

Research Article

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Photoconductivity of Low-Bandgap Polymer and Polymer: Fullerene Bulk Heterojunction Studied by Constant Photocurrent Method

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Abstract: Optical and photoelectric properties of modern photosensitive polymers are of great interest due to their prospects for photovoltaic applications. In particular, an investigation of absorption and photoconductivity edge of these materials could provide valuable information. For these purpose we applied the constant photocurrent method which has proved its efficiency for inorganic materials. PCDTBT and PTB7 polymers were used as objects for the study as well as their blends with a fullerene derivative PC₇₁BM. The measurements by constant photocurrent method (CPM) show that formation of bulk heterojunction (BHJ) in the blends increases photoconductivity and results in a redshift of the photocurrent edge in the doped polymers compared with that in the neat polymers. Obtained from CPM data, spectral dependences of absorption coefficient were approximated using Gaussian distribution of density-of-states within HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) bands. The approximation procedure allowed us to evaluate rather optical than electrical bandgaps for the studied materials. Moreover, spectra of polymer:PC₇₁BM blends were fitted well by the sum of two Gaussian peaks which reveal both the transitions within the polymer and the transitions involving charge transfer states at the donor-acceptor interface in the BHJ.

Keywords: photoconductivity; constant photocurrent method; organic solar cell; density-of-states; PTB7; PCDTBT; bulk heterojunction

1 Introduction

The development of polymeric solar cells has received a great deal of attention from both academic and industrial laboratories because of low cost, flexibility, abundant availability and simple solution-processed technologies applicable for the preparation of organic-based devices. Many recent successes in organic solar cells have been achieved due to the use of bulk heterojunction (BHJ) which is formed in a polymer composite at the interface between the mutually penetrating phases of an electron-donating semiconducting polymer and an electron-accepting fullerene. A specific feature of nonequilibrium charge generation in polymeric semiconductors is that the optical absorption at room temperature generates a neutral particle (exciton) rather than free electron and hole. This occurs due to the rather small value of the dielectric constant in polymers (~3–4 [1]) and consequently the relatively high Coulomb binding energy of the generated electron–hole pair (up to 0.5 eV [2, 3]). The dissociation of the exciton into an electron and a hole occurs at the heterojunction. The diffusion length of excitons in the disordered organic (polymeric) medium does not exceed 13–15 nm [4]. The formation of BHJ in the photoactive layer of a polymer solar cell increases the probability of exciton reaching the interface between donor and acceptor components of the BHJ.

Up to date the physical processes governing the generation, transport and recombination of nonequilibrium charge carriers in the BHJ layer are not completely understood. In particular, there is lack of information on the

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photoconductivity and absorption on the absorption edge of low-bandgap polymer materials. However the BHJ formation should affect materials properties in the spectral region close to the absorption edge. Various techniques, both experimental one such as electrochemical method [5] and numerical simulation by Monte Carlo method [6], are developed for the investigation of the electrical bandgap in such polymer materials and BHJ. Yet, accurate measurements in the low-energy spectral region are difficult to accomplish due to weak absorption of thin films. One of the techniques used to study the absorption edge region in photosensitive materials is constant photocurrent method (CPM) [7]. The method allows one to obtain the spectral dependence of the absorption coefficient, α_{CPM} , for optical transitions leading to the photoconductivity. It allows one to avoid the influence of the spectral dependence of the charge carriers lifetime that occurs when the photoconductivity spectra are used to determine the absorption coefficient spectra. More details on the CPM are described elsewhere [7].

In the study, we examined photoelectric properties of low-bandgap polymers having π -conjugated electrons and their donor-acceptor composites with a fullerene derivative, which form a bulk heterojunction. Specimens of planar configuration instead of sandwich configuration were used. The planar electrodes geometry with ohmic contacts allowed us to avoid the nonlinearity of the current–voltage characteristic of solar cell and, therefore, simplified the analysis of experimental data. Photocurrent spectra measured by CPM were fitted assuming the Gaussian distribution of density-of-states (DOS) of HOMO and LUMO bands.

2 Experimental Procedures

In the work, two promising low-bandgap polymers Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) from 1-Material Inc. and Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) from Ossila Ltd. used as electron donor materials. Intensely studied [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM) from SES Research was used as an acceptor material. The chemical structures of these materials are shown in Figure 1.

The PTB7:PC₇₁BM (1:1.5 by weight) and PCDTBT:PC₇₁BM (1:4 by weight) composites as well as the individual polymers were dissolved in chlorobenzene and the solutions were stirred for 12 h. The layers with a thick-

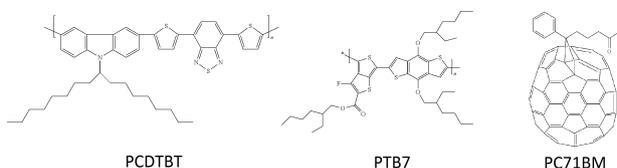


Figure 1: Structure of the chemicals under study.

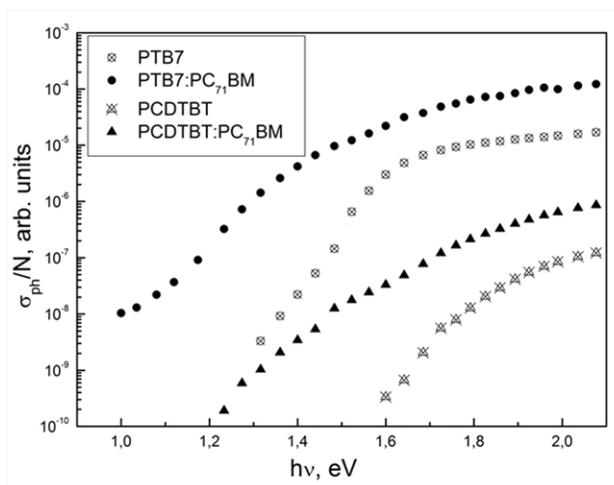


Figure 2: Spectral dependences of the photoconductivity for layers of the PTB7 and PCDTBT polymers and their blends with PC₇₁MB.

ness of 50 nm (polymers) and 100 nm (polymer-fullerene blends) were prepared by spin-coating the solutions onto quartz substrates. The layers were dried in air at room temperature for 24 h. The thickness of the film was measured with a Bermad 2000 atomic force microscope. The couples of planar electrodes (20 nm of gold followed by 40 nm of aluminum) were deposited on the top of the active layers by thermal evaporation in vacuum (at a residual pressure of 10⁻⁴ Pa). The length of the planar electrodes was 10 mm and the distance between them was 0.5 mm. The value of an electric field applied to a sample was 100 V/cm. This value corresponded to the ohmic range of $I - V$ curves. All the measurements were carried out in air at room temperature. VIS-NIR Cornestone 130 monochromator system (LOT-Oriel) with halogen light source and two-color detector K1713-09 (Hamamatsu) were used in photoconductivity measurements. CPM in dc mode was used to obtain data on spectral absorption coefficient of absorption coefficient.

3 Results and Discussion

Figure 2 shows spectral dependences of the photoconductivity $\Delta\sigma_{ph}$ normalized to the number of incident photons (N) for the samples of PTB7 and PCDTBT and their com-

posites with PC₇₁BM. It is seen that in the entire spectral range under study, the photoconductivity of the polymers is lower than that of their associated composites with PC₇₁BM. The result confirms the conventional concept that the formation of BHJ of the donor and acceptor components provides enhanced separation of photogenerated excitons into free electrons and holes at the heterojunction interface and, as a consequence, increases the photoconductivity of such composite material. It is also seen in Figure 2 that for the both polymer composites the photoconductivity edge is shifted to lower photon energies with respect to the individual polymers. Reason for such redshift of the photoconductivity edge is still discussed [8]. In most studies, the reason is assumed to be caused by the generation of charge carriers in the BHJ region via the charge-transfer (CT) states, with the energy of formation of the CT states being lower than that of exciton formation in the individual materials constituting the blend [9]. Figure 3 shows a schematic energy diagram of the BHJ structure illustrating the band offset between the two materials and optical transitions corresponding to bulk and interface of the materials. The interface band gap, E_{gl} , and possible distribution of the states $N(E)$ in the bands [10] are also shown in Fig. 3. The direct excitation of electron-hole pairs at the interface should be efficient because it does not require an exciton to migrate to the interface for dissociation. In common with other studies of the photoconductivity in the low-energy range [10], we attribute the photoconductivity edge in the spectra under the study to charge-transfer excitations across the interface band gap from HOMO of the polymer to LUMO of PC₇₁BM.

It is important to mention that CPM is sensitive only to the light absorption which results in photoconductivity. Therefore measured absorption coefficient α_{CPM} can differ from the conventional α . Anyway, the results of CPM measurement should provide data on electrical band gap rather than optical one. The spectral dependences of the absorption coefficient α_{CPM} near the photoconductivity edge are shown in Figures 4(a) and 5(a). The edge of the each polymer composite is shifted toward long wavelengths compared with that for the corresponding individual polymer. The spectral dependences of the absorption coefficient in disordered organic semiconductors make it possible to determine the band gap width providing the distribution of DOS $N(E)$ of electrons in the valence and conduction bands of a material is known. In such a case, the spectral dependence of the absorption coefficient obeys the relation (1):

$$\alpha(h\nu) \sim \int \frac{N_V(E)N_C(E+h\nu)|M|^2}{h\nu} dE \quad (1)$$

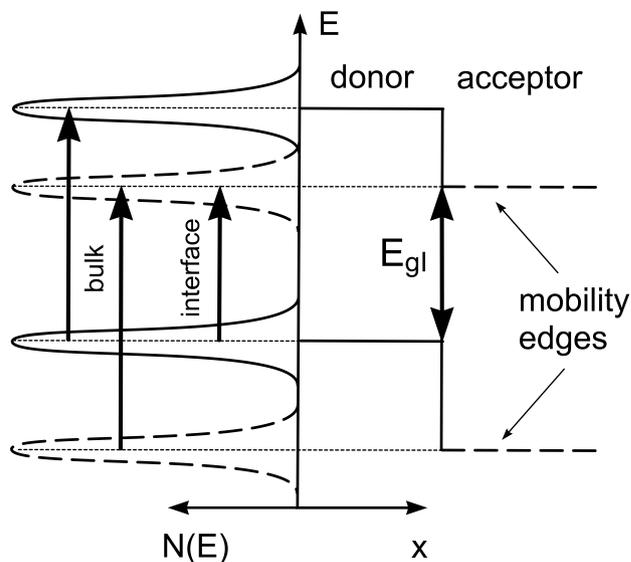
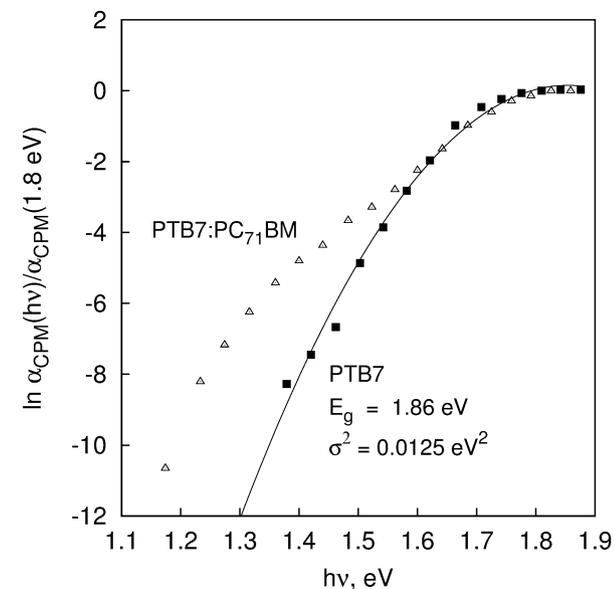


Figure 3: Schematic band diagram illustrating the band offset, interface band gap E_{gl} and distribution of the states $N(E)$ of the component materials. Optical transitions are also shown.

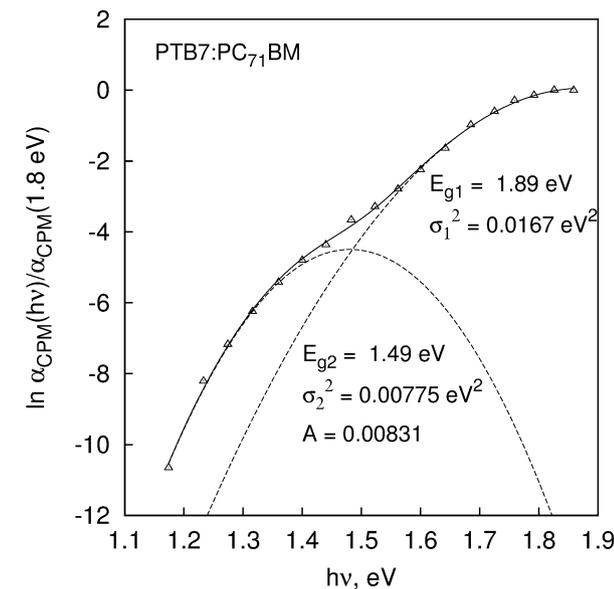
where $h\nu$ is the photon energy, M is the transition matrix element, $N_V(E)$ and $N_C(E)$ is the energy distribution of DOS for HOMO and LUMO, respectively. For the most organic semiconductors, the $N(E)$ distribution in the band is considered to have Gaussian dependence on energy [10] (Fig. 3). For PTB7, PCDTBT and their composites with PC₇₁BM, we also used the Gaussian DOS to determine electrical band gap widths by approximating the spectral dependences of the absorption coefficient α_{CPM} .

If both DOS for the lower and upper levels are Gaussian ones, then the absorption coefficient also has a Gaussian shape (divided by $h\nu$, in agreement with eq. 1) centered around E_g with variance σ^2 being the sum of the corresponding values for two DOS. We assumed here that the matrix element M has no significant dependence on E . For this reason we fitted the experimental data for the neat polymers assuming the Gaussian shape of α_{CPM} .

The optimal magnitudes of E_g are 1.86 eV and 2.18 eV for PTB7 and PCDTBT, respectively (see Fig. 4(a) and Fig. 5(a)). Within the limits of experimental error, the magnitude of $E_g = 1.86$ eV for PTB7 agrees very well with the energy corresponding to the optical absorption peak of the film [11] and with electrochemical bandgap (1.84 eV) determined by cyclic voltammetry [11, Supporting Inf.]. For PCDTBT, the magnitude of E_g (Fig. 5(a) and (b)) is exactly the maximum of the (excitonic) absorption of the film at 576 nm [12] but it differs from the optical bandgap (1.88 eV) and electrochemical bandgap (1.87 eV) presented in the same work [12]. The difference may originate from the more complicated distributions of DOS in the HOMO and LUMO



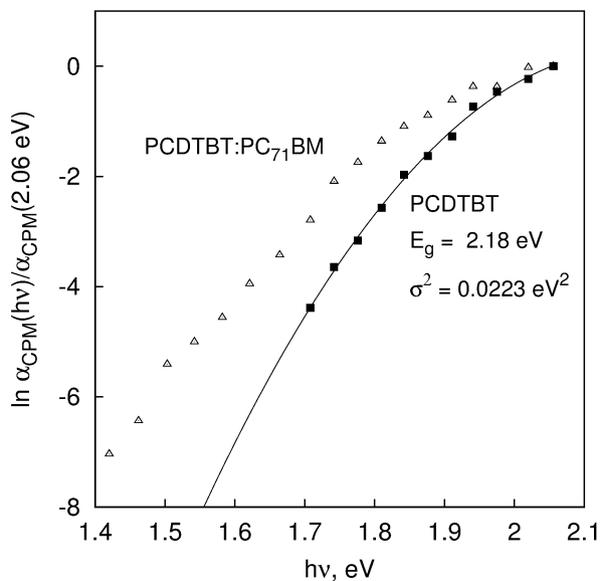
(a)



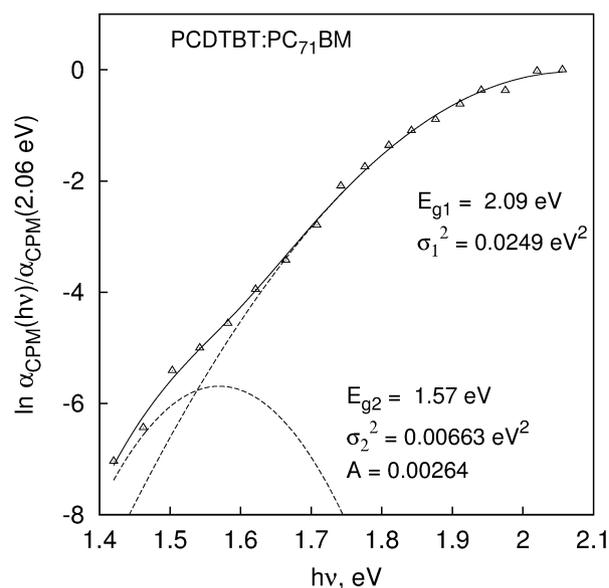
(b)

Figure 4: Spectral dependences of α_{CPM} for layers of the polymer PTB7 (a) and its blend with PC₇₁MB (b). Solid curves show the best fit for one (a) or two (b) Gaussian peaks using eq.2, broken curves show contributions from the individual peaks (b).

bands of PCDTBT than those in PTB7. Another reason is possible inaccuracy in determining the values of band gap from cathodic and anodic onsets which may be defined somewhat arbitrary. Thus, the bandgaps E_g obtained for the polymers by the application of Gaussian DOS correspond to the S0-S1 0-0 optical transition manifested itself as a long-wave peak in the UV-vis spectra.



(a)



(b)

Figure 5: Spectral dependences of α_{CPM} for layers of the polymer PTB7 (a) and its blend with PC₇₁MB (b). Solid curves show the best fit for one (a) or two (b) Gaussian peaks using eq.2, broken curves show contributions from the individual peaks (b).

We expected that absorption of polymer-PC₇₁MB composites in the long-wave range should consist of both transitions within the polymer and transitions involving CT-states at the donor-acceptor interface in the BHJ (see Fig. 3). For the PTB7:PC₇₁MB and PCDTBT:PC₇₁MB blends the fit of α_{CPM} was performed for the sum of two Gaussian

peaks (Fig. 4(b) and Fig. 5(b)):

$$\alpha_{CPM}(h\nu) = \frac{const}{h\nu} \left\{ \exp \left[-\frac{(h\nu - E_{g1})^2}{2\sigma_1^2} \right] + A \exp \left[-\frac{(h\nu - E_{g2})^2}{2\sigma_2^2} \right] \right\} \quad (2)$$

and A is a relative weight of the low energy peak. The high-energy peak (around E_{g1}) corresponds to the transitions between HOMO and LUMO levels of the polymers and have common parameters with Gaussian obtained for the individual polymers. The peak in the low-energy range (around E_{g2}) more likely corresponds to the transitions from HOMO levels of the polymer to LUMO levels of PC₇₁BM. Thus, as seen from Fig. 4(b) and Fig. 5(b), the spectral dependences of α_{CPM} can be approximated well with two Gaussian peaks. This demonstrates the relevance of proposed DOS model.

4 Conclusions

The study demonstrated that insertion of an electron-acceptor fullerene derivative PC₇₁BM into an electron-donor polymer PTB7 or PCDTBT enhances the photoconductivity and shifts the photosensitivity edge towards longer wavelengths, which is presumably due to the generation of excitons at the interface of the bulk heterojunction. The application of the constant photocurrent method made it possible to get spectral dependences of the absorption coefficient determined by nonequilibrium charge carriers transitions in low absorption region close to the absorption edge of thin films. The bandgaps of studied organic materials were determined from the analysis of their spectra. The values of bandgap E_g and bandwidth σ determined under the assumption of the Gaussian shape of DOS distribution for HOMO and LUMO bands agree well with the similar parameters obtained by other methods.

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