

Potentialities of weak charge-transfer complexes based on conjugated polymers in plastic solar cells

D.S. Martyanov, A.A. Bakulin, A.N. Khodarev, S.G. Elizarov, I.V. Golovnin, D.Yu. Paraschuk
International Laser Center, Moscow State University, Moscow 119992, Russia

M.M. Triebel, I.V. Tolstov, E.L. Frankevich
*Institute of Energy Problems of Chemical Physics, Russian Academy of Sciences,
Leninsky prospect 38/2, Moscow 119334, Russia*

S.A. Arnautov, E.M. Nechvolodova, K.A. Ryzkova, N.V. Zhidkova
*Semenov Institute of Chemical Physics, Russian Academy of Sciences,
ul. Kosygina 4, Moscow 119991, Russia*

Combination of conductivity, optical properties, mechanical flexibility, and ease of processing of conjugated polymers make them promising materials for large-scale solar cells. It is generally accepted that photoinduced charge transfer from a conjugated polymer acting as a donor to an acceptor, for example, a fullerene molecule, is an effective way to generate mobile charges [1]. On the other hand, it is possible a more direct way from an incident photon to mobile charges using weak charge-transfer complexes (CTC) of Mulliken type [2]. CTC optical absorption formally implies donor-acceptor electron transfer and as a result a pair of separated charges can be formed. Furthermore, as known for short conjugated molecules, the CTC absorption band can be tuned in the region where both the donor and acceptor are transparent [2,3]. This can be used for tailoring low bandgap absorbing materials to match the solar spectrum. For example, a weak CTC between C₆₀ and Zn-phthalocyanine molecules was recently reported in [4]. Furthermore, a promising approach in plastic photovoltaics is using a bulk heterojunction in which photoexcitations dissociate into mobile charges throughout a donor-acceptor blend. However, the bulk heterojunction approach perturbs the working layer morphology lowering the device efficiency due to donor-acceptor phase segregation. As a CTC implies donor-acceptor attraction, it may be used to obtain a homogeneous working layer avoiding phase separation. In this work we were motivated by attractive potentialities of weak CTCs for using in plastic photovoltaics.

We studied blends of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) with 2,4,7-trinitrofluorene (TNF) or 2,6-dinitroantraquinone (DNAQ) by a number of optical and photoelectric methods at room temperature. Drop-cast films of MEH-PPV/TNF and MEH-PPV/DNAQ blends were prepared from different solvents. For photocurrent studies we fabricated single layer diodes in the sandwich structure on ITO-coated glass substrates. A top Al-electrode was deposited on the polymer film.

Figure 1 demonstrates optical absorption spectra of the donor-acceptor blends. It is seen that the blends have a long absorption tail extending into the near-IR spectral range. This change in the MEH-PPV absorption spectra indicates noticeable donor-acceptor interaction in their ground electronic states. Furthermore, a number of bands in the vibrational IR absorption spectra of the blends do not show additivity of those of MEH-PPV and the acceptor. These observations are a typical signature of a CTC [3]. We found that the photoluminescence efficiency of MEH-PPV is quenched in the blends up to three orders of value suggesting donor-acceptor charge transfer.

Figure 2 shows photoinduced absorption (PIA) spectra of pristine MEH-PPV and TNF/MEH-PPV blends. Bands at ≈ 0.65 and ≈ 1.3 eV in Fig. 2 indicate charge generation in the presence of the acceptor [1]. Essentially, these bands appear for both visible and infrared pump wavelengths with comparable efficiency per absorbed pump photon. Note, that for the infrared pump the PIA bands appear only in the blends.

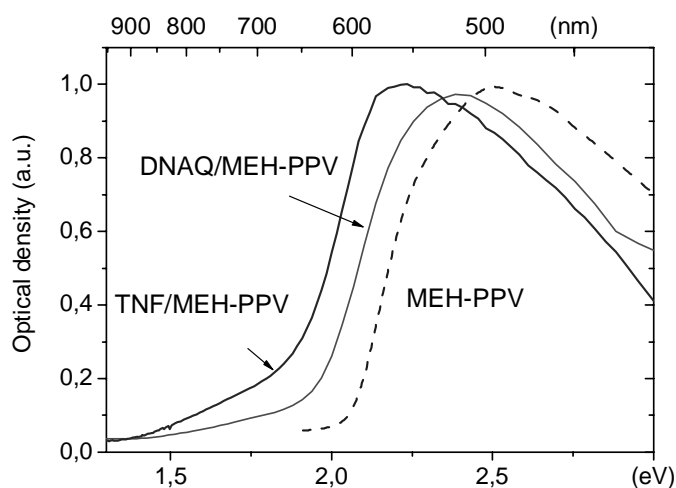


Fig.1. Absorption spectra of pristine MEH-PPV (dashed) and 1:1 acceptor/MEH-PPV (solid) films prepared by drop-casting from toluene.

We found that photoconductivity in the blends strongly increases compared to pristine MEH-PPV. We observed that the photocurrent photoexcitation spectrum of the 1:1 TNF/MEH-PPV blend closely follows its absorption spectra in the range 570-700 nm. In addition, to probe the charge photogeneration mechanisms, a magnetic field spin effect (MFSE) technique was applied [5]. This technique shows that the charge photogeneration mechanism is essentially different in the blends compared to pristine MEH-PPV. Strong correlation between the value of the MFSE and the acceptor concentration was detected.

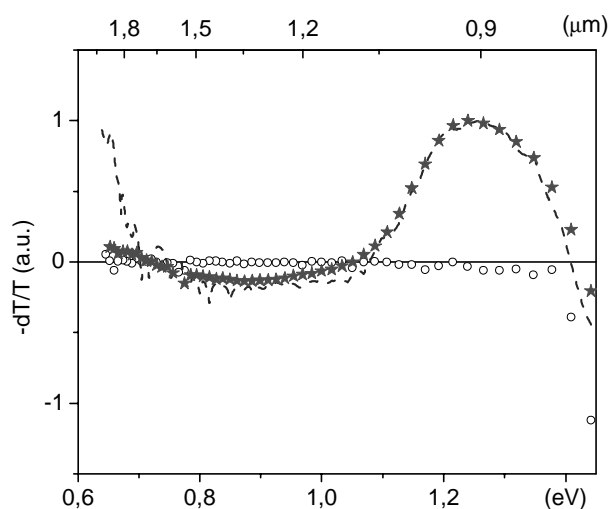


Fig.2. PIA spectra for MEH-PPV(\circ) and 1:1 MEH-PPV/TNF(\star) blend for photoexcitation at 810 nm. The dashed line shows the PIA spectrum of the blend for pump at 532 nm.

Thus, our data show that a weak CTC can be formed between TNF or DNAQ and MEH-PPV with noticeable absorption in the near-IR range. We found that photoexcitation in the CTC band can relax in charged states. Therefore, CTCs based on conjugated polymers are promising for plastic solar cells to extend their sensitivity in the near-IR range.

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