Macromol. Symp. **2004**, *212,* 369-374

Photoelectric Properties of Tetracene-Pentacene Heterojunction

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Summary: We investigated vacuum-evaporated sandwich systems formed by two organic layers of pentacene and tetracene. We measured spectral dependences of photovoltaic short-circuit currents and photocurrents as well as current-voltage dependences. In the case of systems equipped with Au and CuI electrodes the structure of spectral characteristics is determined by exciton release of trapped charge carriers either in the bulk of tetracene or near tetracene-pentacene interface and by photogeneration in pentacene layer. For systems with two Au electrodes we can also observe an influence of exciton injection of holes into tetracene on spectral characteristics. The measurements of dark current-voltage characteristics allow to observe the presence of a potential barrier between tetracene and pentacene.

Keywords: charge transport; heterojunction; pentacene; tetracene; thin films

Introduction

Attractive photoelectric and electric properties of organic heterojunction, such as photovoltaic effects, electroluminescence or current rectification are the subject of great interest of scientists. Some features of these phenomena are difficult to explain due to great amount of charge carrier traps and uncontrolled impurities, which lead to complex processes of photogeneration and transport of charge carriers. Heterojunctions formed from organic materials therefore still require intensive investigation.

The object of our paper is to examine photoelectric properties of a heterojunction formed from polycrystalline layers of tetracene (Tc) and pentacene (Pn). Absorption spectra of Tc and Pn are distinctly separated and, as a result, we can analyze the mechanisms of charge carrier photogeneration and find the position of photoactive region in the system [1]. This heterojunction has not been investigated yet although we have already investigated the heterojunction formed from other oligoacenes (anthracene and tetracene) [2].

DOI: 10.1002/masy.200450844

Experimental

Measurements were performed on sandwich samples evaporated in vacuum with the following materials: Au on a glass substrate, Pn, Tc and Au (Au/Pn/Tc/Au samples) or Au on a glass substrate, Pn, Tc and Cu, which were treated with the vapour of iodine (Au/Pn/Tc/CuI samples). The thicknesses of single organic layers in one junction were the same and amounted to 100 nm or 200 nm. The sample was illuminated with monochromatic light in the range 370 nm - 740 nm, which includes singlet exciton absorptions of both Tc and Pn. Exemplary experimental results, including spectra of absorption, of short-circuit current and of photocurrent as well as dark current-voltage characteristics, are presented in Figs. 1-5. For all the spectra of the currents shown in this work, the flux density of monochromatic light penetrating into organic layers was 10^{13} photons/(cm^{2}s).

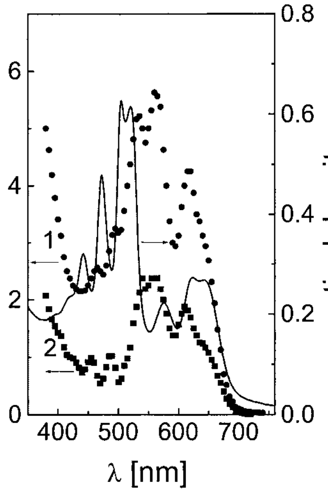

Figure 1. Short-circuit current spectrum of Au/Pn/Tc/CuI cell with 100 nm-thick organic layers illuminated through Au (1) and through CuI (2) and absorption spectrum of Pn/Tc bilayer (solid line).

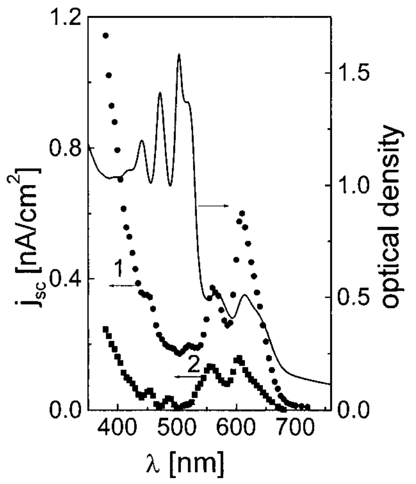

Figure 2. Short-circuit current spectrum of Au/Pn/Tc/CuI cell with 200 nm-thick organic layers illuminated through Au (1) and through CuI (2) and absorption spectrum of Pn/Tc bilayer (solid line).

The spectra of short-circuit currents of Au/Pn/Tc/CuI cells with 100 nm-thick (Fig. 1) or 200 nm-thick (Fig. 2) organic layers are plotted together with absorption spectra of the respective organic bilayers. Characteristics 1 refer to illumination from the Pn side of the sample while characteristics 2 refer to illumination from the Tc side.

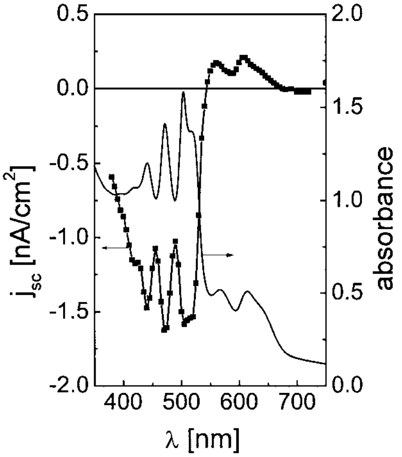

Figure 3. Short-circuit current spectrum of Au/Pn/Tc/Au cell illuminated from the Tc side and absorption spectrum of Pn/Tc bilayer (solid line).

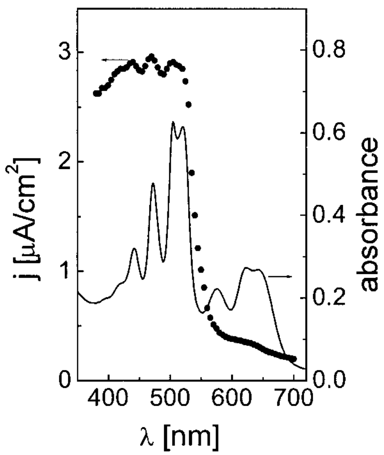

Figure 4. Photocurrent spectrum of Au/Pn/Tc/CuI cell with bias and absorption spectrum of Pn/Tc bilayer (solid line).

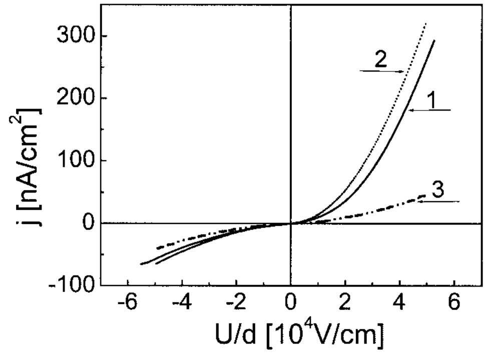

Figure 5. Dark current as a function of average electric field for Au/Pn/Tc/CuI with thicknesses of Tc and Pn 100 nm (1) or 200 nm (2) and for Au/Pn/Tc/Au with 200 nm-thick Tc and Pn layers (3).

Figure 3 shows the spectrum of short-circuit currents of Au/Pn/Tc/Au cell with 200 nm-thick organic layers illuminated from the Tc side. Positive values of short-circuit currents in Figs. 1-3 relate to the current flowing from Pn to Tc.

Figure 4 shows photocurrent spectrum of Au/Pn/Tc/CuI in the presence of bias equal to 0.5 V. The sample was illuminated through the Au electrode, which was negatively polarized. Thicknesses of organic layers were 100 nm.

Dark currents as a function of average electric field ($E=U/d$, where d is the sum of thicknesses of Tc and Pn layers) are presented in Fig. 5. Curves 1 and 2 refer to Au/Pn/Tc/CuI cells with 100 nm-thick (curve 1) or 200 nm-thick (curve 2) organic layers, while curve 3 refers to Au/Pn/Tc/Au cell with organic layers of 200 nm.

Discussion

The investigations of transport of charge carriers in organic systems require the use of appropriate electrodes. To examine the junction of Tc and Pn, between which a potential barrier for holes can be estimated as ca 0.3 eV (the difference between ionization energy of Tc, 5.3 eV, and Pn, 5.0 eV)[3], ohmic electrodes (such as CuI and Au) suitable for these materials should be applied[4]. Then only hole currents can flow through our systems.

Taking into account Figs. 1 and 2 in the range of tetracene absorption, we observe a correlation between maxima of short-circuit currents and minima of absorption spectra for both directions of illumination (antiparallel relations)[5]. Such profiles of short-circuit current spectra indicate that this current is determined by exciton release of charge carriers from traps in the whole bulk of Tc layer or near the Tc/Pn interface. In the case of thinner organic layers (Fig. 1), we do not observe pure antiparallel structure of short-circuit current spectrum for illumination through the Pn layer, which can result from a sequence of exciton detrapping of charge carriers occurring in the whole Tc layer and near the Tc/Pn junction. Comparing Figs. 1 and 2 we also come to the conclusion that the increase in layer thickness leads to a weakening of the spectrum structure in the range of Tc absorption.

On the other hand, in the case of Au/Pn/Tc/Au cell illuminated from the Tc side (Fig. 3) in the same range of absorption, maxima of short-circuit current correspond to maxima of absorption spectrum (parallel relation)[5] and the short-circuit current flows in opposite direction. This relation suggests that for the cell with two Au electrodes the short-circuit current is limited by exciton dissociation and hole injection occurring at the Au/Tc interface, so there is an additional barrier in Tc near Au electrode. The height of this barrier can be estimated as ca 0.3 eV (the difference between ionization energy of Tc (5.3 eV) and work function of Au (5.0 eV)).

Within the region of pentacene absorption (λ > 540 nm), all spectra of short-circuit currents (Figs. 1-3) correlate reasonably well with the absorption spectra of bilayers. This parallel structure of short-circuit current becomes more noticeable for a thicker layer, where short-circuit current associated with pentacene absorption dominates over the one associated with tetracene absorption. So, in the range of Pn absorption, spectra of short-circuit current are determined by charge carrier generation in the bulk of Pn[3,6]. Simultaneously, the importance of charge carrier injection from electrodes can be excluded because this process does not depend on the sample thickness.

Under the illumination through negatively polarized Au electrode, photocurrent of Au/Pn/Tc/CuI is evidently determined by exciton detrapping of charge carriers in Tc near the Tc/Pn interface (parallel relation in the range of tetracene absorption in Fig. 4) and charge carrier photogeneration in the bulk of Pn can be neglected.

The dependences of dark currents on average electric field are presented in Fig. 5. Curves 1 and 2 obtained from the cells with CuI are similar indicating that the electric properties of these systems are reproducible. Some difference between both curves results partly from the inaccuracy in determining the active surface of the samples and current density. The asymmetry of characteristics 1 and 2 observed for different directions of electric field results from the presence of Pn/Tc barrier, which should be overcome by holes flowing from Pn to Tc (range of negative electric fields). Such a barrier does not exist for the opposite direction of current (range of positive electric fields). On the other hand, in the case of the cell with two Au, a barrier at the Au/Tc interface exists also for positive fields. Therefore characteristic 3 is nearly symmetrical.

Conclusions

Our experimental investigation leads to the following conclusions:

- in the region of Tc absorption, the short-circuit current of Au/Pn/Tc/CuI is determined by charge carrier detrapping by excitons in the whole Tc layer or near the Tc/Pn interface,

- in the region of Pn absorption, the short-circuit current of Au/Pn/Tc/CuI is determined by charge carrier photogeneration in the Pn bulk,
- it is impossible to examine the transport of charge carriers through Pn/Tc heterojunction using Au as electrode for the Tc layer,
- in the presence of bias the photocurrent is determined by exciton detrapping of charge carriers in Tc near the Tc/Pn junction,
- asymmetry of dark current-voltage characteristics of systems with ohmic electrodes (Au and CuI) results from the presence of a potential barrier at the Pn/Tc interface.

Acknowledgements

Work was supported by KBN under Program No. 4 T11B 057 22.

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