Research Article

Opto-Electrical Properties of Composite Materials Based on Two Benzotrithiophene Copolymers and Fullerene Derivatives

N. Radychev 1, M. L. Keshtov, 2 H. Borchert, 1 Y. Bondarchuk, 1 S. A. Kuklin, 2 A. Korotaeva, 3 Z. Xie, 4 D. Godovsky, 2 A. R. Khokhlov, 2 and J. Parisi 1

1University of Oldenburg, Department of Physics, Energy and Semiconductor Research Laboratory, Carl-von-Ossietzky Str. 9-11, 26129 Oldenburg, Germany
2Vavilovast., 28, Institute of Organoelement Compounds of the Russian Academy of Sciences, 119991 Moscow, Russia
3University of Oldenburg, Department of Computing Science, Escherweg 2, 26121 Oldenburg, Germany
4Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, No. 5625 Renmin Rd., Changchun, Jilin 130022, China

Correspondence should be addressed to N. Radychev; nicolay.radychev@uni-oldenburg.de

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Two donor–acceptor copolymers based on a benzotriophene acceptor unit and an electron-donor segment of 4,8-didodecyloxybenzo[1,2-b;4,5-b']dithiophene were investigated in the view of photovoltaic application. We provided the complete synthesis procedure supported with NMR spectra of the monomers obtained. The resulting copolymers, labeled P1 and P2 in this work, exhibit strong absorption in the visible region with a similar band gap of about 2.2 eV. In spite of the chemical similarity of both copolymers, the photovoltaic and carrier transport properties of the P1- and P2-based devices demonstrated a noticeable difference. Applying an optimization procedure, a power conversion efficiency of 4.6% has been achieved for the P2/PC 71BM solar cells.

1. Introduction

Over the past years, since Tang et al. reported on a breakthrough in the polymer solar cells, a lot of efforts have been put into the development of organic photovoltaics [1–10]. Although electronic characteristics of the organic materials are still below those of usual inorganic semiconductors, such drawbacks might be compensated by fabrication on flexible substrates via inexpensive solution-phase techniques common in plastic manufacturing, e.g., applying roll-to-roll printing technology. The effective strategy to improve the performance of organic solar cells is the development of novel materials with promising photovoltaic properties. The power conversion efficiency (PCE) in the range of about 8–12% has been achieved for a number of bulk heterojunction solar cells based on novel absorbers with enhanced intrinsic properties [11–16]. One of the promising building blocks for the donor–acceptor copolymers is the benzothiophene (BTT) structure, which demonstrates encouraging characteristics for organic electronics technology [17–22]. A large BTT structure is planar and leads to an effective intermolecular packaging in the solid state. Thereby, BTT-based copolymers have a highly ordered crystal structure and usually exhibit a high mobility of charge carriers in organic field-effect transistors [20, 21].

In spite of BTT blocks having an evident perspective for efficient photovoltaic devices, the synthesis and investigation of the BTT-containing copolymers are rather limited in comparison with the extensively studied benzodithiophene derivatives. In a recent report, we demonstrated that a BTT fragment, which is usually serving as a donor unit for the synthesis of conjugated copolymers, might perform the function of the electron acceptor moiety owing to the carbonyl group attached [23]. In that work, we described the general pathways of the synthesis procedure and performed a few initial tests towards the application potential of two corresponding donor–acceptor copolymers (labeled P1 and P2 in the following, respectively) in the field of organic photovoltaics.
Polymer–fullerene solar cells with P1 and P2 yielded up to 1.7% and 2.5% power conversion efficiency (PCE), respectively [23]. These experimental findings motivated us to focus current research on the opto-electrical properties of both P1 and P2 materials and their mixtures with fullerene derivatives.

2. Experimental

2.1. Experiments and Characterization Methods. 1H and 13C NMR spectra of the initial reagents and copolymers have been recorded on a spectrometer (Bruker Avance-400) operating at 400.13 and 100.62 MHz, respectively. The optical properties of the copolymers have been investigated with a Varian Cary 50 Scan spectrophotometer. The films were prepared by spin-casting of either P1 or P2 copolymers dissolved in anhydrous 1,2-dichlorobenzene (DCB) with a concentration of 6 mg/ml on quartz substrates. A xenon lamp has been used as an excitation source. The electrochemical properties have been examined by cyclic voltammetry (CV). Cyclic voltammograms were recorded on a CH Instruments (CHI660C) electrochemical work station with a three-electrode cell at a scan rate of 100 mV s\(^{-1}\) (glassy carbon electrode, Pt wire, and saturated calomel electrode). \(\text{Bu}_4\text{NPF}_6\) (0.1 mol\(\cdot\)l\(^{-1}\)) was used as an electrolyte, and anhydrous acetonitrile (drying with CaH\(_2\)) was used as the solvent. Copolymers dissolved in DCB were drop-casted on the working electrode and dried under vacuum (~10\(^{-2}\) torr) for 30 minutes. Transmission electron microscopy (TEM) of the active layers was performed on JEOL JEM-1011 operated at an acceleration voltage of 100 kV. Polymer–fullerene films for TEM were prepared in identical conditions to those prepared for device fabrication. The samples were immersed in water, and the active layer floating on the water surface was transferred to a TEM grid.

2.2. Fabrication and Characterization of Thin Film Transistors and Organic Solar Cells. The thin film transistors (TFTs) were prepared in order to examine the transport properties of both P1 and P2 copolymers. TFTs were fabricated on heavily n-doped silicon wafers with 230 nm thermally grown SiO\(_2\) dielectric layers and equipped with 16 transistors per substrate. Source and drain contacts are interdigitated structures (10 nm ITO, 60 nm Au) with channel lengths \(L = 2.5, 5, 10,\) and 20 \(\mu\)m and channel width \(W = 1\) cm. All of the transistors were in the bottom-contact configuration with gold electrodes. The substrates were purchased from Fraunhofer IPMS (Dresden). The gate dielectric capacitance was calculated to be 17 nF/cm\(^2\). The wafers were cleaned in acetone and isopropyl alcohol in an ultrasonic bath. This procedure was finished with Tauc’s model [26]. Figures 2 and 3 demonstrate the plot of \((\alpha t h v)^2\) versus \(hv\) corresponding to the allowed
direct optical transitions for both P1- and P2-based thin films. The values of the energy gaps of $E_{g1}^{opt} = 2.25$ eV (for P1 copolymer) and $E_{g2}^{opt} = 2.12$ eV (for P2 copolymer) were derived by extrapolating the linear segments to the hv axis.

The electrochemical properties of the copolymers have been examined by CV measurements. Figure 4 shows exemplarily cyclic voltammograms of thin films spin-casted from DCB solutions. Both copolymers revealed reversible redox properties due to the high electroactivity. We attribute the cathodic reduction peak to the formation of thiophene radical anions, while the anodic oxidation peak likely corresponds to the radical cations of the thiophene moiety. The position of the energy levels was calculated from the oxidation potential $E_{ox}$ and the reduction potential $E_{red}$ in accordance with the equations:

$$E_{Homo} = -e(E_{ox} + 4.8) \text{ eV},$$

$$E_{Lumo} = -e(E_{red} + 4.8) \text{ eV}.$$

Taking here the onset potentials, the ionization potential ($E_{Homo}^{1}$) and electron affinity ($E_{Lumo}^{1}$) values of P1 were found to be $-5.2$ eV and $-3.0$ eV, respectively. The corresponding values for P2 were $-5.1$ eV and $-2.8$ eV, respectively. The bandgaps obtained ($E_{g}^{ech}$) from CV measurements are in close agreement with the optical bandgaps estimated. The electrochemical parameters and the bandgaps derived from Tauc plots are summarized in Table 1.

### Table 1: Electrochemical parameters and optical bandgaps of P1 and P2.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{Homo}$ (eV)</th>
<th>$E_{Lumo}$ (eV)</th>
<th>$E_{g}^{ech}$ (eV)</th>
<th>$E_{g}^{opt}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>$-5.2$</td>
<td>$-3.0$</td>
<td>$2.2$</td>
<td>$2.25$</td>
</tr>
<tr>
<td>P2</td>
<td>$-5.1$</td>
<td>$-2.8$</td>
<td>$2.3$</td>
<td>$2.12$</td>
</tr>
</tbody>
</table>

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### 3.2. Charge Transport Properties. The potential of two donor–acceptor copolymers as hole transporting materials has been evaluated in TFT structures. Analyzing transistor characteristics, we extracted parameters such as the field-effect mobility ($\mu_{fe}$) and threshold voltage ($V_{th}$), which in turn have a strong influence on the solar cell performance.
The value of $\mu_{fe}$ can be extracted from either the saturation or linear regime of the current-voltage characteristics. However, it was shown that field-effect mobility determined from the linear regime characterizes more precisely the intrinsic properties of a material and estimates the maximum mobility value in a real transistor [27]. Hence, in this work, $\mu_{fe}$ has been derived from the linear regime in accordance with [28].

The typical transfer curves and output characteristics of both P1 and P2 materials at room temperature are shown in Figure 5. In the linear regime, $\mu_{fe}$ was evaluated from the current-voltage characteristics of the FET using the following equation, when the source-drain current $I_{sd}$ is plotted against the gate voltage $V_{gs}$ at a low, constant source-drain voltage $V_{sd}$:

$$\frac{\partial I_{sd}}{\partial V_{gs}} = \mu_{fe} W C_i \frac{V_{sd}}{L},$$

where $W$ is the width of the channel, $C_i$ is the capacitance per unit area of the oxide layer, and $L$ is the length of the channel. The average value of $\mu_{feP1}$ obtained for the device based on P1 copolymer was $4.1 \times 10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$ with a threshold voltage of $-34$ V. The transport characteristics of the P2 samples revealed us a considerable enhancement of the hole mobility. The current measured in P2-based FETs was about a factor of 3 greater when compared with P1-based transistors. The average value of $\mu_{feP2}$ was found to be $2.5 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$, while the threshold voltage remained almost unchanged. We note here that, contrary to expectations, structurally very similar organic materials demonstrated significant difference in charge transport properties. It is reasonable to attribute the phenomenon observed to variable positions of the sulfur atom in copolymers investigated, which plays a key role in the formation of intermolecular interactions and, consequently, impact on the hole transport properties [29, 30].

3.3. Photovoltaic Response of P1-Based Devices. The photovoltaic response of the copolymers was investigated by fabricating conventional bulk heterojunction solar cells with fullerene derivatives. In order to optimize the performance of the solar cells prepared, the polymer–fullerene weight ratio and the thickness of the active layer were stepwise varied. At the initial stage of the solar cell investigation, we observed a poor performance of the devices based on P1. Specifically, we obtained extremely low fill factor (FF) of about 0.4 and the maximum PCE of 1.6% even when the optimization procedure has been applied (Figure S4). We assume that limited hole mobility of P1 (obtained in Section 3.2) results in an inefficient charge carrier collection process and, hence, significantly reduces both the FF and photocurrent of P1-based solar cells [31–34]. Moreover, the low value of $\mu_{feP1}$

![Figure 5: Output (a and c) and transfer (b and d) characteristics of thin film transistors based on either P1 (a and b) or P2 (c and d) copolymers.](image-url)
can aggravate the problem of balanced charge mobility in the bulk leading to the creation of a space charge region, which may limit the photovoltaic performance as well. Owing to these causes, the photovoltaic parameters presented in Figure S4 are far behind in comparison with state-of-the-art devices based on BTT materials \cite{18, 35}. The current density-voltage characteristics of the P1-based devices are summarized in Table S1.

### 3.4. Performance of P2-Based Solar Cells

In contrast, the laboratory devices mixed with P2 demonstrated reasonable photoresponse, pointing to a promising potential for PV application. Taking these results into account, we focused our efforts on the P2-based solar cells.

According to a number of studies, the polymer:fullerene ratio in the organic solar cells is generally spread in the range of 1:3 \cite{36}. Slight variations of the fullerene ratio with respect to the conjugated polymer demonstrate noticeable impact on the photovoltaic parameters. As shown in Figure 6(a), the short-circuit current density ($J_{sc}$) increases from 5.3 mA/cm$^2$ to 6.1 mA/cm$^2$ for a polymer:fullerene ratio of 1:1 and 1:1.5, respectively. Subsequent growth of the fullerene content in the organic mixture results in slight reduction of the photovoltaic characteristics. The noticeable influence of the higher PC$_{61}$BM blending ratio on the density of free charge carriers extracted at the electrodes is represented in Figure 6(b). The advanced devices demonstrate broad photoresponse in the visible part of the spectrum with external quantum efficiency (EQE) up to 52%. It is important to note that we observed about 10% enhancement in EQE within the wavelength range of 450–600 nm for the samples with optimized fullerene content. The corresponding photovoltaic performance values of the solar cells with different ratios are summarized in Table S2.

![Figure 6](image1.png)

**Figure 6:** $J$-$V$ and EQE characteristics of P2/PC$_{61}$BM solar cells with different polymer–fullerene weight ratios. Thickness of the active layer is 110 nm.

![Figure 7](image2.png)

**Figure 7:** TEM picture of P2/PC$_{61}$BM active layers.

It is known that either polymer–fullerene or hybrid solar cells work best across a narrow range of the active layer thickness. However, due to different charge transport characteristics of materials investigated, there is still a wide spread of results discussed in the literature for the appropriate thickness of the absorber, values ranging from 55 nm to 200 nm \cite{36–41}. Applying a favorable polymer:fullerene ratio of 1:1.5 and keeping all other conditions of the solar cell preparation constant, the photovoltaic properties of samples set with different active layer thickness were investigated. As can be seen from Table S3, the variation of the active layer did not result in evident improvement of $J_{sc}$ and open-circuit voltage ($V_{oc}$), which were in the range of 5.8–6.1 mA/cm$^2$ and 0.82–0.85 V, respectively. However, the fill factor (FF) increases from 58% for a thickness of 130 nm to 65% for an 80 nm thick active layer, leading to...
a PCE enhancement from 2.7% up to 3.3% (Figure S5). For devices with an absorber layer thinner than 80 nm, we observed a dramatic drop of the photocurrent that is attributed, in the first place, to an insufficient light-harvesting process. The results obtained are in good agreement with theoretical modeling done for polymer–fullerene solar cells and with our previous studies devoted to the inorganic–organic solar cells [42, 43]. The active layer morphology of P2/PC_{61}BM was controlled by microscopic analysis. According to the differences in the electron scattering densities, the bright and dark regions observed in the TEM picture correspond to polymer and fullerene rich domains, respectively [44]. Figure 7 shows similar bicontinuous blends consisting of P2 and PC_{61}BM nanostructured clusters and pointing to appreciable miscibility between the copolymer and fullerene acceptor. However, it is important to note that we observed a poor fibrillar structure associated with the P2 crystalline phase. This finding can cause suppressed charge transport across the polymer matrix and limited photovoltaic performance of P2/PC_{61}BM solar cells.

Next, we also examined a combination of P2 with the PC_{71}BM acceptor. It is well established that PC_{71}BM has similar to PC_{61}BM electronic properties but demonstrates a stronger absorption in the visible region [44]. The current density versus voltage characteristics (J–V) of the P2/PC_{61}BM and P2/PC_{71}BM solar cells fabricated in accordance with optimized parameters are shown in Figure 8(a). The application of PC_{61}BM did not significantly influence $V_{oc}$ and FF of the P2/PC_{71}BM devices when compared with P2/PC_{61}BM solar cells (Table 2). However, we observed considerable improvement of the $J_{sc}$ from 6.1 mA/cm$^2$ to 8.8 mA/cm$^2$, which is confirmed by the EQE spectrum as well (Figure 8(b)). The external quantum efficiency of the P2/PC_{71}BM devices exhibits superior photoresponse when compared with P2/PC_{61}BM samples, approaching a value of the EQE of about 60% in the wavelength range from 420 nm to 550 nm. The integration of the EQE spectra for the devices investigated with AM 1.5G solar spectrum revealed us slightly smaller $J_{sc}$ than the values gained from J–V curves (see Table 2), but these differences are not significant and theoretical values of $J_{sc}$ are in good agreement with the experimental data. Controlling the morphology of the P2/PC_{61}BM active layers, we observed pronounced nanomter-scale phase separation. However, in comparison with P2/PC_{61}BM, P2/PC_{71}BM-based films demonstrated rather unique morphology, where bundles of P2 fibrils can be distinguished. We speculate that advanced performance of the P2/PC_{71}BM solar cells originates not only from the stronger absorption of PC_{71}BM in the visible range but also from enhancement of the charge-transfer pathways shown in Figure 9. Omitting the introduction of processing additives in the bulk heterojunction solution, the best samples based on the P2/PC_{71}BM active layers achieved PCE of 4.6%. The photovoltaic parameters obtained are comparable with the results discussed in similar studies and related to BTT-containing organic solar cells [35, 45]. We should note that photovoltaic response achieved in this work is still behind the PCE of the champion device based on BTT building blocks [46]. Additional strategies, like solvent additives and extra purification of P2 copolymer, might bring further advance in the photovoltaic performance of the devices investigated.

### Table 2: Photovoltaic parameters of P2-based solar cells mixed with different acceptors.

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$J_{sc}^{a}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC_{61}BM</td>
<td>0.84</td>
<td>6.1</td>
<td>5.9</td>
<td>62.5</td>
<td>3.2</td>
</tr>
<tr>
<td>PC_{71}BM</td>
<td>0.83</td>
<td>8.8</td>
<td>8.5</td>
<td>63.1</td>
<td>4.6</td>
</tr>
</tbody>
</table>

*Calculated from EQE.

### 4. Conclusion

We have designed and synthesized two BTT-based D-A copolymers, labeled P1 and P2. The optical and electrochemical properties of the copolymers demonstrated a strong...
absorption in the UV-visible region with similar bandgap values of about 2.2 eV. The potential of both copolymers as hole transporting materials has been evaluated in TFT structures. The average values of the field-effect mobility obtained for the device based on either P1 or P2 were 4.1 × 10⁻⁶ cm² V⁻¹s⁻¹ and 2.5 × 10⁻⁶ cm² V⁻¹s⁻¹, respectively. Thus, although the structure of the polymers is rather similar, a pronounced difference of the hole mobility was found. In spite of the fact that we did not achieve a reasonable photovoltaic response for the laboratory devices with a bulk heterojunction composed of the P1 copolymer and fullerene derivatives, the solar cells based on P2:fullerene blends revealed us promising photovoltaic characteristics. P2/PC₆₁BM devices demonstrated performance parameters of a short-circuit current density up to 8.8 mA/cm², an open-circuit voltage of 0.83 V, a fill factor of about 63%, and up to 4.6% power conversion efficiency. The photovoltaic parameters obtained are comparable with known BTT-based organic solar cells so that the new BTT-based copolymer P2 appears as a perspective material for further investigation and advancement in the field of organic electronics.

Data Availability

The absorption data, the data related to transfer characteristics of thin film transistors, and J-V and EQE characteristics of the solar cells investigated are available from the corresponding author upon request. The data describing the chemical structure of the copolymers might be found in Supplementary Materials.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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Supplementary Materials

The synthesis pathways of copolymers investigated and characterization of the intermediate compounds by elemental analysis, IR spectroscopy, ¹H and ¹³C NMR are described. Additional photovoltaic characterizations of P1/PC₆₁BM and P2/PC₆₁BM solar cells are available as well. Figure S1: the synthesis pathways of monomers 5 and 8. Figure S2: ¹H (a) and ¹³C NMR (b) spectra of 2,5-dibromo-8-dodecanoylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene (5). Figure S3: ¹H NMR of the polymers P1 (a) and P2 (b). Figure S4: J-V and EQE characteristics of P1/PC₆₁BM solar cells with different polymer–fullerene weight ratios. Figure S5: J-V and EQE characteristics of P2/PC₆₁BM solar cells with different active layer thickness. Table S1: photovoltaic characteristics of P1/PC₆₁BM devices with different polymer–fullerene weight ratios. Table S2: photovoltaic characteristics of P2/PC₆₁BM devices with different polymer–fullerene weight ratios. Table S3: photovoltaic characteristics of P2/PC₆₁BM devices with different thickness of the active layers. (Supplementary Materials)

References


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