

Low bandgap photovoltaic polymer films based on intermolecular charge-transfer complex

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Conjugated polymers combine optical absorption, conductivity, mechanical flexibility, and ease of processing promising applications in photovoltaics especially in large-scale low-cost solar cells. The spectral range of photosensitivity of such devices is determined by the optical gap of a conjugated polymer used. However, they usually have the optical gap about 2 eV, while it needs to be considerably lower to match the solar spectrum. On the other hand, as is well known for small aromatic conjugated molecules, they can easily form intermolecular charge-transfer complexes (CTC) with a molecule having higher electron affinity [1]. These CTCs usually have characteristic optical absorption in the visible range inside the optical gap both the donor and acceptor. The important question is: could the spectral range of a conjugated polymer be extended into its optical gap using an appropriate CTC? Yes, we have recently found that a soluble derivative of poly(2,5-dihydroxy-1,4-phenylenevinylene) (MEH-PPV) can form intermolecular CTCs with wide bandgap low-molecular organic acceptors 2,4,7-trinitrofluorene (TNF) or 2,6-dinitroantraquinone (DNAQ) [2]. The optical absorption of these CTCs reaches the maximum in the red remaining noticeable down to the near IR. In this work, we discuss the ability of a conjugated polymer CTC relax to separated and mobile charges at photoexcitation. Additionally, ground-state charge-transfer interaction possibly could be used to control the phase separation which is ubiquitous in films where the donor and acceptor do not interact in their electronic ground states. Phase separation is well known to be one of the key factors determining the nanomorphology of these films and, therefore, the efficiency of the bulk-heterojunction approach. In this work, we discuss how attractive interaction between the donor and acceptor in the ground state CTC can affect phase separation.

CTC excited states: a pathway to separated and mobile charges

Photoluminescence of MEH-PPV is strongly quenched upon adding TNF or DNAQ (Fig. 1) [3]. Since the optical absorption spectra of TNF or DNAQ do not overlap with the emission spectrum of MEH-PPV, quenching of the MEH-PPV singlet excitation implies electron rather

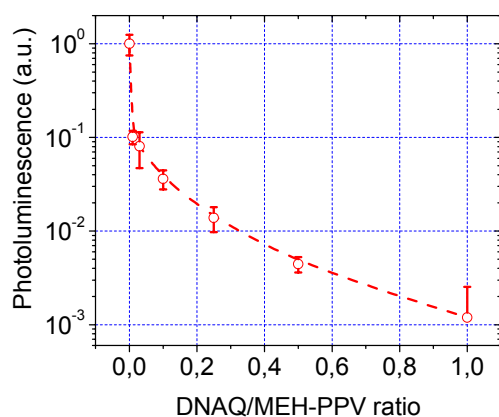


Fig. 1. Peak photoluminescence intensity excited at 532 nm versus molar donor-acceptor ratio for MEH-PPV/DNAQ films prepared from chlorobenzene. The line is a guide to the eye.

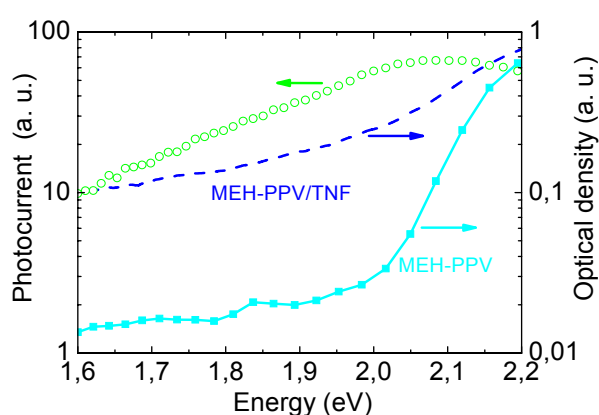


Fig. 2. Photocurrent action spectrum of a 1:1 MEH-PPV/TNF film (points) and its absorption spectrum (dashes). Solid line shows the absorption spectrum of pristine MEH-PPV.

than energy transfer. Further evidence of photoinduced charge separation was obtained from photoinduced absorption spectroscopy studies [3]. In particular, we have observed that photoexcitation of MEH-PPV/TNF films in the spectral range 500–800 nm result in effective generation of long-lived charged-separated states. Furthermore, the efficiency of charges photogeneration per absorbed pump photon almost did not depend on its energy in this spectral range. These observations imply the same relaxation process of the CTC and donor excited states leading to photoinduced charge transfer. Fig. 2 demonstrates the photocurrent excitation spectrum of a ITO/MEH-PPV:TNF/Al device. It is seen that it fairly follows to the CTC absorption below the absorption edge of MEH-PPV. Thus, the charge-transfer excitons responsible for absorption below the optical gap of MEH-PPV have an appreciable relaxation pathway into a state in which the charges are separated and mobile.

CTC ground state: towards control of phase separation

To evaluate phase separation in MEH-PPV/acceptor films with ground-state charge-transfer interaction, we have applied Rayleigh light scattering and differential scanning calorimetry (DSC) techniques. Light scattering and absorption in MEH-PPV/acceptor films with various donor-acceptor molar ratio were measured at several laser wavelengths corresponding to the CTC absorption band (Fig. 3). We have found that the level of light scattering abruptly increases for the MEH-PPV/TNF ratio lower than ≈ 3 . We associate this increase with a separate (uncomplexed) TNF phase which is not involved in the CTC. The content of the uncomplexed TNF in MEH-PPV/TNF films can also be monitored by using DSC. In fact, a strong endotherm peak corresponding to the melting point of the crystalline TNF phase essentially decreased in 1:1 MEH-PPV/TNF films and fully disappeared in 5:1 MEH-PPV/TNF films (Fig. 4). Thus, the light scattering and DSC data are well correlated. On the other hand, the fraction of complexed TNF in MEH-PPV/TNF films can be evaluated using the sensitivity of vibrational frequencies of MEH-PPV to the degree of charge transfer in the ground state. We have observed that the frequency shift of the strongest MEH-PPV Raman band resulting from the ground-state charge transfer saturates at TNF/MEH-PPV ratio higher than ≈ 0.3 . We have concluded that this ratio corresponds apparently to the maximum concentration of CTC in the film. Thus, our data implies that charge-transfer interaction in the electronic ground state could be a means to control phase separation in donor-acceptor films.

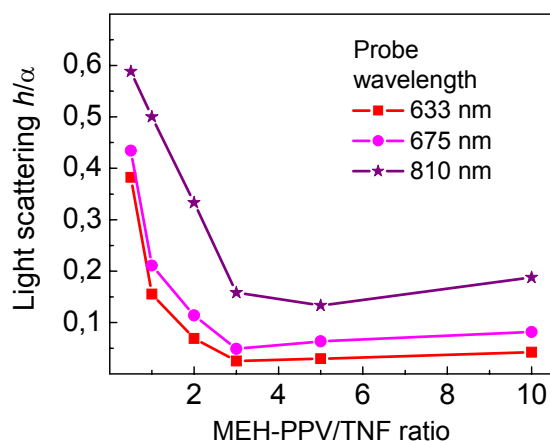


Fig. 3. The light scattering index h normalized to the absorption index α versus the donor-acceptor ratio.

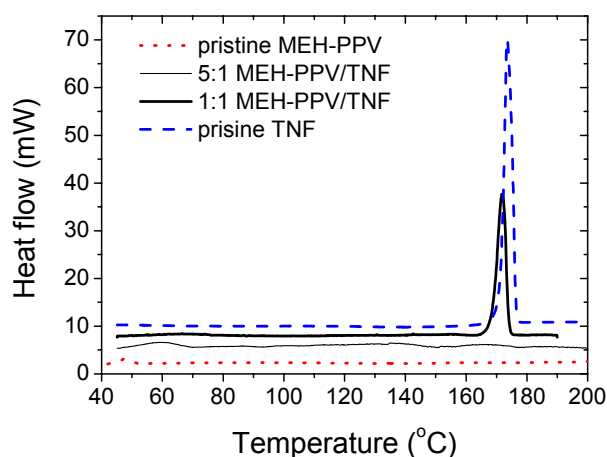


Fig. 4. DSC traces for MEH-PPV/TNF, MEH-PPV and TNF films. All curves are normalized to equal sample weight and are offset vertically for clarity.

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