Solar cells based on poly(3-alkyl)thiophenes and [60]fullerene: a comparative study

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Photovoltaic cells made, at ambient conditions, from blends of regioregular poly(3-alkylthiophenes) and soluble fullerene derivatives are compared. It is shown that the cell performance is affected by the length of the donor side-chain, as it occurs in devices based on pure polythiophenes. The highest value of power conversion efficiency (0.84%) were obtained by using poly(3-hexylthiophene) and a fullerene concentration of 33–40% by weight. We anticipate a significant further improvement in power conversion efficiency upon a mild thermal treatment of the cells.

Introduction

Interpenetrating blends of conjugated polymers and functionalised fullerenes have emerged as promising materials for photovoltaic devices.[1] Upon photoexcitation, an ultrafast electron transfer[2] takes place from the polymer (the electron-donor component, D) to the fullerene (the electron-acceptor, A).[3] The process is reversible, metastable with a quantum yield close to 100%. In particular, mixtures of conjugated polymers and soluble functionalised fullerene derivatives have been employed for the preparation of high-performance plastic solar cells that, recently, reached power conversion efficiencies up to 2.5% under AM1.5 solar irradiation.[4] Systematic optimisation of the characteristics of the D\A couple and of the devices architecture were carried out by several groups.[5]

In this article the performance of D/A solar cells based on blends of three regioregular poly(3-alkylthiophenes) (PATs) and soluble fullerene derivatives are compared. While the film-forming characteristics and properties of other conjugated polymers, such as poly(p-phenylenevinylene) derivatives, with the fullerenes have been thoroughly investigated, devices based on PATs and fullerene have not been studied as extensively. It is therefore interesting to extend the studies to this class of conjugated polymers and to highlight possible structural implications with respect to their photovoltaic behaviour in composite films with functionalised fullerenes.

The three soluble fullerene derivatives 1–3 (Scheme 1) were used as acceptors, and regioregular poly(3-butylthiophene) (PBT), poly(3-hexylthiophene) (PHT) and poly(3-octylthiophene) (POT) as donors. Fullerene derivatives 1–3 have been selected for their good solubility in common organic solvents. This is, among others, a fundamental requisite of the fullerene component for an homogenous mixing with the polymer phase. Regioregular PATs have been used in this investigation because of the their high hole mobility. In the case of regioregular poly(3-hexylthiophene), field-effect mobilities of up to 0.1 cm^2 V^{-1} s^{-1} have been reported.[6,7] Very sensitive photosensors based on thin film D/A composites, in which regioregular PHT has been used as a donor, have been demonstrated, as well as the feasibility of large-area image sensing photodiodes.[8]

Scheme 1

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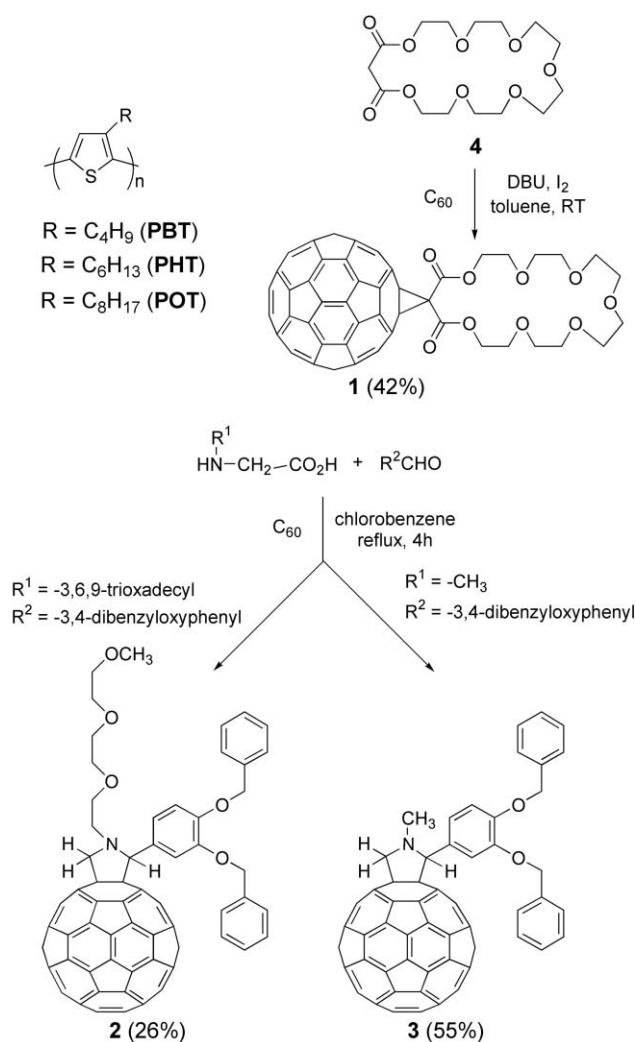
Experimental

General

Details regarding the instrumentation used in this work to characterise compounds **1–3** and the polythiophenes PBT, PHT and POT have been reported elsewhere.[9] Absorption spectra were recorded with Perkin–Elmer $\lambda 6$ and $\lambda 9$ spectrophotometers. The molecular weights of PBT, PHT and POT were determined by gel permeation analysis (GPC) relative to polystyrene standards. The measurements were carried out by using a SEC System Waters GPCV 2000 apparatus equipped with a differential-refractometer 410 on-line detector and Waters Styragel columns at room temperature using THF as eluent.

Photodiodes were prepared by spin-coating (2000–3000 rpm) the fullerene–polymer blends from chloroform onto the top of PEDOT-PSS/ITO/glass electrodes (PEDOT = poly(ethylenedioxythiophene); PSS = polystyrene sulfonic acid), and coating these layers with a semi-transparent Al electrode (about 10 nm) by thermal evaporation. For each Al deposition, a glass plate was positioned next to the device. This Al-covered plate was used as a reference in order to make the proper correction for the Al layer absorption. The fullerene–polymer film thickness, measured with a Tencor Alphastep 200 profilometer, was around 100 nm.[10] The active area of the devices was 3.14 mm^2. Device fabrication was performed, apart from the cathode deposition, at ambient conditions. The electrical characterisation of the devices was performed with a Keithley 2400 source-measure-unit in a home-made measurement chamber under a pressure of 10^{-3} Torr and at ambient temperature. The frame of the chamber did not allow the illumination from the ITO electrode side. Therefore the junctions were illuminated through the Al side with a 300 W Xe arc lamp. The light intensity was adjusted by using neutral density filters. The optical bench was equipped with a water filter to cut off IR radiation. The intensity of the incident light was measured with an Oriel thermopile and corrected for the Al layer absorption, as previously described, at the maximum visible absorption wavelength of the active layer. No correction was made for light reflection. A Pt100 thermoresistor was used for the measurement of the temperature of the cells.

Materials

[60]Fullerene (99.5%) was purchased from Bucky-USA, Houston, USA. PEDOT : PSS was purchased from Bayer AG, Germany. All other reagents were purchased from Aldrich Chemical Co. and used without further purification. All solvents used for UV-Vis measurements and cells active layer depositions were spectrophotometric-grade solvents. 1,4,7,10,13,16,19-Heptaoxacyclodocosane-20,22-dione **4**[11] and N-(3,6,9-trioxadecyl)glycine[12] used for the preparation of methanofullerene **1** and fulleropyrrolidine **2** respectively, were synthesised as described in the literature.

Methanofullerene (1)

Azabicyclo[5.4.0]undec-7-ene (76 mg, 0.5 mmol) in 5 mL toluene was added to a solution of **4** (70 mg, 0.2 mmol), [60]fullerene (145 mg, 0.2 mmol) and I$_2$ (50 mg, 0.2 mmol) in 130 mL of toluene and the mixture was stirred for 12 h under a nitrogen atmosphere. The reaction mixture was loaded on top of a short SiO$_2$ flash chromatography column and eluted with toluene to remove unreacted [60]fullerene. Further elution with toluene–propan-2-ol 9 : 1 afforded 90 mg (42%) of methanofullerene **1**. IR (KBr) 2869, 1743, 1429, 1135 cm^{-1}. UV-Vis (CH$_2$Cl$_2$) λ (nm) ε (cm^{-1} M^{-1}): 257 (111054), 326 (32390), 426 (4218). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 3.5 (m, 16H), 3.75 (m, 4H), 4.48 (m, 4H). ^{13}C NMR (100.62 MHz, CDCl$_3$): δ (ppm) 163.42, 145.15, 145.06,

145.04, 144.78, 144.57, 144.54, 144.51, 143.77, 142.96, 142.90, 142.87, 142.09, 141.79, 140.83, 139.01, 71.34, 70.80, 70.77, 70.72, 70.67, 68.65, 66.54. ESI-MS (C$_{75}$H$_{24}$O$_9$ (M_W = 1068)) m/z 1091 [M + Na]$^+$, 1107 [M + K]$^+$.

N-(3,6,9-Trioxadecyl)-2-[(3',4'-dibenzyloxy)phenyl]fulleropyrrolidine (2)

A solution of [60]fullerene (500 mg, 0.69 mmol), 3,4-dibenzyloxyphenylbenzaldehyde (144 mg, 0.45 mmol) and N-(3,6,9-trioxadecyl)glycine (80 mg, 0.36 mmol) in 250 ml of chlorobenzene was stirred at reflux temperature for 4 h then the solvent was removed *in vacuo*. The solid residue was purified by SiO$_2$ flash-column chromatography (eluent toluene–ethyl acetate 9 : 1, R_f = 0.47) affording 113 mg (26%) of fulleropyrrolidine **2**. IR (KBr) v (cm^{-1}): 3430, 2868, 1511, 1429, 1267, 1133, 1025, 734, 696. UV-Vis (CH$_2$Cl$_2$) λ (nm) ε (cm^{-1}M^{-1}): 255 (99079), 308 (34138), 431 (3656), 706 (142). ^{1}H NMR (250 MHz, CD$_2$Cl$_2$/CS$_2$) δ (ppm): 2.78 (m, 2H), 3.31 (s, 3H), 3.52–3.48 (m, 2H), 3.67–3.63 (m, 2H), 3.73 (s, 2H), 3.92–3.81 (m, 2H), 4.22 (d, J = 9.8 Hz, 1H), 5.00 (s, 1H), 5.07 (s, 2H), 5.09 (s, 2H), 5.15 (d, J = 9.8 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 7.42–7.22 (m, 11H). ^{13}C NMR (62.9 MHz, CDCl$_3$/CS$_2$) δ (ppm): 52.12, 58.81, 67.57, 68.97, 70.62, 70.75, 71.06, 71.31, 71.99, 76.23, 77.20, 81.88, 114.64, 115.86, 122.62, 127.11, 127.18, 127.71, 128.33, 128.37, 130.21, 136.46, 136.93, 137.11, 139.75, 139.94, 140.03, 141.50, 141.96, 142.46, 142.56, 142.86, 143.00, 144.25, 144.59, 145.10, 145.38, 145.80, 146.07, 147.15, 148.93, 153.43, 153.56, 154.15, 156.37. MALDI MS (C$_{89}$H$_{35}$NO$_5$ (M_W = 1197)) m/z 1198 [M + H]$^+$.

N-Methyl-2-[(3',4'-dibenzyloxy)phenyl]fulleropyrrolidine (3)

A solution of [60]fullerene (500 mg, 0.69 mmol), 3,4-dibenzyloxyphenylbenzaldehyde (110 mg, 0.34 mmol) and N-methylglycine (93 mg, 1.0 mmol) in 250 ml of chlorobenzene was stirred at reflux temperature for 4 h then the solvent was removed *in vacuo*. The solid residue was purified by SiO$_2$ flash-column chromatography (eluent toluene, R_f = 0.4) affording 200 mg (55%) of fulleropyrrolidine **3**. IR (KBr) 3430, 2776, 1507, 1427, 1265, 1126, 1021, 731, 693. UV-Vis (CH$_2$Cl$_2$) λ (nm) ε (cm^{-1} M^{-1}): 255 (99079), 308 (34138), 431 (3656), 706 (142). ^{1}H NMR (250 MHz, CDCl$_3$/CS$_2$) δ (ppm): 2.75 (s, 3H), 4.23 (d, J = 9.3 Hz, 1H), 4.81 (s, 1H), 4.93 (d, J = 9.3 Hz, 1H), 5.02–5.20 (m, 4H), 6.90 (m, 1H), 7.03–7.51 (m, 12H). ^{13}C NMR (62.9 MHz, CDCl$_3$/CS$_2$) δ (ppm): 39.69, 68.56, 69.70, 70.76, 70.96, 82.83, 122.26, 127.01, 127.04, 127.60, 128.04, 128.22, 128.25, 129.74, 135.48, 136.19, 136.76, 136.82, 139.36, 139.94, 141.30, 141.66, 141.77, 141.83, 141.86, 141.98, 142.31, 142.34, 142.41, 142.87, 144.10, 144.38, 144.89, 144.97, 144.99, 145.21, 145.24, 145.31, 145.45, 145.65, 145.84, 145.88, 145.96, 146.97, 148.76, 153.24, 153.66, 155.87. MALDI MS (C$_{83}$H$_{23}$NO$_2$ (M_W = 1065)) m/z 1065 [M]$^+$.

Molecular weight determination of PBT, PHT and POT

The molecular weights of the polythiophenes used in this work were found to be M_n = 12500, M_w = 18000 (PBT); M_n = 18000, M_w = 29500 (PHT) and M_n = 18100, M_w = 33400 (POT). Polydispersity index was 1.44 (PBT), 1.64 (PHT) and 1.85 (POT).

Results and discussion

The functional molecules used in the preparation of the solar cells employed in this study are shown in Scheme 1.

The regioregular PATs (PBT, PHT and POT) were prepared following the procedure reported by McCullough and co-workers.[13] Proton and carbon NMR data were identical to those reported in the literature. The molecular weights of PBT, PHT and POT and their respective polydispersity index (see

Experimental Section) are in the range of those reported by McCullough and coworkers[14] and Rieke and coworkers.[15] Derivative **1** is a methanofullerene that was prepared in 42% isolated yield through a standard cyclopropanation reaction[16] to [60]fullerene using the iodomalonate derivative of **4** that formed *in situ* upon treatment of **4** with iodine and the base azabicyclo[5.4.0]undec-7-ene. Derivatives **2**[17] and **3** are fulleropyrrolidines that were synthesised in 26 and 55% isolated yields *via* the dipolar cycloaddition to [60]fullerene of the azomethine ylide[18] that formed when 3,4-dibenzyloxyphenyl-benzaldehyde was treated with *N*-(3,6,9-trioxadecyl)glycine[12] or *N*-methylglycine respectively in refluxing chlorobenzene. All analytical and spectroscopic data were consistent with the structures illustrated in Scheme 1.

It is interesting to note that fulleropyrrolidine **3**, lacking the oxyethylene solubilizing chain, gives slightly better devices than **1** and **2**. Although the difference is not substantial, it indicates that a solubility enhancement of the fullerene partner could not be necessary if a reasonably soluble fullerene derivative is employed. On the other hand, one would expect that a highly functionalised fullerene derivative may disturb the polythiophene main chain conformation, thus altering the conditions for efficient charge transport. It is worth mentioning that under an optical microscope the films appeared dense and smooth without aggregates, macroscopic domains or pinholes, irrespective of the nature of the fullerene derivative or polymer.

The absorption spectra of PBT, PHT and POT are reported in Fig. 1.

The absorption maxima shift to lower energy by increasing the side-chain length. This indicates an increasing of the extent of conjugation for longer substituents, likely due to a more planar backbone conformation. Contrary to the spectrum of PBT, that of PHT and POT show two typical absorption bands at about 550 and 600 nm that could be associated with long-range ordered structures.[15,19]

For this comparative study, devices made from a single polymer component were first fabricated. Studies on the comparison of the photoelectrical performance of cells based on regio-random PATs, with different length of the alkyl substituent, have already been reported.[20,21] In those investigations, it was shown that the junction performance increased by shortening the alkyl side-chain. In particular, the photovoltaic efficiency of cells based on regio-random PBT films was found to be higher than that of cells realised with PHT or other regio-random PATs with a longer alkyl group. It was proposed to be due to a decreased interchain hopping mobility with side-chain lengthening, because of the increased interlayer spacing.[22] In the present case one would also expect the polymer with the
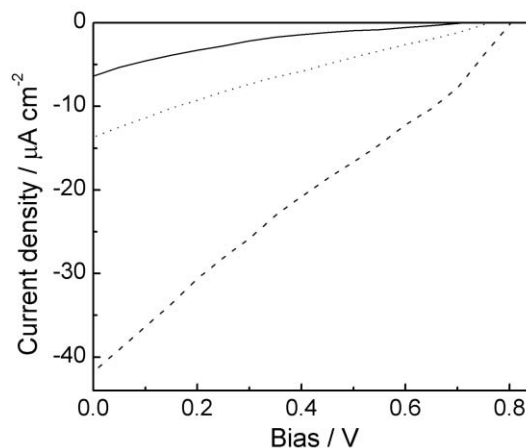
Fig. 2 Current density–voltage characteristics (fourth-quadrant only) of cells based on regioregular PBT (dotted line), PHT (dashed line) and POT (full line). White-light irradiation power: *ca.* 20 mW cm^{-2}. Ambient temperature. The values of the photovoltaic parameters are listed in Table 1.

shortest alkyl chain to display the best photoelectric performance. Contrary to this assumption, the highest values for all photovoltaic parameters were recorded for PHT-based cells. The current–voltage characteristics of the devices made from the three considered PATs, under white-light illumination, are presented in Fig. 2.

The reason for the better performance of PHT relative to PBT could be related to the different optical features shown in their respective absorption spectra. The maximum absorption wavelength of PHT is red-shifted by 27 nm if compared to that of PBT. Additionally, no fine structure is visible in the spectrum of PBT. It could be argued that both the mean conjugation length and the extent of the long-range order are very different in the two cases, leading to the better performance of PHT based cells. Furthermore, a decreased solubility of PBT could be expected, because of the shorter side-chain, leading to reduced film forming properties. The overall photovoltaic performance of this type of devices (Table 1) was, as expected, very poor.

The fullerene acceptors **1**–**3** were compared by realising D/A cells with PHT as donor and with a 1 : 1 PHT–fullerene weight ratio. No substantial differences were observed in the device photovoltaic performance (Fig. 3).

Cells based on **3** were characterised by the highest values of the open-circuit voltage (V_{oc}), fill factor (*FF*) and conversion efficiency (η), although higher short-circuit current densities (j_{sc}) were observed in the other two cases (Table 1). Recently, a study on the origin of the V_{oc} of conjugated polymer–fullerene bulk heterojunctions has been reported.[23] In that investigation, cells based on different soluble fullerene derivatives and a common polymer (a poly(*p*-phenylenevinylene) derivative) were considered. Furthermore, different metals were used for the cathode electrode. A direct correlation of the V_{oc} of the cells
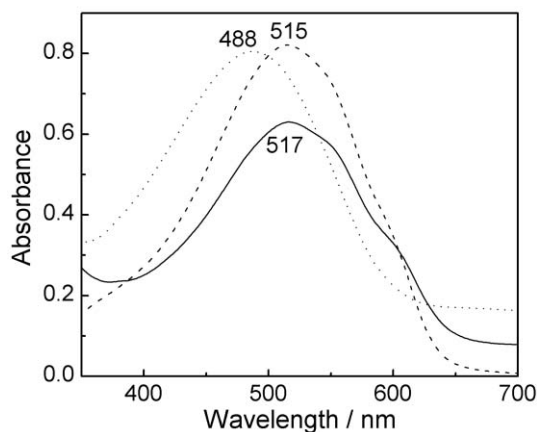

Fig. 1 Absorption spectra of regioregular PBT (dotted line), PHT (dashed line) and POT (full line) spin-cast films from chloroform. Film thickness: about 100 nm.

Table 1 Photovoltaic parameters of cells based on pure polythiophenes and on PHT–fullerene blends. j_{sc}: short-circuit current density; V_{oc}: open-circuit voltage; *FF*: fill factor; η: photovoltaic conversion efficiency. White-light irradiation power: *ca.* 20 mW cm^{-2}. Ambient temperature

Active layer	j_{sc}/A cm^{-2}	V_{oc}/V	*FF*	η (%)
PBT	1.4×10^{-5}	0.76	0.22	1.1×10^{-2}
PHT	4.2×10^{-5}	0.80	0.25	3.2×10^{-2}
POT	6.4×10^{-6}	0.70	0.15	3.7×10^{-3}
PHT–**1** (1 : 1)	9.8×10^{-4}	0.50	0.20	0.37
PHT–**2** (1 : 1)	8.3×10^{-4}	0.58	0.18	0.48
PHT–**3** (1 : 1)	6.2×10^{-4}	0.71	0.27	0.56

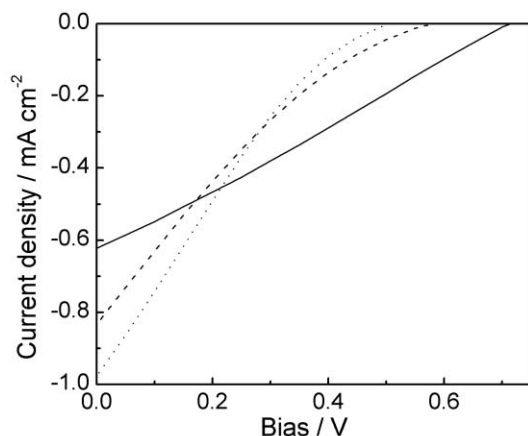**Fig. 3** Current density–voltage characteristics (fourth-quadrant only) of cells based on PHT–**1** (dotted line), PHT–**2** (dashed line) and PHT–**3** (full line). D/A weight ratio: 1:1. White-light irradiation power: *ca.* 20 mW cm^{-2}. Ambient temperature. The values of the photovoltaic parameters are listed in Table 1.
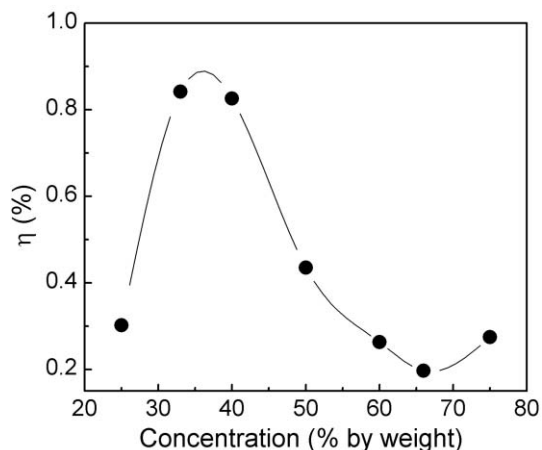

Fig. 4 Power conversion efficiency as a function of the acceptor concentration for PHT–**3** cells. White-light irradiation power: *ca.* 20 mW cm^{-2}. Ambient temperature. The line is drawn to guide the eye. The values of the other photovoltaic parameters are listed in Table 2.
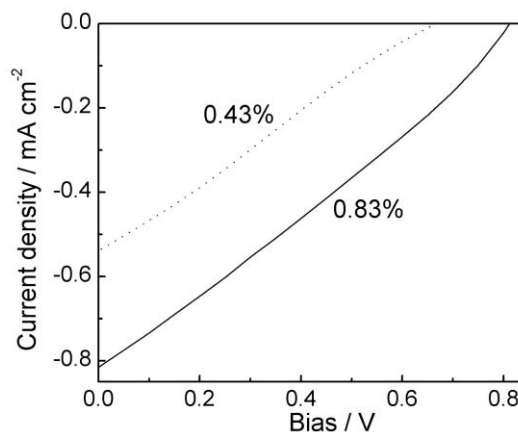
with the electron-acceptor strength of the fullerene derivative was demonstrated. On the other hand, it was found that V_{oc} was rather insensitive to variations of the work function of the negative electrode. In that paper a dependence of V_{oc} on the oxidation potential of the polymer donor was also hypothesised.

The dark current–voltage characteristics of cells made from pure PATs are characterised by a higher rectification ratio (more than one order of magnitude at |2| V) relative to that of devices made from D/A blends. Upon addition of the fullerene derivatives, a decrease in the V_{oc} was observed. This effect was attributed to the lowering of the quasi-Fermi level due to the electron energy loss during electron transfer.[24]

A substantial amount of the fullerene component is usually present in the active layer of high performance D/A cells. For instance, the weight percentage of the functionalised fullerene PCBM ([6,6]-phenyl-C$_{61}$-butyric acid methyl ester) in PCBM–MDMO-PPV blends (MDMO-PPV, poly[2-methyl-5-(3′,7′-dimethyloctyloxy)-p-phenylenevinylene]) of the 2.5% efficient cells was 75%. A study of cell performance as a function of the D/A weight ratio was carried out with the PHT–**3** couple. Blends were prepared with a fullerene content (by weight) ranging from 25 to 75%. The results, averaged over three cells, are summarised in Table 2.

The strongest variations were observed for j_{sc} and η. Fig. 4 shows the trend of cell efficiency with fullerene concentration.

The best cell performance was obtained with blends in which the amount of fullerene was in the 33–40% range. The values obtained for the power conversion efficiency are comparable with those already reported[25] for similar cells prepared at ambient conditions and at the same intensity of the irradiation power.[26]

Cells made from PHT–**3** and POT–**3** at a 3:2 D/A weight ratio were also compared. The effect of the nature of the donor

Fig. 5 Current density–voltage characteristics (fourth-quadrant only) of cells based on POT–**3** (dotted line) and PHT–**3** (full line). D/A weight ratio: 3:2. White-light irradiation power: *ca.* 20 mW cm^{-2}. Ambient temperature. The values of the power conversion efficiency are indicated in the figure. Other photovoltaic parameters: $V_{oc} = 0.66$ V, $j_{sc} = 0.54$ mA cm^{-2}, $FF = 0.25$ for the POT–**3** cell; $V_{oc} = 0.81$ V, $j_{sc} = 0.82$ mA cm^{-2}, $FF = 0.28$ for the PHT–**3** cell.

polymer is not negligible as illustrated in Fig. 5 which shows that the power conversion efficiency of a PHT-based cell is almost twice as much as that made from POT.

Preliminary results indicate that a dramatic improvement of the device performance could be achieved after a mild thermal treatment of the cells. Fig. 6 shows the current–voltage characteristics of a 3:2 PHT–**3** cell, taken before and after heating the device to about 55 °C for 30 min. Both j_{sc} and η underwent a threefold increase upon thermal treatment (from 0.86 to 2.52 mA cm^{-2} and from 0.82 to 2.50%, respectively).

Also the fill factor improved from 0.28 to 0.35 after treatment. On the other hand, a decrease of V_{oc} was observed (from 0.76 to 0.63 V).[27]

The absorption spectra of both PHT and POT were found to change upon blending the polymers with the fullerene component. In particular, the peak wavelength of the interband transition of the PATs shifted towards shorter and shorter wavelengths by increasing the fullerene concentration. As an example, the absorption spectrum of 3:2 PHT–**3** film is reported in Fig. 7. The same spectral behaviour has already been reported in the case of blends between regio-random PATs and [60]fullerene.[28,29]
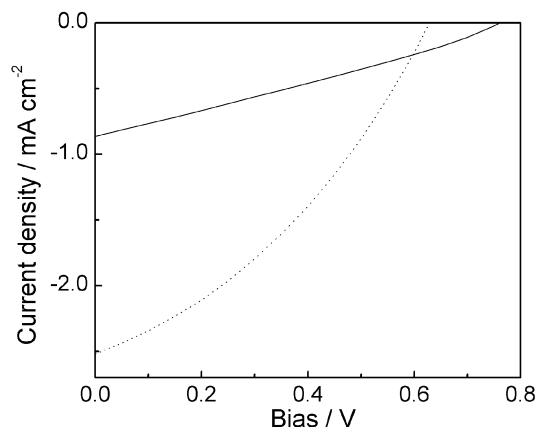
Table 2 Photovoltaic parameters of cells based on blends of PHT–**3** in different weight ratios. White-light irradiation power: *ca.* 20 mW cm^{-2}. Ambient temperature

PHT–**3** weight ratio	j_{sc}/A cm^{-2}	V_{oc}/V	FF	η (%)
3:1	5.4×10^{-4}	0.68	0.18	0.30
2:1	9.2×10^{-4}	0.68	0.21	0.84
3:2	8.4×10^{-4}	0.79	0.28	0.83
1:1	5.2×10^{-4}	0.71	0.24	0.44
2:3	3.9×10^{-4}	0.74	0.26	0.26
1:2	2.1×10^{-4}	0.63	0.24	0.20
1:3	3.1×10^{-4}	0.74	0.26	0.27

Fig. 6 Current density–voltage characteristics (fourth-quadrant only) of cells based on 3 : 2 PHT–**3** before (full line) and after (dotted line) the thermal treatment (*ca.* 55 °C, 30 min) of the device. White-light irradiation power: *ca.* 20 mW cm^{-2}. Ambient temperature.
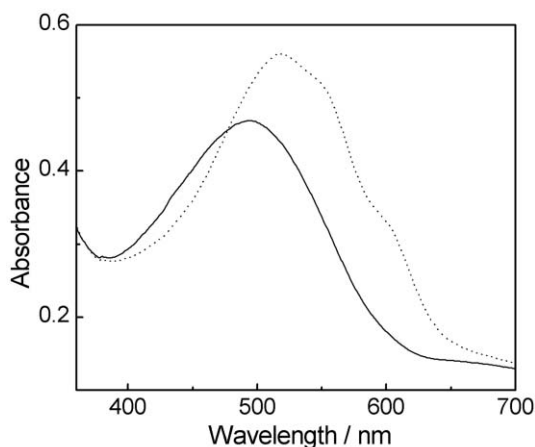

Fig. 7 Absorption spectra of 3 : 2 PHT–**3** films before (solid line) and after thermal treatment (dotted line) to about 55 °C for 30 min, respectively. Film thickness: *ca.* 100 nm.

Relevant changes in the absorption spectrum of the PHT–**3** blend were recorded after thermal treatment. In particular, the maximum absorption wavelength, in the visible range, underwent a red-shift (from 495 to 516 nm, in the case shown in Fig. 7) and the appearance of the characteristic vibronic structure of the pure donor was observed, along with an overall increase of the absorption intensity. A better organisation of the polymer donor, with a concomitant beneficial effect in terms of charge transport properties, most likely takes place during the heating process, although other effects cannot be excluded at this stage.

Conclusions

Bulk heterojunction solar cells, realised at ambient conditions and made from three regioregular PATs and soluble fullerene derivatives, were compared. The D/A couple PTH–**3** showed the best photovoltaic performance having, for instance, a power conversion efficiency about twice as much as that showed by the POT–**3** couple. The highest power conversion efficiencies, recorded for an incident, white-light, irradiation power of 20 mW cm^{-2}, were obtained with a fullerene concentration ranging between 33 and 40% in the active layer. Preliminary results of an ongoing study indicate that a dramatic improvement of the cell performance could be achieved after a mild thermal treatment of the device. Power conversion efficiencies up to 2.5% were recorded upon heating

to 55 °C for 30 min a cell made from 3 : 2 PHT–**3** (20 mW cm^{-2} incident white-light irradiation power).

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