Low bandgap 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_{61} – butyric acid methyl ester (PCBM), a soluble fullerene derivative) photoinduced absorption (PIA) characteristic for charged excitations together with photoluminescence (PL) 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^2 under AM 1.5 white-light illumination. The photocurrent spectrum of the photovoltaic device shows an onset at about 1.65 eV (750 nm) which corresponds to the absorption spectrum of the polymer.
Keywords: Poly(Thienylene Vinylene), low bandgap polymer, photovoltaics

1. INTRODUCTION

One of limitations for organic photovoltaic devices is the mismatch of the absorption of the active layer and the solar emission spectrum AM1.5. The use of low bandgap polymers (Eg < 1.8 eV) allows for an improvement in photon harvesting, enriching in the number of photons absorbed which would enhance in the power conversion efficiency of photovoltaic devices. Conjugated poly (thienylene vinylene) (PTV)s with bandgaps below 1.8 eV [1] show high-charge-carrier-mobility ($\sim 1 \times 10^{-3}$ cm^2 v^{-1} s^{-1}).[2] These properties make PTVs promising materials for photovoltaic applications. 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.[3,4] This 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 demonstrate the utilisation of the low bandgap PTV for organic solar cells using a bulk heterojunction concept [5] which exploit a large donor-acceptor interfacial area for efficient charge generation. Photomodulation spectroscopy was used to study the photoinduced charge generation and transfer of photoexcited PTV in its composite with an acceptor [6,6]-phenyl C_{61} – butyric acid methyl ester (PCBM). The results show evidence of photoinduced charge transfer which is a prerequisite for solar cells operation. The obtained PTV exhibits a maximum absorption λ_{max} up to 550 nm and a broad absorption band extending into the near IR with an onset of about 750 nm (1.65 eV). The photovoltaic performance of the PTV with PCBM in bulk heterojunction concept was optimized achieving power efficiency of 0.6 % with short circuit current of about 4 mA/cm^2. These results are significantly high compared to recent reports for PTVs [3,6] and for other low bandgap polymers. [7]

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2. EXPERIMENTAL PART

The precursor polymer with an average molecular weight M_w of 13000 and a polydispersity of 1.3 used in this study was synthesized via the dithiocarbamate route.[3b] The chemical structures of the compounds investigated in this study are shown in Figure 1 together with the conversion process of the precursor to PTV.
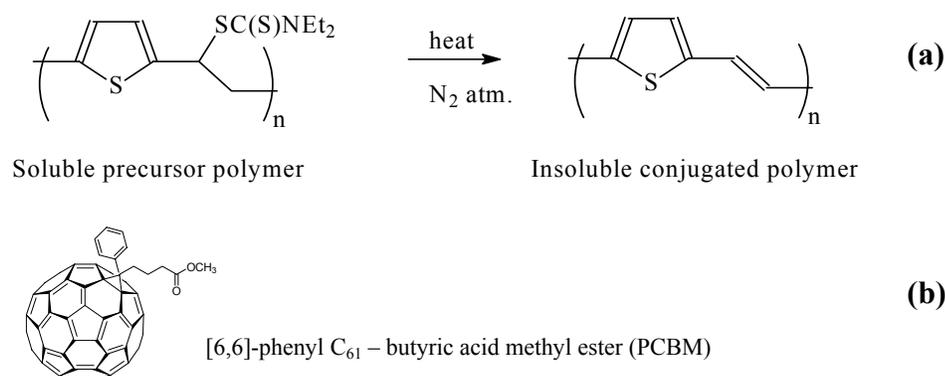

Soluble precursor polymer   Insoluble conjugated polymer   **(a)**

[6,6]-phenyl C_{61} – butyric acid methyl ester (PCBM)   **(b)**

Figure 1: a) Conversion reaction of the precursor polymer towards conjugated PTV; b) chemical structure of [6,6]-phenyl C_{61} – butyric acid methyl ester (PCBM).

2.1. 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.

2.2. 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 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 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. Photoinduced absorption was measured by probing the absorption of light from the tungsten halogen lamp during laser photoexcitation. The transmission T and the photoinduced changes ΔT 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.

2.3. 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 cholorobenzene as solvent. 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 (~25 Ω/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 at 160 °C for 15 min in inert atmosphere (argon) in a dry glove box. Then 6 Å of lithium fluoride (LiF) and a 80 nm thick Al electrode was deposited onto the blend film by thermal evaporation at ~5x 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 $mWcm^{-2}$ 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. 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.

2.4. Atomic force microscopy (AFM)

Atomic Force Microscopy 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.[3,4] Optimization of the converting conditions for the precursor polymer was required to gain the photovoltaic performance. In conjugated polymers the distribution of effective conjugation lengths directly affects the observed energy of $\pi-\pi*$ transition.[8] 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. Figure 2 shows optical spectra of PTV and the PTV:PCBM blend converted at different heat treatments. 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 regards 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.
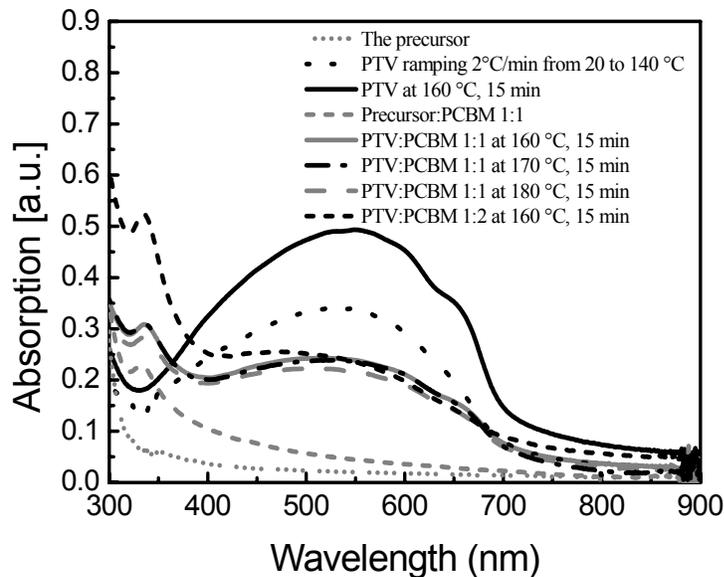

Figure 2: UV-Vis spectra of the precursor, pristine PTV and the PTV precursor:PCBM blends at weight ratios of 1:1 and 1:2 converted at various heat treatment conditions

Figure 3 shows the absorption (dashed line) 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 photoluminescence of PTV is quenched by a factor of 4 in the PTV:PCBM blend (dashed dot line, Figure 3). Photoluminescence quenching is often indicative of a charge transfer for many donor-acceptor blends.[9]
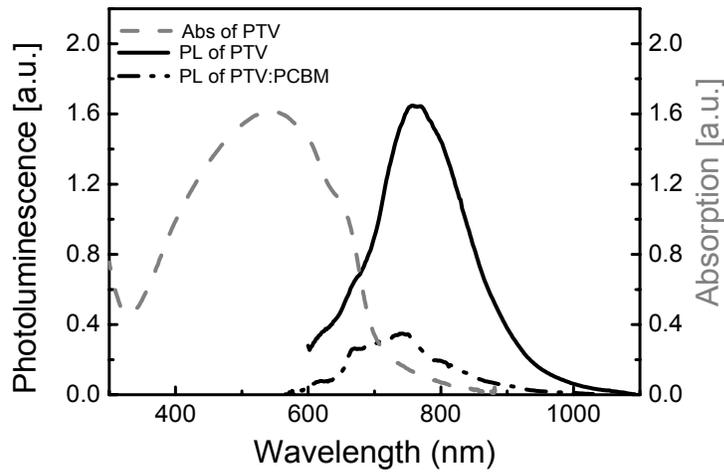

Figure 3: Optical absorption of PTV (gray dashed line); Photoluminescence of PTV (solid line) and its blend with PCBM (1:2 wt) (dashed dot line) converted at 160 °C for 15 min, excited at 514 nm, 38Hz and 80K.

Photoinduced absorption (PIA) studies for pristine PTV (gray line) and PTV:PCBM (1:2 wt) blend (black line) are shown in Figure 4. The PIA for pristine PTV exhibits two peaks at <0.6 eV and 1.04 eV which can be assigned to charged species (polaronic state). The PIA spectrum of the blend shows peaks at <0.6 eV, 1.04 eV, 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) photoinduced absorption 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.[10] 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.
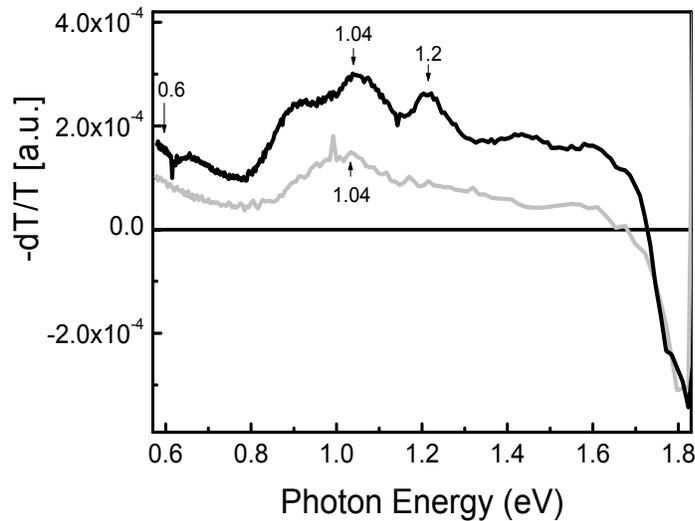

Figure 4: Photoinduced absorption spectrum of PTV:PCBM at 1:2 wt recorded at 80K following chopped cw excitation at 514 nm, 218 Hz.

3.2. Photovoltaic devices

I-V characteristics of a ITO/PEDOT/PTV:PCBM/LiF/Al 1:1 and 1: 2 device are shown in Figure 5a and 6a both in dark and under AM 1.5 illumination (100 mW/cm^2). Values obtained for the main parameters of 1:1 device are open-circuit voltage V_{OC}= 350 mV, short-circuit current I_{SC}= 3.9 mA/cm^2, fill factor FF= 0.4 and conversion efficiency η= 0.5 % (Figure 5a). The values of the V_{OC} (~350 mV) were comparable regardless of different acceptor ratios. The 1:2 device shows lower current density (3.5 mA/cm$^{2)}$ but higher FF (0.5), leading to higher efficiency (0.6 %). The morphology of the active layer in both cases shows a smooth surface with no phase separation (Figure 5b and 6b). The morphology of the 1:2 device is much smoother and more homogeneous which can be a reason for an increase in FF (0.5) and therefore a higher efficiency. In comparison to other low bandgap polymer/PCBM systems such as polyfluorene/PCBM[11] and poly[5,7-bis-(3-octylthiophene-2-yl)thieno{3,4-b}pyrazine]/PCBM[12] the short circuit currents achieved in this study with the PTV/PCBM blend is significantly higher.
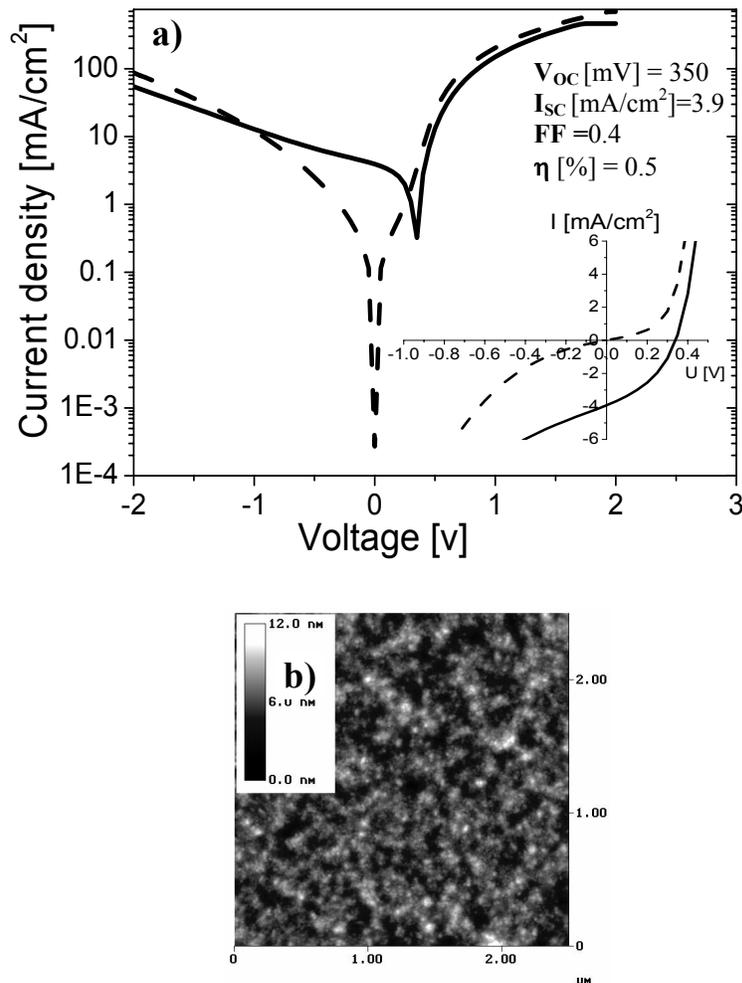

Figure 5: a) Semilogarithmic and linear (inset) I-V characteristics of the PTV:PCBM 1:1 device measured in the dark (dashed lines) and under 100 mW/cm^2 solar simulator illumination (solid line). b) AFM morphology of the active layer of PTV:PCBM 1:1 device.

Figure 6c 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 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 photovotaic devices generate electrons over a wide range of wavelengths which expand into the near-infrared.
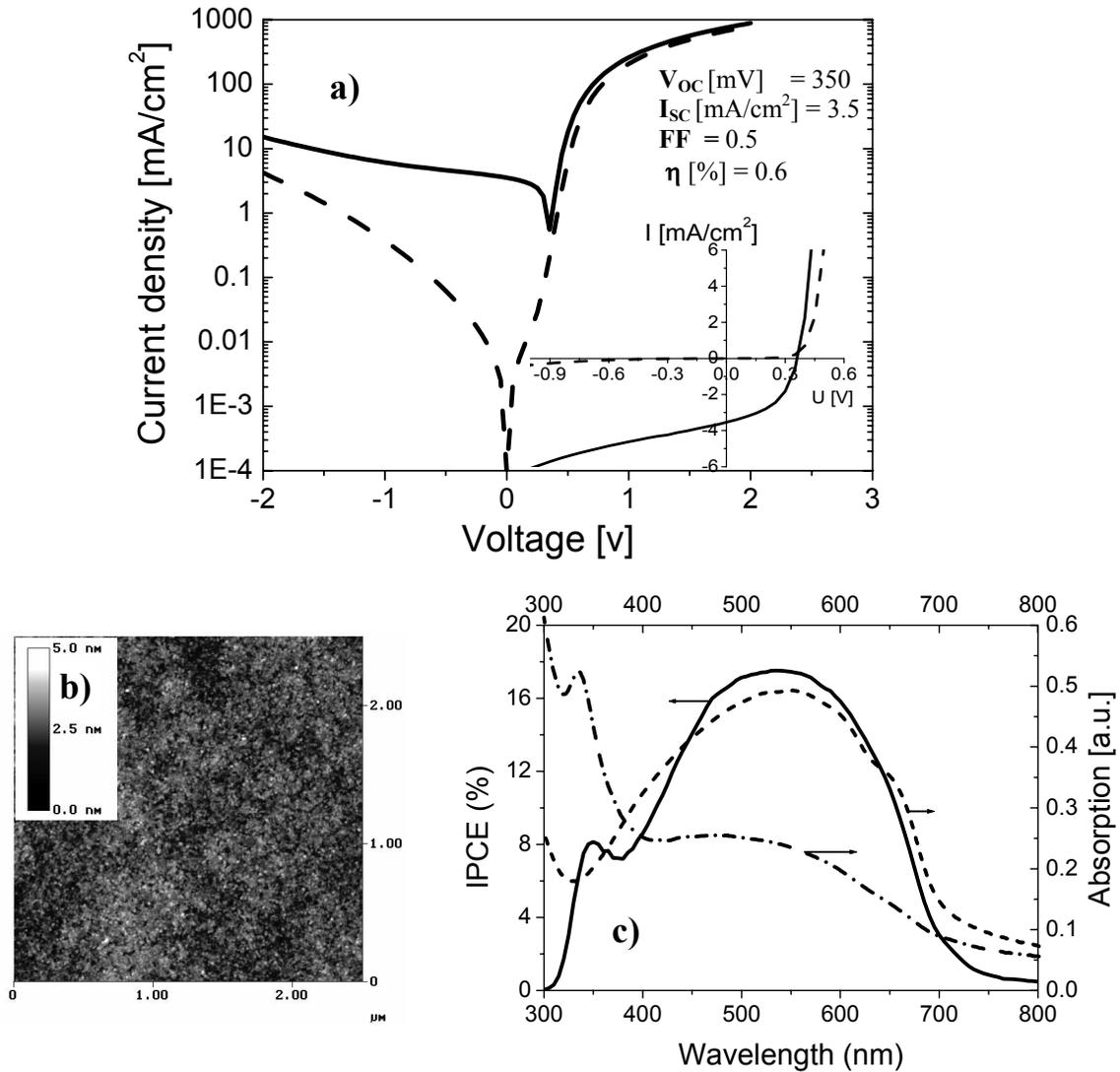

Figure 6: a) I-V characteristics (AM 1.5, 100 mW/cm^2) of the PTV:PCBM 1:2 device prepared from 1 wt.-% solution in CB; b) Morphology of the active film; c) IPCE % spectrum of the device (solid line) and the corresponding optical absorption for the pristine PTV (dashed line) and PTV:PCBM blend (1:2 wt) (dashed dot line) films.

In summary, the soluble precursor route has been successfully applied to the preparation of the low bandgap polymer poly(thienylene vinylene) 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 with short circuit currents up to ~ 4 mA/cm^2. 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.

Acknowledgements

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