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# Precursor route poly(thienylene vinylene) for organic solar cells: Photophysics and photovoltaic performance

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## Abstract

Photophysical studies and photovoltaic devices on a low bandgap, high-charge carrier mobility poly(thienylene vinylene) (PTV), prepared from a soluble precursor polymer synthesised via the “dithiocarbamate route”, are reported. In composites with an electron acceptor ([6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM), a soluble fullerene derivative), photoinduced absorption characteristic for charged excitations together with photoluminescence quenching are observed indicating photoinduced electron transfer. The “bulk heterojunction” photovoltaic devices using PTV and PCBM composites show short-circuit currents up to 4 mA/cm<sup>2</sup> under AM 1.5 white-light illumination. The photocurrent spectrum of the photovoltaic device shows an onset about 1.65 eV (750 nm), which corresponds to the absorption spectrum of the polymer.

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**Keywords:** Poly(thienylene vinylene); Low bandgap polymer; Photovoltaics

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## 1. Introduction

Organic photovoltaic devices are promising candidates for renewable sources of electrical energy because of ease in fabrication and low production cost as well as light weight and flexibility. The best-reported devices are today able to achieve 2.5–5% power efficiency [1,2]. One of the limitations for organic photovoltaic devices is the mismatch of the absorption spectrum of the active layer and the solar emission spectrum AM1.5. Low bandgap ( $E_g < 1.5$  eV) polymers are needed for strongly absorbing sunlight near the peak of the photon flux from sun. Therefore, it allows for an increase in the number of absorbed photons by more closely matching the donor–polymer absorption spectrum to the solar spectrum. Besides their promising use in organic photovoltaics [3–6], low bandgap-conjugated polymers are also of great interest for many applications as all-polymer-integrated circuits [7] and field-effect transistors [7–9] because of their versatile electronic and optical properties. Conjugated poly(thienylene vinylene) (PTV) and its derivatives possess nonlinear optical responses [10] and electroluminescence properties [11]. Several reports have shown that PTVs exhibit smaller bandgap (below 1.8 eV) [12–14] than the polyaromatic polythiophene (PT) and the PT derivatives [15].

Moreover, PTVs show relatively high-charge carrier mobility ( $\sim 1 \times 10^{-3} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$  measured in field effect transistor geometry) [8,9], which is one of the prerequisites for high efficient solar cells and field effect transistors. PTV is insoluble and thus not processable, but can be prepared via a soluble precursor route. In the final stage, the precursor polymer can be thermally converted into the conjugated polymer PTV by elimination of a leaving group rendering it insoluble in the solid state [16–18]. This extraordinary, unique property of PTV compared to other low bandgap-conjugated polymers allows new potential device architectures in order to improve device performance.

In this paper, we report on the photophysical properties of PTV using photomodulation spectroscopy to study the photoinduced charge generation in photoexcited PTV in its composite with the acceptor [6,6]-phenyl  $C_{61}$ -butyric acid methyl ester (PCBM). The results show evidence of photoinduced charge generation and transfer which is a prerequisite for solar cells operation. Exploiting a large donor–acceptor interfacial area of the bulk heterojunction concept [19,20] for efficient charge generation, the photovoltaic devices were fabricated from a blend of PTV and PCBM and investigated. PTV used in this work was prepared from the precursor which was obtained from dithiocarbamate route [16b,17]. Optimization of the converting conditions for the precursor polymer was required to optimize the photovoltaic performance. In conjugated polymers, the distribution of effective conjugation lengths directly affects the observed energy of  $\pi - \pi^*$  transition [21]. Hence, the optical absorptions were studied for the converted polymers obtained at different heat treatments. The obtained PTV exhibits a  $\lambda_{\text{max}}$  up to 550 nm and a broad absorption band extending into the near IR with an onset of about 1.65 eV. Power conversion efficiencies of around 0.6% with short-circuit currents of about  $4 \text{ mA/cm}^2$ , significantly higher compared to recent reports for PTVs [16,22] and for other low bandgap polymers [4,16,23], were obtained.

## 2. Experimental part

The precursor polymer used in this study was synthesized via the dithiocarbamate route which was published elsewhere [16b,17a], a full paper with a detailed description of the

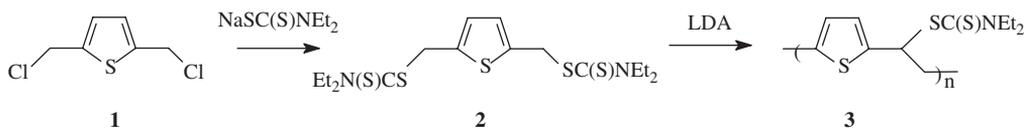
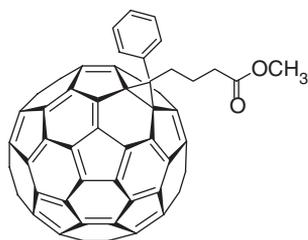
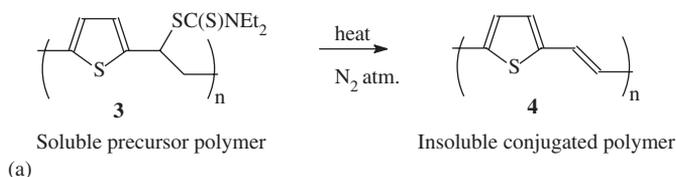


Fig. 1. Synthesis method towards the PTV precursor polymer.

[6,6]-phenyl C<sub>61</sub> – butyric acid methyl ester (PCBM)

(b)

Fig. 2. (a) Conversion reaction of the precursor polymer towards conjugated PTV; (b) chemical structure of [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM).

synthesis method including characterization of the PTV material used in this paper is now submitted to Thin Solid Films [17b]. The structure and the synthesis route are shown in Fig. 1. The chemical structures of the compounds investigated in this study are shown in Fig. 2 together with the conversion process of the precursor polymer to the conjugated polymer PTV. A short description of the synthesis with main characterization data of the polymer is following.

### 2.1. Synthesis of 2,5-bis(chloromethyl)-thiophene (1)

To a cooled (0 °C), stirred solution of 2,5-thiophene dimethanol [17b] (0.9 g, 5 mmol) in THF (20 ml) was slowly added a solution of SOCl<sub>2</sub> (0.9 ml, 1.49 g, 12.5 mmol) in THF (5 ml). The temperature of the reaction mixture was allowed to increase to room temperature under continuous stirring for 1 h. Then, the mixture was cooled down again at 0 °C and a saturated sodium carbonate solution was added dropwise until neutral. The mixture was extracted with ether and dried over MgSO<sub>4</sub>. The solvent was evaporated and the highly reactive dichloride **1** was obtained as a yellow oil.

## 2.2. Thiophene-2,5-diylbismethylene *N,N*-diethyl dithiocarbamate (**2**)

To a solution of bischloromethyl (0.7 g, 4 mmol) **1** in ethanol (10 ml), sodium diethyldithiocarbamate trihydrate (or diethyldithiocarbamic acid sodium salt trihydrate) (5 g, 12 mmol) was added as a solid. The mixture was stirred at ambient temperature for 2 h. Then, water was added and the desired monomer was extracted with ether (3 × 100 ml) and dried over MgSO<sub>4</sub>. Evaporation of the solvent yielded (81%) of the pure product as a white solid used as it is. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 6.84 (s, 2 H), 4.69 (s, 4 H), 4.01 (q, *J* = 7.2 Hz, 4 H), 3.69 (q, *J* = 7.2 Hz, 4 H), 1.26 (t, *J* = 7.2 Hz, 12 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 194.29, 138.76, 126.77, 49.46, 46.70, 36.72, 12.46, 11.53; MS (EI, *m/e*): 258 (M+—SC(S)NEt<sub>2</sub>), 148 (SC(S)NEt<sub>2</sub>).

## 2.3. Precursor polymerization **3**

A solution of monomer **2** in dry THF (the monomer concentration was set at 0.2 M) was degassed by passing through a continuous nitrogen flow. LDA (2 M solution in THF/*n*hexane) was added in one go to the stirred monomer solution. The mixture was kept either at −78 °C, or room temperature or 0 °C, for 90 min under continuous nitrogen flow. The solution was then allowed to come to 0 °C. When the reaction temperature is −78 °C, firstly ethanol (6 ml) is added to stop the reaction. The polymer was precipitated in ice water and the water layer was neutralized with diluted HCl, then extracted with chloroform (CF). The solvent of the combined organic layers was evaporated under reduced pressure and a second precipitation was performed in a 1/1 mixture (100 ml) of diethyl ether and hexane at 0 °C. The polymer was collected and dried in vacuo.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 6.56–6.72 (br s, 1 H), 6.72–6.36 (br s, 1 H), 5.22–5.55 (br s, 1 H), 3.81–4.12 (br q, 2 H), 3.48–3.81 (br q, 2 H), 3.11–3.40 (br s, 2 H), 1.01–1.37 (br t, 6 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): 193.61, 140.77, 140.36, 126.15, 125.89, 52.50, 49.20, 46.73, 38.37, 12.45, 11.60.

GPC: PS standard, DMF as solvent, room temperature, *M*<sub>w</sub> = 13,096, DP = 1.3.

TGA: The conversion reaction of the precursor polymer to the conjugated PTV takes place in the range of temperature 140–200 °C with its maximum at 195 °C. An elimination at 62 °C can be also observed which is related to the evaporation of remaining traces of solvent and to the evaporation of very small oligomers. A third elimination peak at higher temperature of 424 °C corresponding to the thermal degradation of the polymer backbone is also present.

## 2.4. Conversion reaction toward the conjugated polymer **4**

The soluble precursor polymer **3** was thermally converted to the insoluble conjugated PTV in situ in thin film from room temperature to 160 °C at 2 °C/min and held at 160 °C for 15 min.

## 2.5. Optical absorption

Thin film samples for optical measurements were prepared by spincoating from chlorobenzene solution onto glass substrates. UV–Vis spectra were recorded using a Varian Cary 3G UV–Vis Spectrophotometer.

## 2.6. Photomodulation spectroscopy

Photoinduced absorption (PIA) measurements were performed on pristine PTV and a blend of PTV and PCBM with a 1:2 weight ratio of precursor:PCBM. The sample prepared as a drop cast film onto glass, after converting, was mounted in a cryostat (Oxford CF 204) and held at 80 K. The vacuum during all measurements was better than  $10^{-5}$  mbar. The samples were excited by a  $\text{Ar}^+$  laser (INNOVA 400) operating at a wavelength of 514 nm and light power of 40 mW. The illumination spot on the sample was around  $4 \text{ mm}^2$ . The pump beam was modulated by a mechanical chopper (Standford SR 540) with a frequency of 218 Hz for PIA and 38 Hz for photoluminescence (PL) measurements. PIA was measured by probing the absorption of light from the tungsten halogen lamp during laser photoexcitation. The transmission  $T$  and the photoinduced changes  $\Delta T$  in the spectral range of 600–2200 nm were measured using a Si-InGaAsSb detector and lock in technique. The PL spectra were recorded without probe beam on the sample using the same settings.

## 2.7. Solar cell fabrication

Photovoltaic devices were prepared from 1 wt% solutions of the precursor and PCBM at weight ratios of 1:1 (named as 1:1 device) and 1:2 (named as 1:2 device) using chlorobenzene (CB) as solvent. Concentrations as 2 wt% solutions in CB and chloroform (CF) were prepared additionally for the 1:2 device. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Baytron P, Bayer Germany) was spin-coated on top of indium-tin oxide (ITO) (Merck, Germany) coated glass ( $\sim 25 \Omega/\text{sq.}$ ) which had been cleaned in an ultrasonic bath with acetone and isopropyl alcohol. The active layer (precursor polymer: PCBM blend) was spin-coated on the PEDOT: PSS layer and converted to PTV by several different heat treatments ( $2^\circ\text{C}/\text{min}$  to  $140^\circ\text{C}$  and held for 10 min (A), for 20 min (B); constant at  $140^\circ\text{C}$  for 10 min (C); constant at  $160^\circ\text{C}$  for 10 min (D) and for 15 min (E)) in inert atmosphere (argon) in a dry glove box. Then,  $6 \text{ \AA}$  of lithium fluoride (LiF) and a 80 nm thick Al electrode was deposited onto the blend film by thermal evaporation at  $\sim 5 \times 10^{-6}$  mbar. All current–voltage ( $I$ – $V$ ) characteristics of the photovoltaic devices were measured using a Keithley SMU 2400 unit under inert atmosphere (argon) in a dry glove box. A Steuernagel solar simulator was used as the excitation source with a power of  $100 \text{ mW cm}^{-2}$  white light illumination (AM 1.5 conditions). A lock-in technique was used to measure the incident photon-to-current efficiency (IPCE). The spectral photocurrent was recorded under illumination by a monochromatized xenon lamp with a typical illumination density  $5\text{--}10 \mu\text{W cm}^{-2}$ . The incident beam was chopped with a mechanical chopper, the photocurrent was detected with a lock-in-amplifier. The Xe-lamp spectrum was measured with a calibrated Si-diode.

## 2.8. Atomic force microscopy

Atomic force microscopy (AFM) studies were performed by using a Digital Instruments Dimension 3100 in the tapping mode. The AFM characterization was performed on an area of the active layer of the photovoltaic device where the electrode was not deposited.

### 3. Results and discussion

#### 3.1. Photophysical properties

The precursor polymer films are converted to PTV in the temperature range of 140–200 °C where the elimination reaction occurred observed by thermogravimetry measurement [17b]. Precursors with different molecular weights require different heat-converting conditions. The optical spectra of PTV films converted at different heat conditions show that the higher the degree of conjugation, the more the absorption maximum shifts to longer wavelengths. The precursor polymer used in this study has an average molecular weight  $M_w$  of 13,100 and a polydispersity of 1.3. Fig. 3 shows optical spectra of PTV converted at different heat treatments such as a temperature ramp with 2 °C/min from room temperature to 140 °C and a constant temperature at 160 °C for 15 min, etc. The optical absorptions spectra of the precursor polymer:PCBM blend at weight ratios of 1:1 and 1:2 converted at different temperatures of 160, 170, 180 °C for 15 min were also studied and plotted in Fig. 3. The onset of the  $\pi$ – $\pi^*$  transition in PTV occurs just below 750 nm (1.65 eV). The spectra show that the conversion at 160 °C for 15 min gave the maximum absorption intensity and broadest absorption spectrum in the pristine polymer and in the blend. As higher temperatures of 170 and 180 °C did not show beneficial effects on absorption and solar cell performance, the lower conversion temperature at 160 °C was chosen in regard to the heat sensitivity of PEDOT layer for photovoltaic devices. The blend of PTV with PCBM is capable of absorbing over the entire visible range of 400–750 nm. However, this spectral broadening approach is only useful if the donor polymer is able to ultimately transfer an electron to PCBM upon photoexcitation.

The PL of PTV and its blend with PCBM was measured to check if there is interaction of the two components in the excited state. PL quenching is often indicative of a charge transfer for many donor–acceptor blends [24]. Fig. 4 shows the absorption (dashed line)

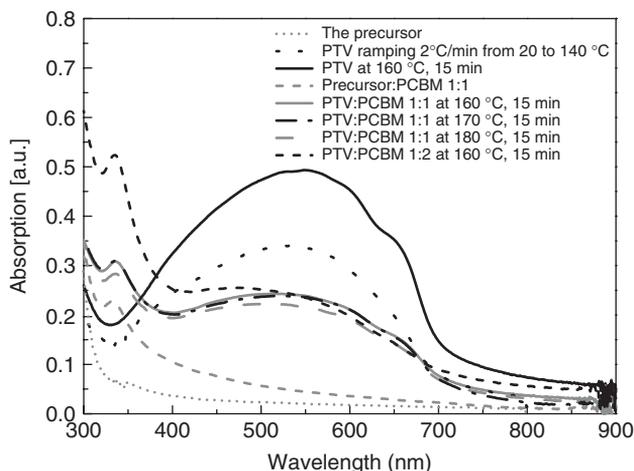


Fig. 3. UV–Vis spectra of the precursor, pristine PTV and the PTV precursor: PCBM blends at weight ratios of 1:1 and 1:2 converted at various heat treatment conditions.

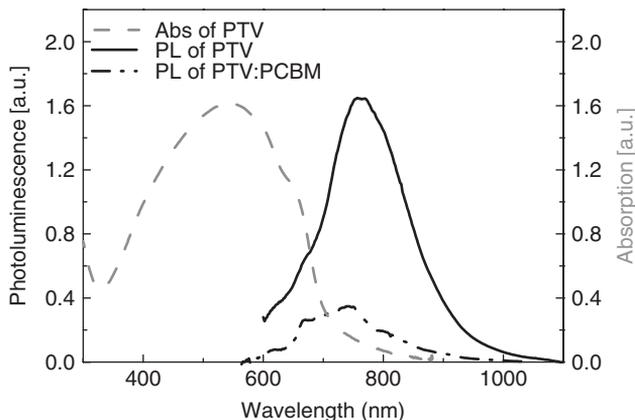


Fig. 4. Optical absorption of PTV (dashed line); PL of PTV (solid line) and its blend with PCBM (1:2 wt) (dashed dot line) converted at 160 °C for 15 min, excited at 514 nm, 38 Hz and 80 K.

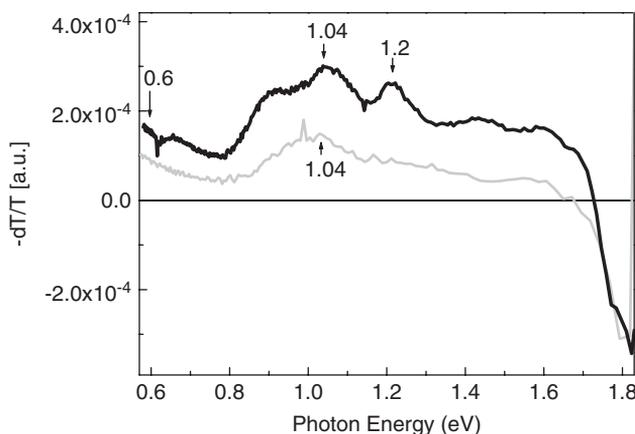


Fig. 5. PIA spectrum of PTV:PCBM at 1:2wt recorded at 80K following chopped cw excitation at 514 nm, 218 Hz.

and PL spectra of PTV and its blend with PCBM at 1:2 weight ratio films of comparable optical thickness. One PL peak was observed at about 760 nm (1.63 eV) for pristine polymer (solid line). The PL of PTV is quenched by a factor of 4 in the PTV:PCBM blend (dashed dot line, Fig. 4).

PIA studies for pristine PTV (gray line) and PTV:PCBM (1:2 wt) blend (black line) are shown in Fig. 5. The PIA for pristine PTV exhibits two peaks at <0.6 and 1.04 eV which can be assigned to charged species (polaronic state). The obtained data are consistent with previous results reported by Friend et al. [25]. The PIA spectrum of the blend shows peaks at <0.6, 1.04, 1.2 eV and a negative peak at 1.85 eV. PIA bands around <0.6 eV and the broad absorption centered at 1.04 eV are proposed to originate from the low-energy (LE) and high-energy (HE) PIA of positive charges (usually described as polarons) on the PTV chain. The relatively sharp peak at about 1.2 eV is assigned to the absorption of the PCBM radical anion which was previously reported as doublet around 1.15 and 1.25 eV [26]. No

clear signature of the PCBM radical anion which is expected at 1.15 eV as in Ref. [26] is observed, but it may well be overlapped by the 1.04 eV band of the PTV radical cation. The C60 anion absorption was often observed at around 1.15–1.2 eV in PIA spectrum of polymer-C60 [27] and polymer-methanofullerene composites [28]. Additionally, a bleaching of the ground state absorption of PTV starting at 1.7 eV with its negative peak at 1.85 eV occurred. PIA spectroscopy supported by PL quenching indicates that upon photoexcitation, PTV acts as donor and transfers charges to PCBM as an acceptor.

### 3.2. Photovoltaic devices

$I$ - $V$  characteristics of a ITO/PEDOT/PTV:PCBM/LiF/Al 1:1 device are shown in Fig. 6a both in dark and under AM 1.5 illumination ( $100 \text{ mW/cm}^2$ ). Values obtained for the main parameters such as open-circuit voltage ( $V_{OC}$ ), short-circuit current ( $I_{SC}$ ), fill

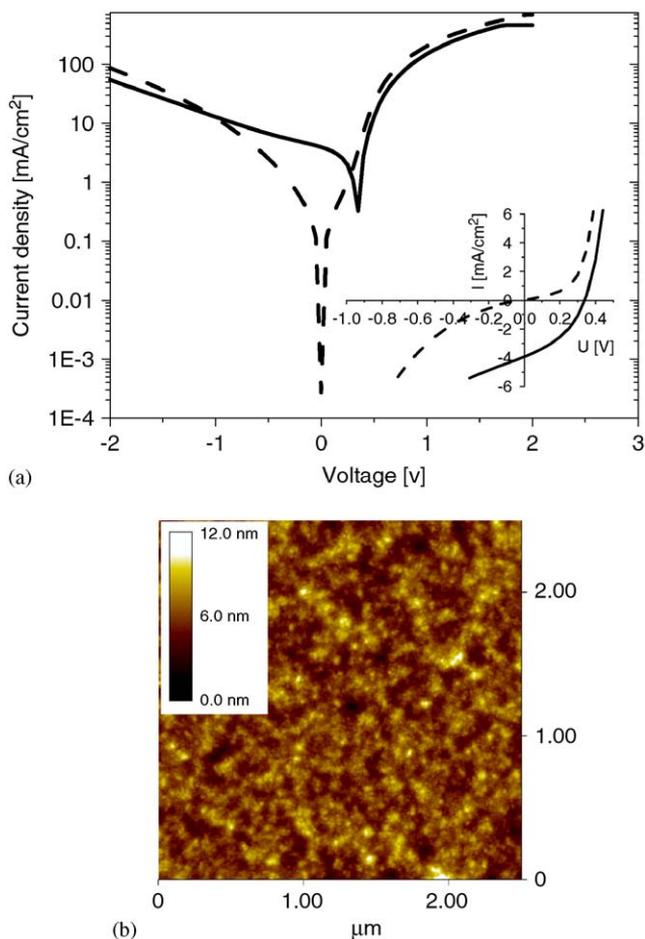


Fig. 6. (a) Semilogarithmic and linear (inset)  $I$ - $V$  characteristics of the PTV:PCBM 1:1 device measured in the dark (dashed lines) and under  $100 \text{ mW/cm}^2$  solar simulator illumination (solid line). (b) AFM morphology of the active layer of PTV:PCBM 1:1 device.

Table 1

Photovoltaic parameters from photovoltaic devices of configuration: ITO/PEDOT:PSS/PTV:PCBM/LiF/Al

Devices	$V_{OC}$ (mV)	$I_{SC}$ (mA/cm <sup>2</sup> )	FF	Efficiency $\eta$ (%)
PTV:PCBM 1:1 1 wt% in CB	350	3.9	0.4	0.5
PTV:PCBM 1:2 1 wt% in CB	350	3.5	0.5	0.6
PTV:PCBM 1:2 2 wt% in CB	260	2.2	0.3	0.2
PTV:PCBM 1:2 2 wt% in CF	250	1.7	0.3	0.1

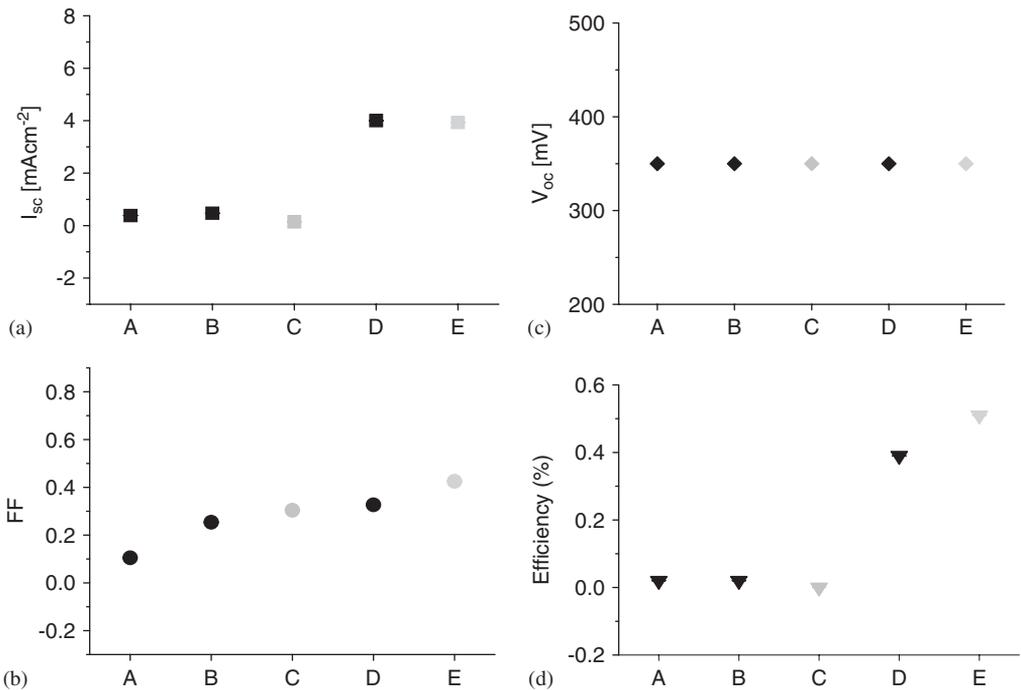


Fig. 7.  $I_{SC}$  (a), FF (b),  $V_{OC}$  (c) and efficiency (d) at different conversion heat treatments for 1:1 device. (A) ramp 2 °C/min from 20 to 140 °C and held at 140 °C for 10 min, (B) ramp 2 °C/min from 20 to 140 °C and held at 140 °C for 20 min, (C) constant temperature at 140 °C for 10 min, (D) constant temperature at 160 °C for 10 min, (E) constant temperature at 160 °C for 15 min.

factor (FF) and conversion efficiency ( $\eta$ ) are  $V_{OC} = 350$  mV,  $I_{SC} = 3.9$  mA/cm<sup>2</sup>, FF = 0.4 and  $\eta = 0.5\%$  (Fig. 6a, Table 1). The morphology of the active layer studied by AFM shows a smooth surface with no phase separation and a height scale of 12 nm (Fig. 6b). The values of the  $I_{SC}$ ,  $V_{OC}$ , FF and  $\eta$  are plotted at various conversion heat treatments: (A) ramp 2 °C/min from 20 to 140 °C and held for 10 min; (B) ramp 2 °C/min from 20 to 140 °C and held for 20 min; (C) held at 140 °C for 10 min; (D) held at 160 °C for 10 min; (E) held at 160 °C for 15 min (Fig. 7). The values of the  $V_{OC}$  (~350 mV) were comparable regardless of different heat treatments. The  $I_{SC}$  reaches maximum values in the case of (D) and (E). Both FF and  $\eta$  exhibit the best performance in the case of 160 °C and 15 min heat treatment (E),

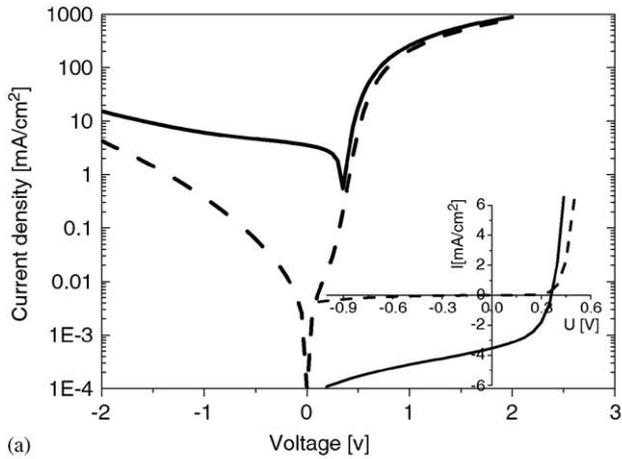
which finds good agreement with the optical absorption studies. The AFM images (not presented) in all cases show a smooth surface and no phase separation occurred for different heat conversion durations. Within the range of necessary conversion temperatures, no conclusive results were obtained for optimal morphology, which is of great interest for the actual performance of the photovoltaic devices. Higher conversion temperatures of 170 and 180 °C were also tested for solar cells but the results showed that the devices were mostly shorted due to pinholes formed in the converted film. Therefore, the conversion temperature of 160 °C was chosen for further investigation. In comparison to other low bandgap polymer/PCBM systems such as polyfluorene/PCBM [29] and poly[5,7-bis-(3-octylthiophene-2-yl)thieno{3,4-b}pyrazine]/PCBM [30], the short-circuit currents achieved in this study with the PTV/PCBM blend is significantly higher.

The relative concentrations of the two components of donor and acceptor can also play an important role in the device performance. Usually, a higher content of PCBM compared with the amount of the conjugated polymer leads to better device performance [31]. Therefore, the higher content of PCBM, as in ITO/PEDOT/PTV:PCBM/LiF/Al 1:2, was tested. The  $I$ - $V$  characteristics are shown in Fig. 8a and gave  $V_{OC} = 350$  mV,  $I_{SC} = 3.5$  mA/cm<sup>2</sup>, FF = 0.5 and  $\eta = 0.6\%$ . The morphology (Fig. 8b) compared to that of the 1:1 device (Fig. 6b) shows that the active layer is much smoother and more homogeneous. The better morphology can be a reason for an increase in FF (0.5) and therefore a higher efficiency despite of the lower  $I_{SC}$  (Table 1).

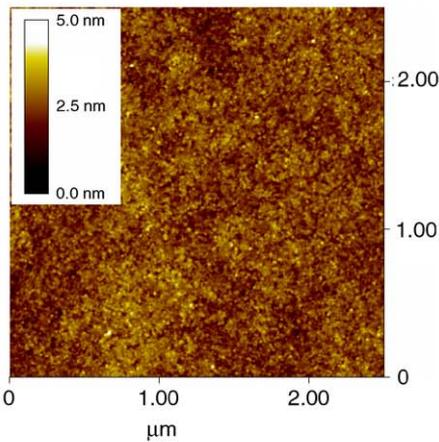
Fig. 8c reports the spectrally resolved photocurrent (IPCE) of the 1:2 device together with absorption spectra of pristine PTV (dashed line) and the blend (dashed dot line). The IPCE spectrum peaks coincide with the absorption of PCBM (350 nm) with subsequent hole transfer to the donor, and PTV absorption (550 nm) resulting in electron transfer to acceptor. The photocurrent spectrum of the device shows an onset of the photocurrent at about 750 nm (1.65 eV) close to the optical bandgap and exhibits a maximum of 17% at 550 nm. Low bandgap PTV leads to the better matching to solar emission spectrum. As a consequence, the photovoltaic devices generate electrons over a wide range of wavelengths which expand into the near-infrared.

The nanomorphology of donor–acceptor composites is known to have an important influence on the device efficiency [1]. Since the morphology also depends on the solvent [1,31], CF was used at 2 wt% solution for comparison. The photovoltaic device prepared from CF gives poorer performance properties listed in Table 1. The comparison of the morphology of the devices prepared from CB and CF (Fig. 9) shows that CB provides a smoother and more homogeneous nanomorphology. Phase separation observed in CF cast blend can be interpreted as the main reason for the reduced photocurrents [32].

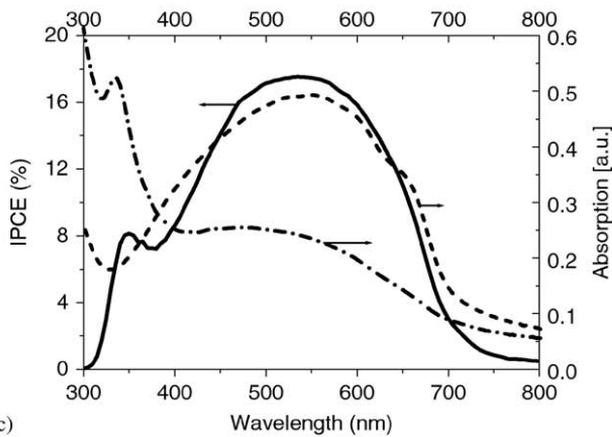
The lifetime of organic photovoltaic devices is known to be short when the devices are operated in atmosphere. PTV appears to be prone to oxidation due to the existence of vinylene groups (like in poly(*p*-phenylene vinylene) (PPV)), which are known to be unstable in air and particularly susceptible to photodegradation induced by oxygen and moisture. PPV-based solar cells usually do not operate for more than a few hours in air [33]. As reported, systems having no side-chain group show to give very stable devices with longer lifetime [34], and therefore improved stability of PTV devices may be expected. Preliminary tests were carried out to this aspect. Fig. 10 shows conversion efficiency and  $I_{SC}$  versus exposure time of the devices without encapsulation measured during the continuous exposure under AM1.5 (1000 Wm<sup>-2</sup>) illumination. For polymer solar cells, the lifetime is commonly defined as the time it takes for the efficiency to decrease to half of its



(a)



(b)



(c)

Fig. 8. (a)  $I$ - $V$  characteristics (AM 1.5,  $100 \text{ mW/cm}^2$ ) of the PTV:PCBM 1:2 device prepared from 1 wt% solution in CB; (b) morphology of the active film; (c) IPCE % spectrum of the device (solid line) and the corresponding optical absorption for the pristine PTV (dashed line) and PTV:PCBM blend (1:2 wt) (dashed dot line) films.

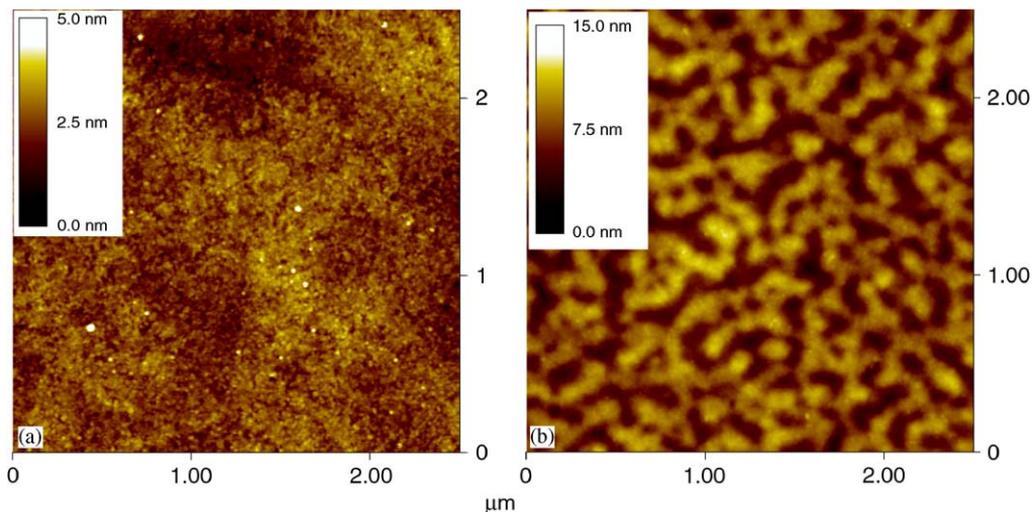


Fig. 9. Morphology of the active films of PTV:PCBM 1:2 device prepared from 2 wt% solution using (a) CB and (b) CF.

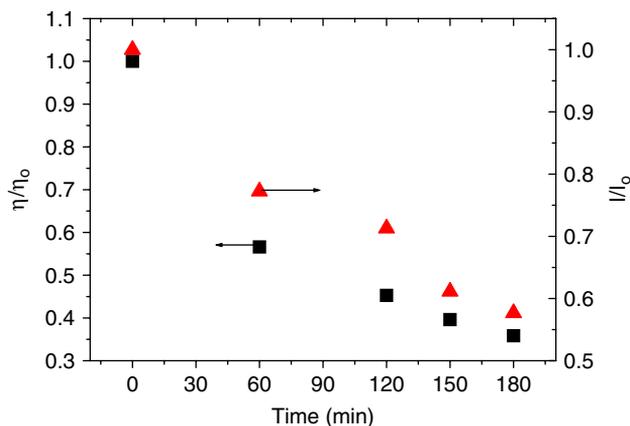


Fig. 10. Conversion efficiency and  $I_{SC}$  versus exposure time when the devices without encapsulation were continuously illuminated under AM1.5 ( $1000 \text{ Wm}^{-2}$ ) in the atmosphere.

initial or maximum value [34]. The operating lifetime of the device without protection against air is about 90 min.  $I_{SC}$  values decreases by 50% in 180 min. Therefore, appropriate encapsulation is mandatory for this type of devices. Dennler et al. [35] reported new encapsulation solution using poly(ethylene naphthalate)-based ultra-high barrier material. With the new encapsulation, the shelf lifetime (non-operating) of solar cells increases from less than 6 h into the range beyond 3000 h. For organic solar cells, an operating lifetime of at least 1000 h is of interest from an application point of view.

In summary, the soluble precursor route has been successfully applied to the preparation of the low bandgap polymer PTV for photovoltaic devices. Spectroscopic investigations show that the PTV:PCBM composite exhibits an efficient photoinduced charge transfer

cross the bulk heterojunction. Polymer solar cells with a spectral response up to 750 nm were fabricated and discussed. Photovoltaic devices with short-circuit currents up to  $\sim 4 \text{ mA/cm}^2$  were prepared. For future applications, the precursor processing route of PTV may be used for the construction of tandem cells due to the insolubility of PTV in the converted state.

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## References

- [1] S.E. Shaheen, C.J. Brabec, N.S. Sariciftci, F. Padinger, T. Fromherz, J.C. Hummelen, *Appl. Phys. Lett.* 78 (2001) 841.
- [2] W. Ma, C. Yang, X. Ong, K. Lee, A.J. Heeger, *Adv. Funct. Mater.* 15 (2005) 1617.
- [3] C. Winder, N.S. Sariciftci, *J. Mater. Chem.* 14 (2004) 1077.
- [4] L. Goris, M.A. Loi, A. Cravino, H. Neugebauer, N.S. Sariciftci, I. Polec, L. Lutsen, E. Manca, L. De Schepper, D. Vanderzande, *Synth. Met.* 138 (2003) 249.
- [5] K. Colladet, M. Nicolas, L. Goris, L. Lutsen, D. Vanderzande, *Thin Solid Films* 451–452 (2004) 7.
- [6] S.E. Shaheen, D. Vangeneugden, R. Kiebooms, D. Vanderzande, T. Fromherz, F. Padinger, C.J. Brabec, N.S. Sariciftci, *Synth. Met.* 121 (2001) 1583.
- [7] M. Matters, D.M. de Leeuw, M.J.C.M. Vissenberg, C.M. Hart, P.T. Herwig, T. Geuns, C.M.J. Mutsaers, C.J. Drury, *Opt. Mater.* 12 (1999) 189.
- [8] H.E.A. Huitema, G.H. Gelinck, J.B.P.H. van der Putten, K.E. Kuijk, C.M. Hart, E. Cantatore, P.T. Herwig, A.J.J.M. van Breemen, D.M. de Leeuw, *Nature* 414 (2001) 599.
- [9] H.E.A. Huitema, G.H. Gelinck, J.B.P.H. van der Putten, K.E. Kuijk, C.M. Hart, E. Cantatore, D.M. de Leeuw, *Adv. Mater.* 14 (2002) 1201.
- [10] T. Kobayashi, *Pure Appl. Chem.* 67 (1995) 387.
- [11] J.L. Segura, *Act. Polym.* 49 (1998) 319.
- [12] W.J. Mitchell, C. Pena, P.L. Burn, *J. Mater. Chem.* 12 (2002) 200.
- [13] Y.-B. Lee, H.-K. Shim, S.-W. Ko, *Macromol. Rapid Commun.* 24 (2003) 522.
- [14] R.S. Loewe, R.D. McCullough, *Chem. Mater.* 12 (2000) 3214.
- [15] J. Roncali, *Chem. Rev.* 97 (1997) 173.
- [16] (a) A. Henckens, M. Knipper, I. Polec, J. Manca, L. Lutsen, D. Vanderzande, *Thin Solid Films* 451–452 (2004) 572;  
(b) A. Henckens, L. Lutsen, D. Vanderzande, M. Knipper, J. Manca, *Proc. SPIE* 5464 (2004) 52.
- [17] (a) A. Henckens, K. Colladet, S. Fourier, T.J. Cleij, L. Lutsen, J. Gelan, D. Vanderzande, *Macromolecules* 38 (2005) 19;  
(b) F. Banishoeib, A. Henckens, S. Fourier, G. Vanhooyland, M. Bresselge, J. Manca, T.J. Cleij, L. Lutsen, D. Vanderzande, L.H. Nguyen, H. Neugebauer, N.S. Sariciftci, *Thin Solid Films* 2006, submitted.
- [18] H.-Q. Xie, C.M. Liu, J.-S. Guo, *Eur. Polym. J.* 32 (1996) 1131.
- [19] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, *Adv. Funct. Mater.* 11 (2001) 15.
- [20] F. Padinger, R.S. Rittberger, N.S. Sariciftci, *Adv. Funct. Mater.* 13 (2003) 85.
- [21] R.S. Loewe, R.D. McCullough, *Chem. Mater.* 12 (2000) 3214.
- [22] A.P. Smith, R.R. Smith, B.E. Taylor, M.F. Durstock, *Chem. Mater.* 16 (2004) 4687.
- [23] A. Dhanabalan, J.K. van Duren, P.A. van Hal, J.L. Van Dongen, R.A.J. Janssen, *Adv. Funct. Mater.* 11 (2001) 255.
- [24] N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, *Science* 258 (1992) 1474.
- [25] A.J. Brassett, N.F. Colaneri, D.D.C. Bradley, R.A. Lawrence, R.H. Friend, *Phys. Rev. B* 41 (1990) 10586.
- [26] K. Lee, R.A.J. Janssen, N.S. Sariciftci, A.J. Heeger, *Phys. Rev. B* 49 (1994) 5781.

- [27] L. Smilowitz, N.S. Sariciftci, R. Wu, C. Gettinger, A.J. Heeger, F. Wudl, *Phys. Rev. B* 47 (1993) 13835.
- [28] K. Lee, E.K. Miller, N.S. Sariciftci, J.C. Hummelen, F. Wudl, A.J. Heeger, *Phys. Rev. B* 54 (1996) 10525.
- [29] F. Zhang, E. Perzon, X. Wang, W. Mammo, M.R. Anderson, O. Inganäs, *Adv. Funct. Mater.* 15 (2005) 745.
- [30] L.M. Campos, A. Tontcheva, S. Günes, G. Sonmez, H. Neugebauer, N.S. Sariciftci, F. Wudl, *Chem. Mater.* 17 (2005) 4031.
- [31] H. Hoppe, M. Niggemann, C. Winder, J. Kraut, R. Hiesgen, A. Hinsch, D. Meissner, N.S. Sariciftci, *Adv. Funct. Mater.* 14 (2004) 1005.
- [32] H. Hoppe, N.S. Sariciftci, *J. Mater. Chem.* 26 (2006) 45.
- [33] F. Padinger, T. Fromherz, P. Denk, C.J. Brabec, J. Zettner, T. Hierl, N.S. Sariciftci, *Synth. Met.* 121 (2001) 1605.
- [34] F.C. Krebs, H. Spanggaard, *Chem. Mater.* 17 (2005) 5235.
- [35] G. Dennler, C. Lungenschmied, H. Neugebauer, N.S. Sariciftci, M. Latreche, G. Czeremuszkin, M. Wertheimer, *Thin Solid Films*, 2006, in press.