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## Acceptor Energy Offset Manages Ultrafast Recombination Dynamics in Donor-Acceptor Mixtures

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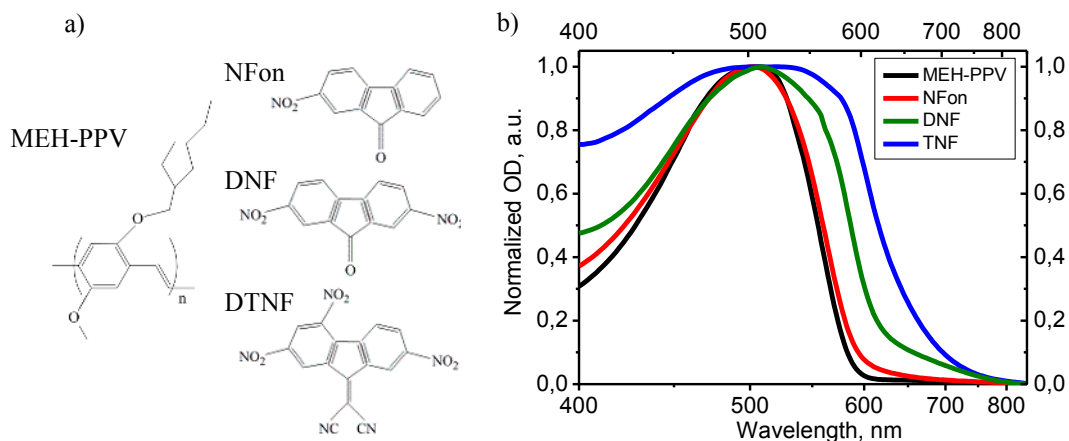
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**Abstract.** We study charge recombination rates in blends of MEH-PPV and a comprehensive set of low molecular-weight fluorine-based acceptors, using visible-pump – IR-probe photoinduced absorption technique. The positions of acceptor's HOMO-LUMO levels are engineered by addition of different chemical substituents. The results clearly show the exponential scaling of the charge recombination rate with the acceptor LUMO energy. The minimal donor-acceptor LUMO energy difference required to form a CTC state is estimated as  $\sim 0.25$  eV.

Ground-state charge transfer complexes (CTCs) lay in heart of many photoinduced processes in physics, chemistry, and biology. The ground-state CTCs are characterized by a partial shift of electronic density from the donor to the acceptor molecule already in the ground state. Upon optical excitation, the electron is transferred to the acceptor almost instantaneously, while back recombination occurs in the finite time. The CTC photophysical 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 (MEH-PPV) with fluorene-type acceptors, the CTC formation can be readily detected visually as a color change. In the latter type of materials, the CTC band is so intense that it could enhance the solar energy harvesting in the bandgap of both the donor and acceptor [2], similarly to push-pull copolymers [3]. Furthermore, the polymer photooxidation stability is drastically increased by the presence of the CTCs [4]. As was recognized in early studies of small-molecule CTCs [5], the acceptor electron affinity is a key parameter that determines the back electron transfer rates.

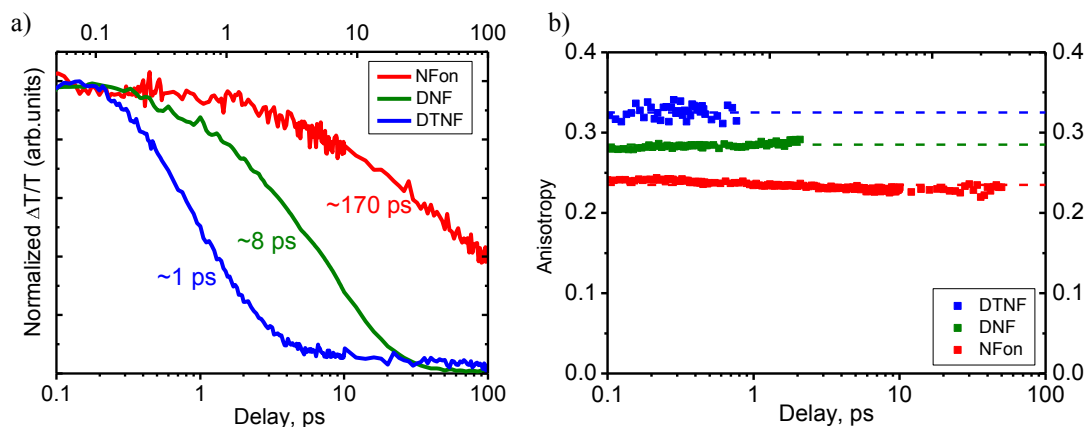
Here we demonstrate that the acceptor electron affinity governs the CTC recombination rate in full accord with the Marcus theory [6]. Donor-acceptor CTCs formed in blends between the conjugated polymer MEH-PPV and a family of low-molecular weight fluorene acceptors was used for their known property to form stable CTCs already in solution. To unravel recombination dynamics of the photogenerated charges, ultrafast visible-pump -- IR-probe photo-induced absorption (PIA) spectroscopy [7] was applied.

The acceptor electron affinity engineering was achieved by attaching a number of electron-negative functional groups (cyano, nitro, and carbonyl) to the fluorene core (Fig.1a), which predictably modify the HOMO-LUMO energies of the acceptors. Both energies were calculated by DFT method at the B3LYP/6-31g(d,p) level of theory.



**Fig.1.** (a) Chemical structures of MEH-PPV polymer (left) and three representative acceptors (named as NFon, DNF and DTNF) with the LUMO energies of -2.8, -3.3, and -4.5 eV respectively. (b) Absorption spectra of CTCs formed by polymer with the three representative acceptors with 1:0.3 weight concentrations (in films).

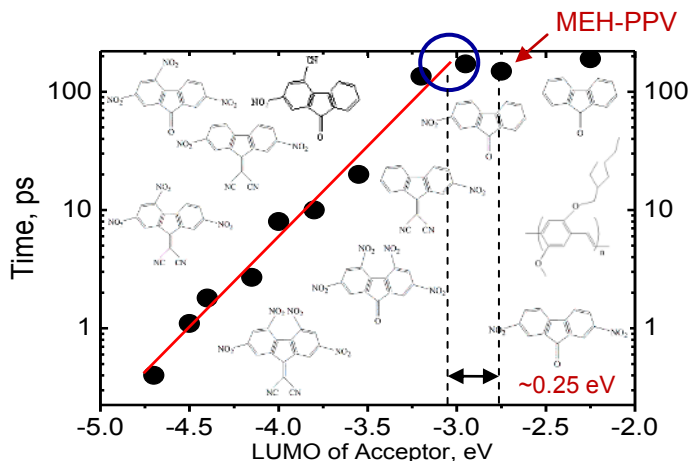
Absorption spectra of the polymer-acceptor films (Fig.1b) exhibit a wing in the red region which is a clear signature of the CTC formation. Isotropic PIA transients (Fig.2a) demonstrate that charge



**Fig. 2.** Normalized to the unity isotropic PIA (a) and anisotropy (b) transients for CTCs of MEH-PPV with three representative acceptors. The excitation and probe wavelengths are 640 nm and 3  $\mu$ m, respectively. In (a), decay lifetimes are shown next to the transients. Anisotropy transients are depicted within the recombination lifetime.

recombination dynamics in different CTCs are markedly different. Here we monitor the time evolution of the IR polaron absorption band associated with generation of the photoinduced charges and their subsequent recombination. In all blends, the PIA transients show exponential decay in the 1-100 ps range that is assigned to charge recombination. Transient anisotropy does not change in time (Fig.2b) which strongly suggests that the charges do not migrate at the time scale of the charge recombination, pointing at high degree of localization of the charge-transfer state. More importantly,

the amplitudes of PIA anisotropy reflect different packing of the polymer and acceptors in the blend, resulting in different orientations of the excitation and polaron transient dipole moments.



**Fig. 3.** Charge recombination time versus position of the acceptors LUMO (points). The solid line shows a linear (in the logarithmic scale) fit to the data points where CTCs with the polymer are formed.

Figure 3 shows the relation between the charge recombination time and the acceptor LUMO energy position. The relation between them is clear: the higher position of the LUMO, the slower the recombination dynamics. Furthermore, the experimental points cluster around a straight line in full agreement with the Marcus model [8]. The linear dependence extends until a point where the intramolecular recombination channel with a characteristic time of  $\sim 150$  ps for neat MEH-PPV begins to prevail. The CTC formation energy can be estimated from the offset of the crossing point as 0.25 eV which is consistent with the slope value of 0.26 eV.

From the ultrafast studies presented here, we arrive at the following conclusion, directly concerning organic photovoltaics. It is well established that increasing the acceptor electron affinity increases the driving force for efficient exciton dissociation of donor-acceptor pair. At the same time, this inevitably increases the unwanted back transfer electron rate unless the blend design provides the efficient charge delocalization [9].

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