

# Ground-state donor-acceptor charge-transfer complexes: intermediates on the route from excitons to free charges in polymer solar cells

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Charge photogeneration in donor-acceptor blends of organic materials is usually considered to occur via two manifolds of electronic states of the donor and acceptor. However, recent studies on polymer/fullerene blends indicate that charge photogeneration involves an intermediate state(s) at the polymer-fullerene interface [1-3]. There is growing evidence that these states belong to a polymer-fullerene ground-state charge-transfer complex (CTC) of the Mulliken type [2, 4-6], the fact that passed indiscernible in earlier studies. As a result, charge photogeneration in polymer/fullerene blends is expected to occur in a ternary system including the donor, CTC, and acceptor (Fig. 1). In some polymer-acceptors blends, e.g. MEH-PPV/TNF and MEH-PPV/DNAQ, the CTC has strong absorption in the optical gap of both the donor and acceptor [7] that could be exploited to extend the photosensitivity of organic solar cells in the red and NIR ranges. Remarkably, the initial charge photogeneration in these CTCs is as efficient as in polymer/fullerene blends [8]. However, the crucial drawback in using these CTCs in solar cells is efficient geminate recombination of photogenerated charges. Fig. 2 shows that the charge-associated photoinduced absorption (PIA) decays on the picosecond time scale in the blends with pronounced CTCs, whereas the PIA decays much slower in the polymer/fullerene blend.

For efficient polymer solar cells, it would be extremely beneficial to combine the extended photosensitivity of polymer-based CTCs with a long carrier lifetime typical for polymer/fullerene blends. This would become possible if one of the photogenerated charges escapes the parent CTC before the recombination occurs (i.e. faster than 5 ps, see Fig. 1). Such an escape route can be realized in a blend of the CTC with a fullerene acceptor to provide a consecutive photoinduced electron transfer from the polymer to the CTC-acceptor and then to the fullerene. In this case, the presence of the CTC-acceptor enhances the

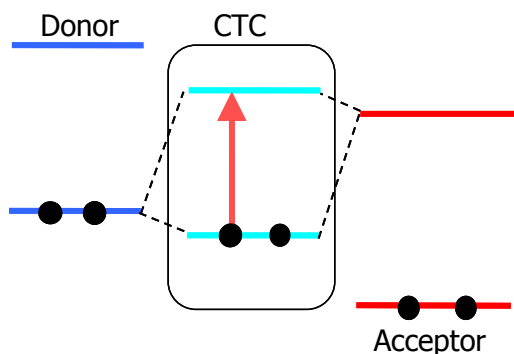


Fig. 1. Schematic of the frontier molecular orbitals of the polymer donor (MEH-PPV), low-molecular-weight acceptor (fullerene, trinitrofluorenone (TNF), dinitroanthraquinone (DNAQ)), and CTC. The arrow illustrates the CTC absorption.

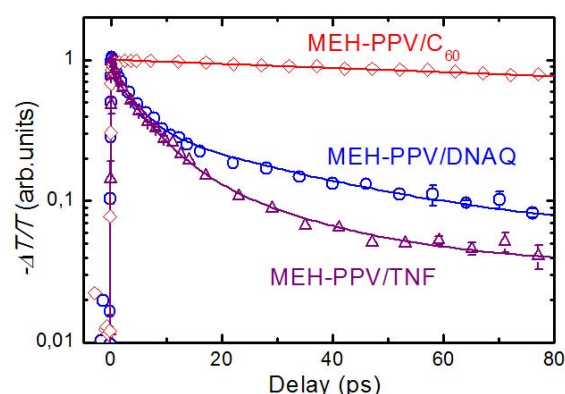


Fig. 2. Dynamics of the photoinduced charges in MEH-PPV/acceptor blends probed by ultra-fast PIA spectroscopy. The MEH-PPV/DNAQ, MEH-PPV/TNF, and MEH-PPV/C<sub>60</sub> blends were excited at 1.9 eV. The probe energy was 0.4 eV.

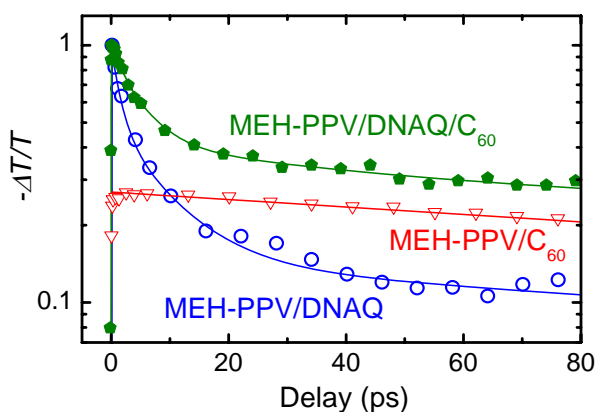


Fig. 3. Transient PIA at 0.4 eV in binary and ternary blends after excitation at 2 eV. The data are normalized to the number of absorbed pump photons.

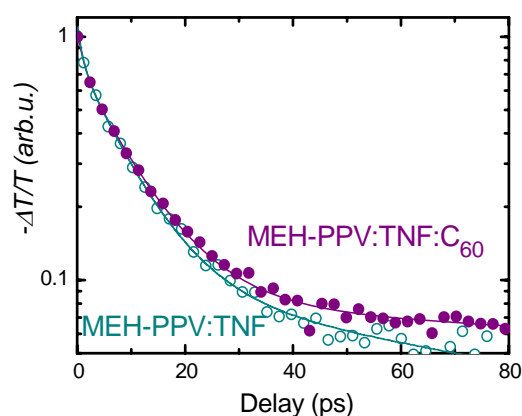


Fig. 4. Same as Fig. 3 but with TNF as the CTC-acceptor. Note only minute difference between the binary and ternary blends.

photosensitivity in the red, while the fullerene accepts the already photogenerated electron and therefore improves the generation of long-lived charges and their collection. We study a two-step charge photogeneration in model CTC-fullerene systems (ternary blends) where easily observable CTCs is formed between MEH-PPV and CTC-acceptor (DNAQ or TNF) [7].

Fig. 3 compares typical PIA transients in the binary and ternary blends. The PIA transient in the ternary blend MEH-PPV/DNAQ/C<sub>60</sub> is significantly different from that in the MEH-PPV/DNAQ CTC. Most striking is the disappearance of the fast (0.7 ps) decay upon doping the CTC with C<sub>60</sub>. As a result of this the amplitude of the long-lived (>300 ps) component of the PIA decay becomes a factor of three higher in the ternary blend than in the MEH-PPV/DNAQ CTC. This indicates an appreciable increase in the survival probability of the photogenerated charges upon doping with C<sub>60</sub>. Similar experiments with another acceptor, TNF, the LUMO of which is situated at about the same energy as the C<sub>60</sub> LUMO, indicated no surplus of the long-lived charges. Therefore, these results confirm the importance of material LUMO level management for providing efficient electron harvesting from the CTC states to the fullerene acceptor. The PIA data on the millisecond time scale for both the CTC-acceptors are in accordance with the ultrafast PIA data and indicate considerably more efficient charge generation in the red spectral range in the ternary blend MEH-PPV/DNAQ/C<sub>60</sub> as compared to the binary MEH-PPV/C<sub>60</sub> blend.

On the basis of the spectroscopic data with different CTC-acceptors, we discuss the importance of the LUMO difference between the CTC-acceptor and fullerene for efficient charge separation in the ternary blends. The photocurrent data in the ternary and binary blends are compared and analyzed. The photophysics in donor-CTC-acceptor systems is discussed.

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