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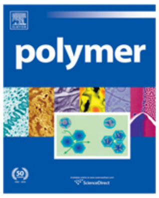

Synthesis of donor–acceptor poly(perylene diimide–altoligothiophene) copolymers as n-type materials for polymeric solar cells

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ABSTRACT

Donor–acceptor alternated copolymers based on perylene diimide units linked in bay positions with oligothiophene units were prepared and used as acceptor material in polymeric solar cells. The copolymers have exhibited ambipolar electrochemical properties, high electronic affinities and wide electronic absorption in the visible spectrum. The spectroscopical characterization of the copolymer blends with poly-3-hexylthiophene showed evidences indicative of a charge transfer from the perylene-based copolymers to the polythiophene. All-polymeric solar cells were prepared with the blends and the photovoltaic characterization of these devices showed conversion efficiencies of 0.8% and 0.4%. The results demonstrate the potentialities of perylene-based copolymers as processable photoactive acceptor in organic solar cells.

1. Introduction

Organic photovoltaic devices are promising candidates for the exploitation of solar energy in a cost-effective way and sustainable source of renewable energy. Intensive research in this field is stimulated by the inherent advantages of organic materials: high absorption coefficients, versatility by chemical tailoring to impart suitable electronic properties, ease of processing in large area as well as low manufacturing costs [1].

Photoelectric conversion in organic material solar cells is based on the photoinduced electron transfer process involving two species with different ionization potential and electron affinity. The active layer of these devices is a donor–acceptor bulk-heterojunction in which a donor compound is mixed with an acceptor organic species. In these photoactive composites the charge separation occurs at the donor–acceptor interface and the charge carriers are transported to the electrodes through the n-type and p-type conducting networks formed by the two phase-segregated species: the positive charge via the donor and the electrons via the acceptor domains.

Different types of organic materials have been used for the fabrication of donor–acceptor bulk-heterojunction active layers either molecules [2], combinations of molecules and conjugated polymers [3], conjugated polymers [4], or combinations of inorganic and organic materials [5]. Usually small molecules suitable for photovoltaics show limited solubility in common solvents and are mainly deposited in thin films by vacuum deposition techniques. In contrast the preparation of large polymeric thin film areas can be made by cheap techniques such as spin-coating, ink jet printing, screen printing or spray coating. The easy processability of the polymeric materials represents an important feature in the preparation of large-area, ultrathin, flexible, and low cost all-polymer-based photovoltaic devices [6].

Conjugated polymers, such as polythiophenes and polyphenylenevinylenes, are particularly suitable for photovoltaic applications as light absorber, electron donor and relative efficient hole-transporting materials. In recent years the development of polymer-based devices has made significant progress with a rapid increase in energy conversion efficiencies up to 6% [7].

Although various conjugated polymers have been explored as electron donor and hole transporter (p-type transport) in bulk-heterojunction, not so many polymers have been used as electron acceptor and transporter (n-type transport). The electron affinity and electron mobility of most conjugated polymers are low and this is the main obstacle for the preparation of polymeric electron acceptors. For this reason only a few publications have reported the preparation of all-polymeric photodiodes made of a p-type polymer and n-type polymer with good efficiencies [8]. Due to the increasing interest in organic transistors and photovoltaic devices, there is an urgent need for new molecules or polymers which show

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n-type transport properties. Although the relevance of such materials is continuously increasing, there are limited efforts toward the development of new synthesis for the preparation of n-type transporter.

The absorption properties are a determinative factor in the design and preparation of the materials used for converting the solar light into electric energy. Conjugated polymers have usually strong absorption in the visible spectral range, while fullerene molecules, the most used class of acceptors and n-type transporter, have quite limited absorption in the visible region. Thus, the replacement of fullerenes with n-type conjugated polymers as electron acceptors in organic solar cells will definitely improve the light absorption of the devices.

Perylene-3,4,9,10-perylene tetracarboxylic acid diimides (PDIs) are a well-known class of industrial dyes [9] and one of the most significant n-type organic semiconductors for organic optoelectronics. PDI molecules exhibit large absorption in the visible to near-infrared region, irradiate fluorescence with quantum yields near unity and in addition they are thermally, chemically and photochemically very stable. Perylene bisimide dyes were used as photoreceptors [10], in organic field effect transistors [11], in light-emitting diodes [12], and in photovoltaic devices with poly(3-hexylthiophene) P3HT [13]. PDI molecules were used in bulk-heterojunction solar cell as acceptor materials because of their electronic properties and their better harvesting of the solar light respect to fullerenes, but the PV devices made with these molecules have shown poor efficiencies. These low photovoltaic performances are mainly due to the difficult PDIs processability and to the poor morphology of the photo-active blends [13].

The interesting electronic properties and the stability of perylene diimide moiety along with its peculiar supramolecular architecture have rendered PDI one of the most promising molecular building blocks for the preparation of photo- and electro-active materials [14].

PDI photophysical and redox properties can be easily modified by introducing substituent groups in the diimide positions or in perylene core (bay positions), this demonstrating the chemical versatility of this dye molecule. In the literature a series of conjugated oligomers [15] and polymers containing perylene diimides have been synthesized in order to increase the solubility, the processability and to modulate the electronic properties and supramolecular architecture of perylene dyes.

Different approaches have been followed to design macromolecules containing perylene diimides' moieties. PDI derivatives have been covalently linked as side chains to both flexible polymers [16] and conjugated backbones [17], or have been incorporated in block copolymers [18] or alternated copolymers [19]. Recently an n-type copolymer made upon alternating PDI linked in bay positions with dithienothiophene moieties has been tested as acceptor component in bulk heterojunction solar cells in combination with a bi(thienylenevinylene)-substituted polythiophene as donor. Conversion efficiencies of up to 1.4% have been obtained with this system [20].

With the aim to obtain new stable photoactive materials with n-type transport properties and good processability, we have prepared two alternated copolymers containing a perylene diimide electron acceptor moiety substituted in bay positions with bithiophene or with terthiophene electron donor moieties. In this paper the molecular characterization and the optical and electronic properties of these materials are reported. These donor–acceptor copolymers have been used as acceptor materials in solar cells, in blend with P3HT, and the photovoltaic devices have shown relatively promising performance although the preparation process of the solar cell has not been optimized.

2. Experimental section

2.1. Materials

All thiophene and perylene reagents were purchased from Aldrich and used as received without further purification unless otherwise specified. The solvents were dried and distilled by the usual methods; all the reactions were run under nitrogen inert atmosphere.

2.2. Characterization

The molecular weight distribution was obtained by means of a size exclusion chromatography (SEC) multi-detector system from Waters, in THF solutions using a calibration curve and polystyrene standards.

^{1}H and ^{13}C NMR (11,7 T) spectra were recorded on 400 and 600 MHz Bruker spectrometers.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA 7 instrument under nitrogen atmosphere at a heating rate of 10 °C/min. TGA and derivate thermogravimetry (DTG) curves were recorded from 50 °C up to 650 °C.

Cyclic voltammetry measurements were performed under nitrogen atmosphere in a three electrode single-compartment cell using platinum electrodes and SCE as standard electrode with a tetrabutylammonium tetrafluoroborate solution (0.1 M) in acetonitrile for experiments in solid state, and in CH_2Cl_2 for solution.

Electronic absorption spectra were performed with a Perkin Elmer Lambda 9 spectrophotometer on chloroform solutions or spin-coated films on quartz (thickness 50 nm).

Photoluminescence (PL) spectra of polymeric solutions were recorded using 490 nm light excitation from a xenon lamp and a monochromator coupled to a N_2 cooled CCD detector.

The photo-induced absorption spectra have been measured in the MIR region with an FTIR spectrometer. The fractional changes in transmission have been measured in response to a 488 nm laser line incident on the sample, by the subsequent accumulation of scans with laser on and laser off; the temperature has been kept at 80 K.

2.3. Fabrication and characterization of solar cells

Solar cells were made with the conventional geometry glass/ITO/PEDOT-PSS/**P**x:P3HT/Al in a MBraum drybox. The active layers were spin-coated from chlorobenzene solution of **P**x:P3HT 1:1 weight ratio (16 mg/ml), with a thickness of 45–50 nm. A thermal treatment was performed at 150 °C, for 30 min, prior to the metal electrode deposition. The current density–voltage measurements were performed directly in the glove box where the cell was assembled and annealed, with a Keithley 2600 source meter, using a tungsten–halogen lamp equipped with a Schott filter KG1 and Balzer filter TL60, to simulate solar radiation. Light power (approx. 100 mW/cm^2) was measured using a calibrated InGaP solar cell as reference. EQE spectral responses were recorded by dispersing a Xe lamp through a monochromator, using a Si solar cell with known spectral response to measure the incident light power intensity at each wavelength. The devices were taken outside the glove box for the EQE measurements, after mounting them on a sealed cell to avoid moisture and oxygen exposure. The photocurrent J_{sc} under AM1.5G solar simulation has been calculated from the envelope of the EQE to the standard AM1.5G spectral radiance, after checking that this method, using our spectral radiance instead of the standard AM1.5G, was indeed providing quite similar values respect to the ones obtained under white light.

2.4. 5,5′-bis-(trimethylstannyl)-2,2′-bithiophene (**1a**)

5,5′-bis-(trimethylstannyl)-2,2′-bithiophene **1a** was obtained according to the literature procedure [21a–d]. To a dry 100 ml Schenk flask containing 2,2′-bithiophene (1 g, 6 mmol) and 25 ml of dry THF, a solution of *n*-butyl lithium in hexane (12 mmol) was dropwise added at −78 °C. The suspension was stirred at −78 °C for an additional 30 min. A solution of trimethyltin chloride in THF (13.3 mmol) was dropwise added. The precipitate reacted slowly and gave a pale yellow solution, which was then allowed to stir for 4 h at −78 °C, then warmed to room temperature and poured into water. The organic layer was separated and dried over $MgSO_4$. After removal of the solvent by evaporation, the residue was recrystallized several times from hexane to obtain 1450 mg (49% yield) of 5,5′-bis (trimethylstannyl)-2,2′-bithiophene as light yellow crystals. ^{1}H-NMR ($CDCl_3$): δ 0.37 (s, 18H), 7.09 (d, 2H), 7.27 (d, 2H). ^{13}C-NMR ($CDCl_3$): δ −8.2, 125.1, 136.3, 137.7, 143.3.

2.5. 5,5″-bis-(trimethylstannyl)-2,2′:5′,2″-terthiophene (**1b**)

5,5″-bis-(trimethylstannyl)-2,2′:5′,2″-terthiophene **1b** was obtained according to the literature procedure [22]. To a solution of 2,2′:5′,2″-terthiophene (250 mg, 1.008 mmol) and 6 ml of dry THF, a solution of *n*-butyl lithium in hexane (2.016 mmol) was dropwise added at −78 °C. The suspension was warmed up at 0 °C and stirred for 30 min and then cooled down to −78 °C. A solution of trimethyltin chloride in THF (2.1 mmol) was dropwise added. The precipitate reacted slowly and gave an orange solution, which was then allowed to stir for 1 h at −78 °C, then warmed to room temperature and stirred for another hour. The reaction mixture was quenched with water and extracted with hexane. The organic layer was separated and dried over $MgSO_4$. After removal of the solvent by evaporation, the residue was recrystallized several times from hexane to obtain 430 mg (74% yield) of 5,5″-bis-(trimethylstannyl)-2,2′:5′,2″-terthiophene as yellow crystals. ^{1}H-NMR ($CDCl_3$): δ 0.35 (s, 18H), 7.10 (d, 2H), 7.11 (d, 2H), 7.30 (d, 2H). ^{13}C-NMR ($CDCl_3$): δ −8.2, 124.0, 124.7, 127.8, 136.2, 136.7, 142.7.

2.6. N,N′-bis-(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide (**2**)

N,N′-bis-(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide **2** was obtained by a modified procedure from the literature [23]. The condensation reaction of 3,4,9,10-perylenetetracarboxylic dianhydride (606 mg, 1.55 mmol) and 10-nonadecanamine [24] (1.07 g, 3.78 mmol) was accomplished by conducting the imidazation reaction in the presence of zinc acetate (214 mg, 1.16 mmol) in quinoline (5 ml) at 160 °C for 4 h under nitrogen atmosphere. The resulting *N,N*′-bis-(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide was isolated in 78% yield as a deep red solid after column chromatography purification (hexane:$CHCl_3$ = 8:2 as eluent). ^{1}H-NMR ($CDCl_3$): δ 0.83 (t, 12H), 1.21 (m, 56H), 1.85 (m, 4H), 2.26 (m, 4H), 5.25 (m, 2H), 8.51 (br, 4H, pery-H), 8.59 (br, 4H, pery-H). IR (KBr, cm^{-1}): υ 2922, 2853, 1694, 1649, 1593, 1465, 1404, 1344, 1254, 1175.

2.7. 1,7-Dibromo-N,N′-bis(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide (**3**)

1,7-dibromo-*N,N*′-bis(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide **3** was obtained as described in literature [25]. A mixture of *N,N*′-bis(nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide **2** (100 mg, 0.108 mmol), bromine (1184 mg, 7.4 mmol) in 2 ml CH_2Cl_2 was stirred at 60 °C in a closed vial for 4 h. The reaction mixture was allowed to reach the room temperature and then, after removing the excess of bromine by air bubbling, the solvent was removed under vacuum. The crude product was purified by column chromatography, using hexane:$CHCl_3$ = 6:4 as eluent. The first band was collected to afford dibromo-*N,N*′-bis(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic diimide (as a mixture of 1,7-dibromo and 1,6-dibromo derivative 3:1) as a deep orange solid (108 mg, 92%). ^{1}H-NMR ($CDCl_3$): δ 0.85 (t, 12H), 1.25 (m, 56H), 1.85 (m, 4H), 2.25 (m, 4H), 5.20 (m, 2H), 8.70 (br, 2H, pery-H), 8.91 (br, 2H, pery-H), 9.52 (d, 2H, pery-H). IR (KBr, cm^{-1}): υ 2919, 2849, 1700, 1660, 1589, 1465, 1382, 1327, 1237.

2.8. Polymerization

A mixture of 1,7-dibromo-*N,N*′-bis(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic diimide **3** and distannylated oligothiophene **1a** or **1b** derivatives (1 equivalent) was dissolved in dry toluene (5 ml for 0.1 mmol of dibromo-*N,N*′-bis(nonadecyl)perylene-3,4,9,10-tetracarboxylic diimide). Catalytic amounts of Pd[PPh_3]$_4$ were added and the reaction mixture was stirred at 90 °C for 48 h. Shortly after the addition of the catalyst, the colour of the mixture starts to change from red to dark red. At the end of the reaction time, the black solution was cooled to room temperature and then washed with a solution of KI for 2 h in order to eliminate the tin impurity. The mixture was extracted with $CHCl_3$, washed with water and concentrated to a smaller volume and dropped into 30 ml methanol. The black precipitate was filtered, dried and extracted in Kumagawa apparatus with methanol and then with acetone.

Poly{[*N,N*′-bis-(10-nonadecyl)-perylene-3,4,9,10-tetracarboxylic diimide-1,7-diyl]-alt-(2,2′-bithiophene-5,5′-yl)} **P1** was obtained as a black solid in 80% yield using the general procedure. ^{1}H-NMR(TCE, 400 MHz): δ = 8.72 (br, 2H, pery), 8.38 (br, 4H, pery), 7.25 (br, 2H, thiophene-H), 7.30 (br, 2H, thiophene-H), 5.10 (br, 2H, −CH−N), 2.25 (br, 4H, $-CH_2-$), 1.85 (br, 4H, $-CH_2-$), 1.25 (br, 56H, $-CH_2-$), 0.85 (br, 12H, $-CH_3$). $M_w = 11{,}800$, $M_w/M_n = 1.70$. UV/VIS ($CHCl_3$): $\lambda_{max}(\varepsilon \times 10^{-4})$ 605 (2.99), 472 (3.50), 357 (5.83).

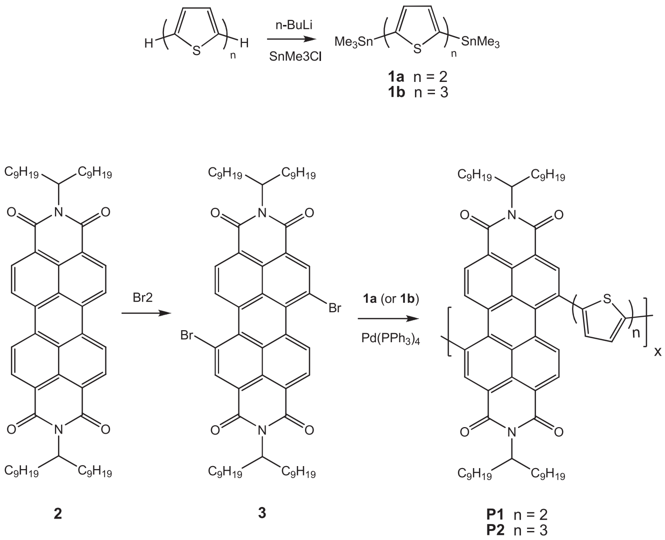
Poly{[*N,N*′-bis-(10-nonadecyl)-perylene-3,4,9,10-tetracarboxylic diimide-1,7-diyl]-alt-(2,2′:5′,2″-terthiophene-5,5′-yl)} **P2** was obtained as a black solid in 83% yield using the general procedure. ^{1}H-NMR(TCE, 400 MHz): δ = 8.55 (br, 2H, pery), 8.25 (br, 4H, pery), 7.20 (br, 2H, thiophene-H), 7.10 (br, 4H, thiophene-H), 5.05 (br, 2H, −CH−N), 2.10 (br, 4H, $-CH_2-$), 1.75 (br, 4H, $-CH_2-$), 1.20 (br, 56H, $-CH_2-$), 0.75 (br, 12H, $-CH_3$). $M_w = 11{,}400$, $M_w/M_n = 1.67$. UV/VIS ($CHCl_3$): $\lambda_{max}(\varepsilon \times 10^{-4})$ 625 (2.94), 495 (4.50), 394 (8.79).

3. Results and discussion

3.1. Synthesis and characterization

The n-type organic semiconductor for optoelectronic application posses higher electron affinity or low LUMO orbital energy level, associated with a good electron mobility in the solid state. An efficient sunlight-harvesting and a good processibility are also very important to use these materials in photovoltaic devices. Perylene diimide (PDI) dye is one of the most promising molecular building block for the preparation of acceptor material with n-type charge transport properties, but the application in organic solar cell is limited by the moderate processability.

One approach to design conjugated polymers with electron acceptor and n-type transport properties is to link a donor monomer with an acceptor unit, which permits to control the HOMO and LUMO levels and therefore, to tune the energy band gaps. Perylene diimide based donor–acceptor molecules have been synthesized by substitution of the perylene core in bay positions with oligothiophene moieties [26] and a polymer was prepared with dithienothiophene group [14,20]. These conjugated systems show interesting



Scheme 1. Synthetic route for monomers and copolymers **P1** and **P2.**

Table 1
Redox potentials of unsubstituted perylene **2**, bithiophene, terthiophene, **P1** and **P2** in the solid state[a].

Sample	E_{ox}[b]	E_{red1}[b]			E_{red2}[b]
	E_p (V)	E_0 (V)	$E_{1/2}$ (V)	E_p (V)	E_p (V)
2	–	−0.56	−0.72	−0.91	–
Bithiophene	0.88	–	–	–	–
Terthiophene	1.18	–	–	–	–
P1	1.70	−0.50	−0.63	−0.72	−0.94
P2	1.62	−0.40	−0.56	−0.78	−0.92

[a] Film on Pt in ACN/Bu_4NBF_4 [0.1 M] versus SCE reference electrode.
[b] E_p peak potentials; E_0 onset potentials; $E_{1/2}$ half-wave potentials.

ambipolar electrochemical properties, high electronic affinities when compared with the most common conjugated polymers, wide electronic absorption in the visible spectrum, and they can be processed easily from solution.

We have synthesized two new alternated donor–acceptor copolymers, **P1** and **P2,** containing in the main chain a perylene diimide unit linked in bay position with bithiophene or terthiophene units. These copolymers have been obtained via Stille reaction between *N*,*N*′-bis(10-nonadecyl)-1,7-dibromo-3,4,9,10-perylene diimide and 5,5′-bis-(trimethylstannyl)-2,2′-bithiophene or 5,5″-bis-(trimethylstannyl)-2,2′:5′,2″-terthiophene (see Scheme 1). Both donor–acceptor copolymers are highly soluble and processable in chloroform, chlorobenzene and THF.

The molecular weight, M_w, and polydispersity, *D*, of the polymers were determined by Size Exclusion Chromatography in THF against polystyrene standards. **P1** shows $M_w = 11{,}800$ g/mol and $D = 1.70$ while **P2** has $M_w = 11{,}400$ g/mol and $D = 1.67$, corresponding to ca. 10 repeating units composed by one perylene and one oligothiophene moiety. ^{1}H NMR spectra recorded on a 400 MHz spectrometer in tetrachloroethane have confirmed the chemical structures of the donor–acceptor copolymers.

The thermal stability of the perylene diimide-based copolymers was determined by TGA considering the onset of thermal decomposition, i.e. the temperature corresponding to initial 5% of weight loss. TGA traces reported in Fig. 1 show that both copolymers are thermally stable in inert atmosphere up to ca. 390 °C.

The cyclic voltammetry experiments on **P1** and **P2** carried out in solution and in the solid state show two reduction processes in the negative potential range and one oxidation process in the positive potential range. In Table 1 are reported the redox potentials of the copolymers and for comparison those of perylene **2**, bithiophene and terthiophene. All **P1** and **P2** electrochemical processes are reversible evidencing the ambipolar properties of the two donor–acceptor copolymers. The two cathodic reductions probably correspond to the formation of the mono- and dianion species on the perylene moieties and the anodic oxidation corresponds to the radical cation on the thiophene moieties.

The UV-VIS spectra of the two copolymers in the solid state, depicted in Fig. 2, show a considerable widening of the spectral absorption region with respect to the unsubstituted perylene diimide compounds **2**. For photovoltaic purposes, these spectroscopic modifications represent a considerable improvement for the

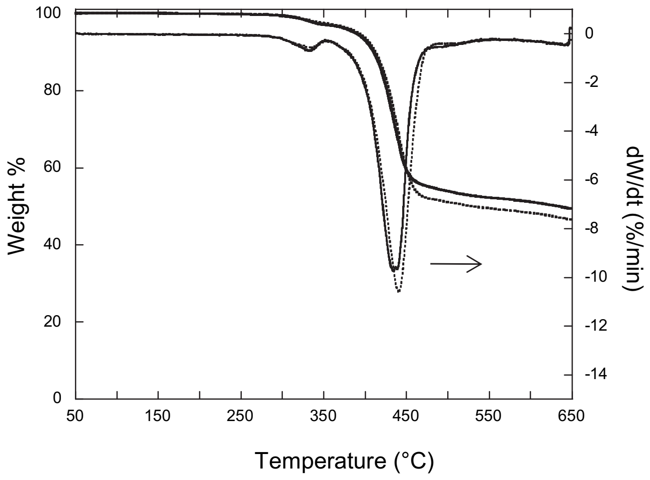


Fig. 1. TGA and DTG curves under nitrogen flow of **P1** (dashed line) and **P2** (solid line).

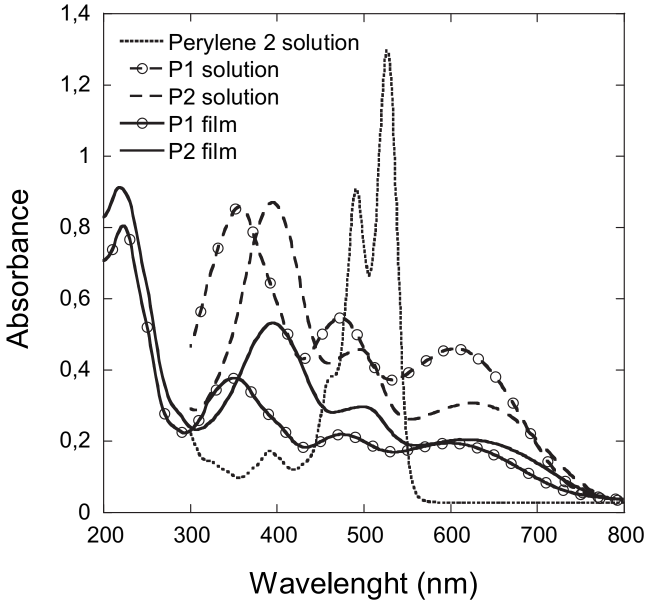


Fig. 2. Electronic absorption spectra of unsubstituted perylene **2** (dotted line), of copolymer **P1** in chloroform (circle dashed line) and in the solid state (circle full line), and **P2** in solution (dashed line) and in the solid state (full line).

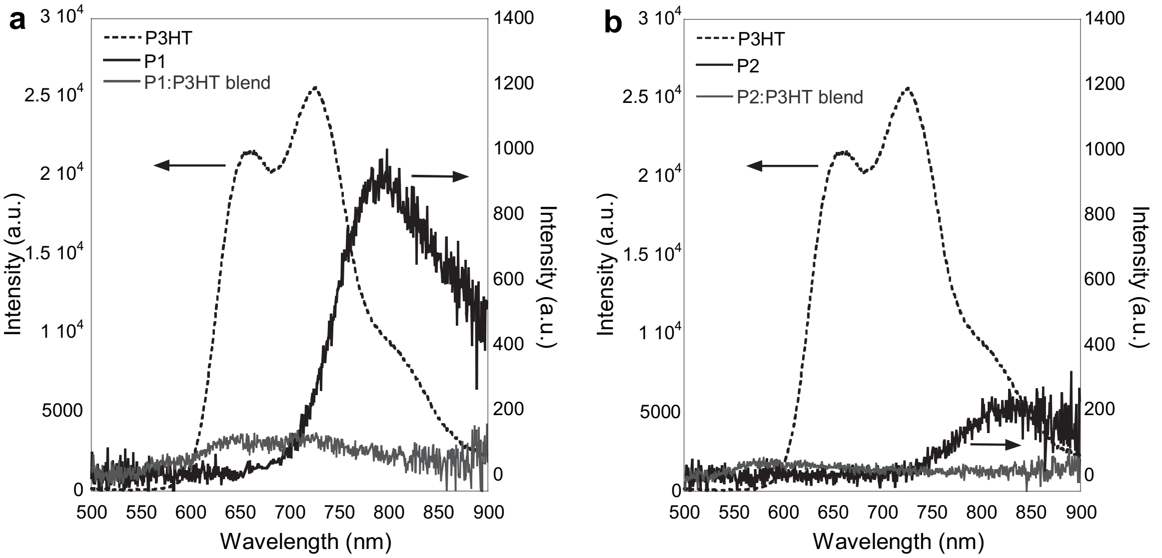


Fig. 3. Photoluminescence spectra of: (a) P3HT (dotted line), **P1** (dark line), **P1**:P3HT blend (grey line) films; (b) P3HT (dotted line), **P2** (dark line), **P2**:P3HT blend (grey line) films. The spectra are normalized to the number of absorbed photons at the incident excitation wavelength (490 nm).

material characteristics, since the solar harvesting plays a significant role in the light energy conversion.

The donor–acceptor copolymer films show four broad absorption bands at 600 nm, 475 nm, 350 nm and 220 nm for **P1**, and 620 nm, 502 nm, 395 nm and 220 nm for **P2**. The two bands at lower energy in each spectrum can be assigned to perylene chromophore system as S_0–S_1 transition polarized along the long molecular axis, and to S_0–S_2 transition with a dipole moment perpendicular to long molecular axis; while the two higher energy bands are related to the π–π^* transitions of the thiophene rings and to the conjugated system. For both the copolymers the band absorption form and the maxima are similar in the solid state and in solution with solvents having different polarity. From the electronic absorption onset at lower energy is possible to derive an energy gap of 1.65 eV for **P1** and 1.60 eV for **P2**.

HOMO and LUMO energy level of the two donor–acceptor copolymers can be calculated from the electrochemical properties and the electronic absorption [27]. LUMO level is obtained from the onset of the first reduction potential during cyclic voltammetry measurements, and HOMO level is obtained from LUMO energy and the optical band gap. The copolymers show the following HOMO and LUMO energy levels: −5.89 eV and −4.23 eV for **P1** and −5.94 eV and −4.34 eV for **P2**. HOMO orbital energy levels of the copolymers are lower than P3HT one and their electronic affinity is higher, thus from the electronic point of view **P1** and **P2** can be used as electron acceptor respect to P3HT.

In order to investigate the potentialities of the two perylene-based copolymers as photoactive acceptor materials we have prepared blends in 1:1 weight ratio with P3HT as a donor.

In order to investigate the potentialities of the two perylene-based copolymers as photoactive acceptor materials we have prepared blends in 1:1 weight ratio with P3HT as a donor.

Both blends of **P1** and **P2** with P3HT show a quenching of the photoluminescence in the solid state compared with the pure polymeric components (see Fig. 3). This PL quenching suggests that photoinduced charge transfer is occurring between the polymeric components and that the charge transfer is fast enough to compete with the radiative recombination of the excitons.

Photoinduced absorption spectroscopy has been used to probe the capability of the perylene-based copolymers to act as acceptor with respect to P3HT. Fig. 4 shows the FTIR PA spectra of **P2**:P3HT 1:1 blend film and of a pristine P3HT film. It can be seen that the blend has the same spectral pattern as P3HT, displaying the signatures of charged polaron cation formation into the P3HT component. The blend spectrum has however a signal which is more intense compared to the spectrum of P3HT.

This feature can be ascribed to an increased number of long-lived cations into P3HT, arising from photoinduced charge transfer between the blend components. Since both components are absorbing light in the visible, this process can be either an electron transfer from P3HT to **P2** or a hole transfer from **P2** to P3HT. Pristine **P2,** unlike P3HT, has no detectable FTIR PA spectrum because the π-electrons are confined within the donor and acceptor moieties at a molecular level. This is reducing drastically the oscillator strength

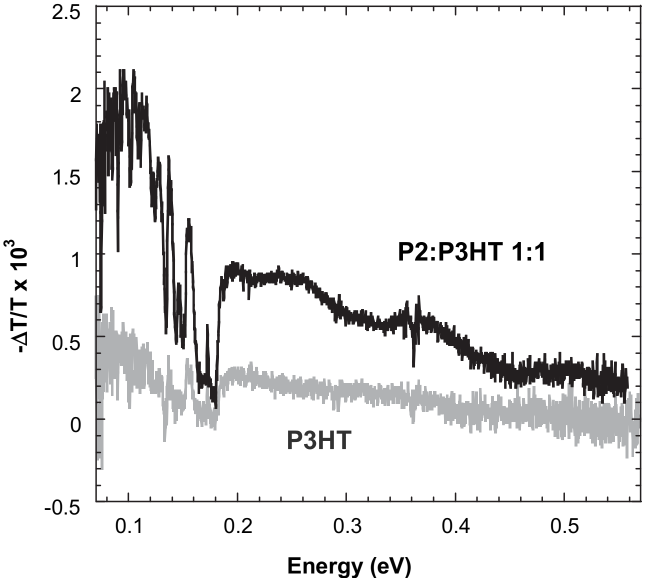


Fig. 4. FTIR photoinduced absorption spectra of **P2**:P3HT 1:1 blend (black) and P3HT (grey); exc. wavelength: 488 nm, 10 mW/cm^2; temperature: 80 K.

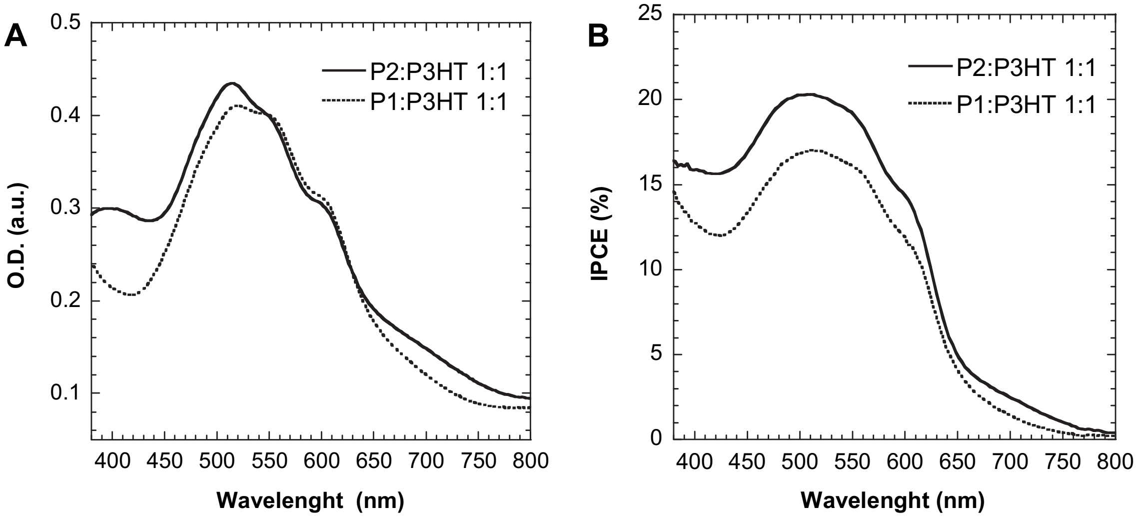


Fig. 5. (A) UV-VIS absorption spectra of blend films 1:1 w/w **P1**:P3HT (dotted line) and **P2**:P3HT (full line); (B) External Quantum Efficiency spectra of **P1**:P3HT (dotted line) and **P2**:P3HT (full line) solar cells after thermal treatment at 150 °C for 30 min.

of the PA bands respect to P3HT and the FTIR PA spectrum is not detectable. For similar reasons, the infrared bands associated to **P2** anions are not detected in the PA spectrum.

3.2. Photovoltaic cells

The copolymers have been tested as active components, in combination with P3HT, in bulk heterojunction solar cells. Photovoltaic devices were assembled with the geometry ITO/PEDOT/**P1** (or **P2**):P3HT/Al and with 1:1 w/w active layers composition. The devices have been thermally treated prior the aluminum electrode deposition.

The UV-VIS absorption spectra of 1:1 (w/w) blend films of **P1**:P3HT and **P2**:P3HT are reported in Fig. 5 along with the External Quantum Efficiency spectral responses. The EQE spectra exhibit Incident Photon to Current Efficiency (IPCE) reaching values around 16% for **P1** device and 20% for **P2** solar cell, that evidence a fairly good charge photogeneration in the blends. The EQE spectra of both the solar cells are slightly broadened but display also a good match to the UV-VIS absorption spectra of the active blends. Therefore the copolymer acceptor components act as sensitizers and as antenna in the photovoltaic devices.

The photovoltaic parameters under 1 sun solar simulation are reported in Table 2 and the I/V curves of the two solar cells are shown in Fig. 6.

The photovoltaic characteristics obtained for **P1**:P3HT and **P2**:P3HT solar cell are quite encouraging, considering these were the first assembled devices. The complete study concerning the solar cell assembling, the blend component ratio and the thermal annealing is at present in progress. The characterization here reported shows that the PCE of photovoltaic devices based on **P1** is lower than that of **P2**. The *J*–*V* curves and the photovoltaic parameters suggest a higher series resistance for the devices based on **P1**, which could be a consequence of either lower charge transport properties of the active layer or a higher contact resistance. We have observed that the behavior of the blends, upon spin-coating deposition, is different: the films made of **P1**:P3HT are less homogeneous and show the tendency to form macroscopic aggregations. Therefore, these aggregates are likely deteriorating the contact to the evaporated Al cathode, leading to high series resistance that reduces the PCE of **P1**:P3HT devices. We cannot exclude that a different optimization of the solar cell assembly may lead to similar photovoltaic performances for the devices based on **P1** and **P2**. Nevertheless this first characterization suggests that **P2** is probably more promising, respect to **P1**, when used in polymeric solar cells with P3HT, because of the better compatibility of the two components in a blend, likely due to the longer thienylene moieties of **P2**.

Table 2
PV parameters of ITO/PEDOT/**P1**(or **P2**):P3HT/Al bulk heterojunction solar cells for 1 sun AM1.5G standard solar radiation.

Device	V_{oc} (V)	FF	J_{sc} (mA/cm^2)	PCE (%)
P1:P3HT	0.54	0.32	2.33	0.40
P2:P3HT	0.56	0.51	2.81	0.80

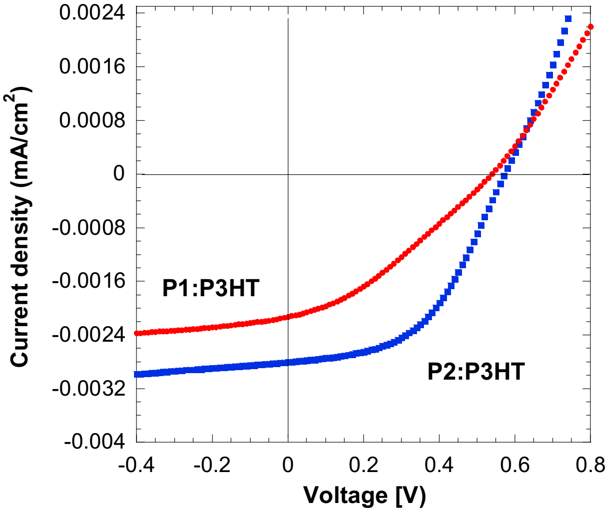


Fig. 6. *J*–*V* characteristics of 1:1 w/w devices under white light illumination: **P1**:P3HT (red circles) and **P2**:P3HT (blue squares). (For interpretation of colour in this figure, the reader is referred to the web version of this article.)

4. Conclusion

We have described the preparation of two donor–acceptor alternated copolymer containing perylene bisimide and oligothiophenes in the backbone. These copolymers are processable and show electrochemical ambipolar properties and a wide electronic absorption in the visible spectral range. The electronic properties of the copolymers, derived from the electrochemical and optical characterizations, show that they can be used as electron acceptor in bulk heterojunction solar cell with P3HT as donor material. The charge photogeneration in the blends is due to photo-induced charge transfer from polythiophene backbone to the perylene-based copolymers and from the perylene-based copolymers to P3HT. We have prepared all-polymer photovoltaic devices with **P1** and **P2**, these not yet optimized solar cells have PCE % of 0.4 and 0.8 respectively. Future optimization of the blend composition and processing, and of the post-assembling thermal treatment will improve the performance of these polymeric devices.

Due to the reasonable photovoltaic properties, this chemical strategy will be applied for the preparation of other donor–acceptor systems, with different donor components. Thus, the chemical tailoring of perylene core in bay positions opens the possibility to obtain via an easy synthesis a wide class of molecular and polymeric materials having n-type transport properties, high light absorptions and good processability available for the preparation of organic photovoltaic devices.

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