduced by suitable processing, some improvement in the performances could eventually occur. However, this is not possible as the film forming properties of P1 based devices are relatively poor and the thermal annealing of P1:PC71BM blend, see ESI,[†] corresponds already to the best processing procedure to optimise the device. In P3 and P4 based active layers, phase segregation is enhanced compared to the P1 blends. As a result, an increase of the FF in P3 and P4 devices is indeed expected.^{10a} Moreover, we have previously assessed that the BDT copolymers have a better delocalisation of the polaron cations. A lower confinement of the photogenerated charges favours electronhole pair separation^{10b} and thus accounts for the higher FF parameters observed in solar cells made with BDT copolymers.

From the above features, it is evident that in **P3** and **P4** based solar cells, the use of BDT is positively affecting the spectral coverage to solar radiation and the FF. These advantages clearly relate to the previously discussed effects of the chemical tailoring on the optical energy gap, delocalisation of the charges and blend morphology. Note that the above correlation has a general validity, despite the non-optimal molecular weight (**P3**) and irrespective of the processing (see below).

Phase segregation in **P3-** and **P4-**based devices leads to relatively low IPCEs and J_{sc} . In the previous section, we have shown that, by using a CN additive, it is possible to reduce the phase segregation in **P3** and **P4** blends. Fig. 5 shows that the reduction of phase segregation is indeed improving effectively the IPCE and J_{sc} of **P3-** and **P4-**based devices, which exhibit almost a two-fold enhancement. Note that to reduce the contact barriers for the final optimisation, see Fig. 5 and Table 2, the devices have been treated with ethanol on the surface.³⁴ As shown and discussed in the ESI,† such treatment does not affect the blend morphology, and has minor effects on the PV performances.

3 Conclusions

This paper reports the design and synthesis of three novel D–A copolymers alternating two acceptors, benzothiadiazole and benzotriazole, to a donor co-unit, and we investigate their use in bulk heterojunction solar cells with $PC_{71}BM$. Some of the key properties for device operation of the polymers and active blends have been assessed, as monitored by optical, electrochemical and photo-physical characterisations, to rationalize the results and to draw a correlation between the chemical tailoring on this series of D–A copolymers and their PV characteristics.

The copolymer containing a thiophene co-unit has reached a power conversion efficiency of 1.88% in optimised devices. The use of BDT instead of thiophene leads to a number of advantages including solubility and blend morphology. Other advantages are also found, such as a lower optical energy gap and a lower confinement of the photo-generated charges. As a result, in the devices the spectral coverage to solar radiation and the FF parameter are positively affected. However, the regular alternation of BT and BTz to BDT co-units leads to a non-optimised copolymer, in terms of molecular weight, that limits the PCE to 1.48%. Passing from regular to random alternation of the acceptor co-units, the high molecular weight and good solubility lead to a significant improvement of the solar cell performances, with PCEs of 5%, higher than its parent-like copolymers with only one acceptor unit.

The above results demonstrate that it is possible to exploit the intrinsic chemical versatility of copolymers containing benzothiadiazole and benzotriazole acceptors to improve their photovoltaic performances.

Finally, the proposed design approach brings the development of novel copolymers with encouraging PCEs, high molecular weight, high solubility and easy preparation procedures which are important features towards industrial scale up.

4 Experimental

The experimental conditions, concerning the preparation and characterisation of the D–A copolymer series under study, are described in detail in the ESI.† The optimised OPV cells reported in Table 2 were assembled with the typical sandwich structure glass/ITO/PEDOT:PSS/active layer/cathode and characterised as described in the ESI.†

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