

Acceptor Electron Affinity Manages Ground- and Excited-State Charge Transfer in Semiconducting Polymer-Acceptor Blends

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The heart of an organic solar cell (OSC) is the donor-acceptor heterojunction where the first steps occur in the multistage charge photogeneration process – exciton dissociation into a bound electron-hole pair and its subsequent dissociation/recombination. Recent studies on various heterojunctions have demonstrated that rather weak donor-acceptor interaction in the electronic ground state, namely formation of Mulliken charge-transfer complex (CTC), cannot be overlooked as it strongly influences charge photogeneration and hence the overall efficiency of the devices. The CTC properties strongly depend on the molecular structure of the donor-acceptor pair. For instance, in polymer-fullerene blends the CTC absorption is extremely weak and hardly detectable [1]. In contrast, in blends of soluble poly(*para*-phenylene vinylenes) with fluorene-type electron acceptors the CTC formation can be readily detected visually as a color change, and the CTC band is so intense that it could enhance the solar energy harvesting in the polymer bandgap [2]. The efficiency of initial charge generation after CTC photoexcitation is about unity; however, the recombination from the CTC state might also be pronounced thereby contrasting requirements for an efficient OSC heterojunction. As recognized in early studies on small-molecule CTCs, the acceptor electron affinity (*EA*) is a key parameter that dictates both the ground- and excited-state electron transfer (ET).

Here we demonstrate how the acceptor electron affinity governs the CTC formation and the recombination rate of photoinduced charges. To unravel the dynamics of the photogenerated charges, we applied ultrafast visible-pump – IR-probe photo-induced absorption (PIA) spectroscopy. Acceptor *EA* engineering was achieved by attaching a number of electron-withdrawing functional groups (cyano, nitro, carbonyl) to the fluorene core (Fig. 1). The blend absorption below the absorption edge of pristine MEH-PPV systematically increased with increasing the acceptor *EA* indicating the more pronounced ground-state CTC.

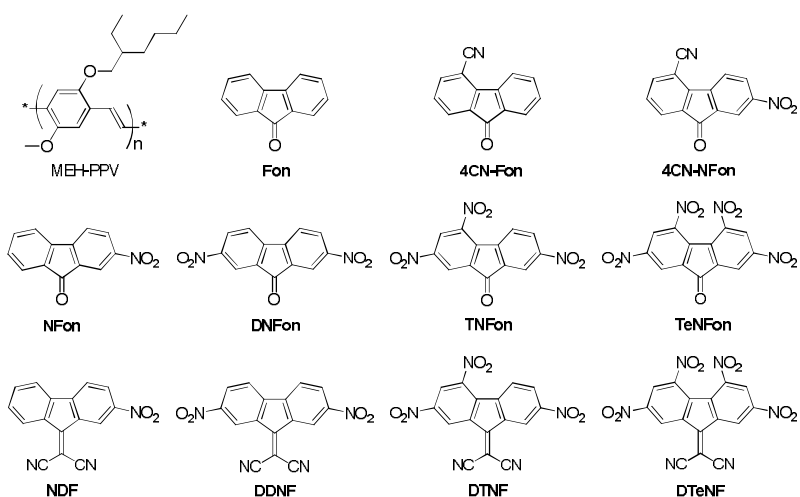


Fig. 1. Chemical structures of studied fluorene acceptors and MEH-PPV.

and the acceptor EA . The experimental points clearly cluster around a straight line in agreement with the inverted regime of the Marcus model. Increasing the acceptor EA is known to increase the driving force for efficient exciton dissociation; however, it inevitably enhances the unwanted recombination due to formation of the ground-state CTC. In order to improve the efficiency of photovoltaic devices, one should balance these two competing factors.

In the ultrafast studies, we monitored the time evolution of the IR polaron absorption band associated with generation of the photoinduced charges and their subsequent recombination (Fig. 2). The dynamics of the PIA transients for different acceptors are strongly different (Fig. 2a). PIA transients for all blends show picosecond exponential decay that is assigned to charge recombination. Figure 2b shows a relationship between the logarithm of the back ET rate and the acceptor EA .

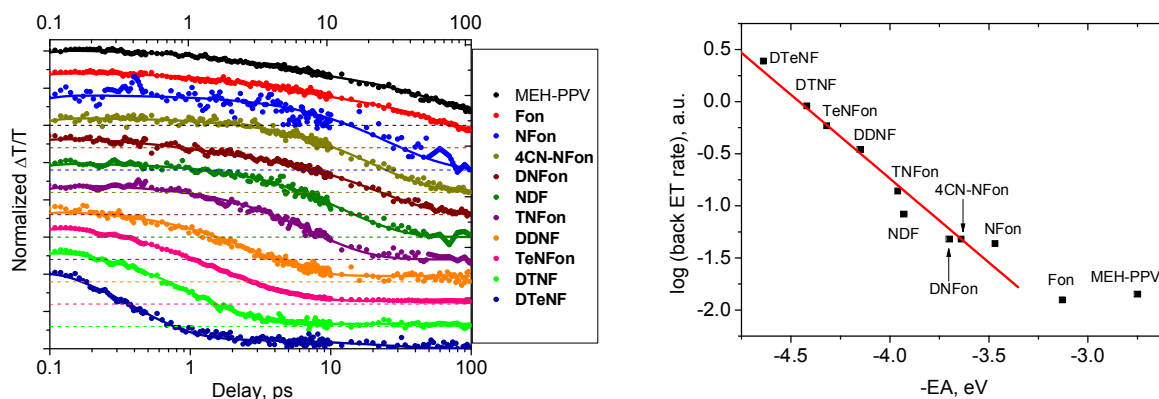


Fig. 2. (a) Normalized PIA transients with characteristic decay times for MEH-PPV/acceptor blends (points) with best fits (lines). The excitation and probe wavelengths were 560 nm and 3 μm , respectively. (b) The logarithm of the back ET rate versus acceptor EA (points) and the fit to the Marcus model (line).

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