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Charge Transfer Dynamics in Donor-Acceptor Complexes between a Conjugated Polymer and Fluorene Acceptors

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ABSTRACT: We report on ground and excited state charge transfer in charge-transfer complexes in films formed between a semiconducting polymer, MEH-PPV (poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene]), and a series of fluorene electron acceptors. The latter were designed to vary systematically the electron affinity (EA) over ~1.5 eV by attachment of various electron withdrawing groups to the fluorene core. The EAs of the acceptors are determined by cyclic voltammetry and

1
2 compared with those from Density Functional Theory calculations. The charge transfer dynamics are
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4 studied using an ultrafast visible-pump – IR-probe photoinduced absorption technique. We demonstrate
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6 that the acceptor EA is the key – but not the only – parameter that governs charge recombination rates
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8 that scale exponentially with the acceptor EA. From the time-resolved data we deduced a model that
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10 describes charge dynamics for acceptors with low and high EAs. The two opposite trends - higher
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12 acceptor EA increases the driving force for charge separation but also inevitably increases the rate of
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14 undesirable charge recombination – should be carefully counterbalanced in designing of novel
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16 polymer-fullerene bulk heterojunctions.
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22 KEYWORDS: charge-transfer complex, electron affinity, ultrafast spectroscopy, polaron dynamics,
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24 polymer-acceptor blends.
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1. INTRODUCTION

The electronic ground state of a molecular charge-transfer complex (CTC) is formed by the transfer of a fraction of the electron charge between the non-covalently bound molecular entities, the donor and the acceptor. CTCs and the very process of electron transfer lay at the heart of many photoinduced processes in physics, chemistry, and biology. According to the Mulliken model,^{1,2} the amount of the donor-acceptor charge transfer in the CTC ground state is mainly controlled by the difference between the donor ionization potential and the acceptor electron affinity (EA) or in first approximation by the energy difference between the acceptor lowest unoccupied molecular orbital (LUMO) and the donor highest occupied molecular orbital (HOMO), also known as the effective HOMO-LUMO gap.³

Upon optical excitation of the Mulliken-type CTCs, a major part of the electron density is transferred from the donor to the acceptor almost instantaneously while the back electron transfer, i.e. charge recombination, occurs within a finite time span.^{4,5} The early studies on dynamics of small-molecule CTCs in solutions^{6,7} demonstrated that the driving force for geminate charge recombination is mainly determined by the acceptor EA. The charge recombination rate was shown to scale exponentially with the acceptor EA, while some deviations were attributed to the reorganization energy variations.⁶

In recent years, a new kind of Mulliken-type CTCs involving conjugated polymers as donors has been identified in a variety of polymer-acceptor blends.⁸⁻¹² A number of unusual properties makes the polymer-based CTCs especially fascinating in comparison to their small-molecule counterparts. Planarization of the polymer chains¹³ and formation of crystalline domains¹⁴ are but two examples. Such properties are closely related to charge delocalization over conjugated polymer chains (non-existing in small-molecule CTCs) so that the electron density from several repeating units of the polymer is transferred to an acceptor molecule.^{13,15}

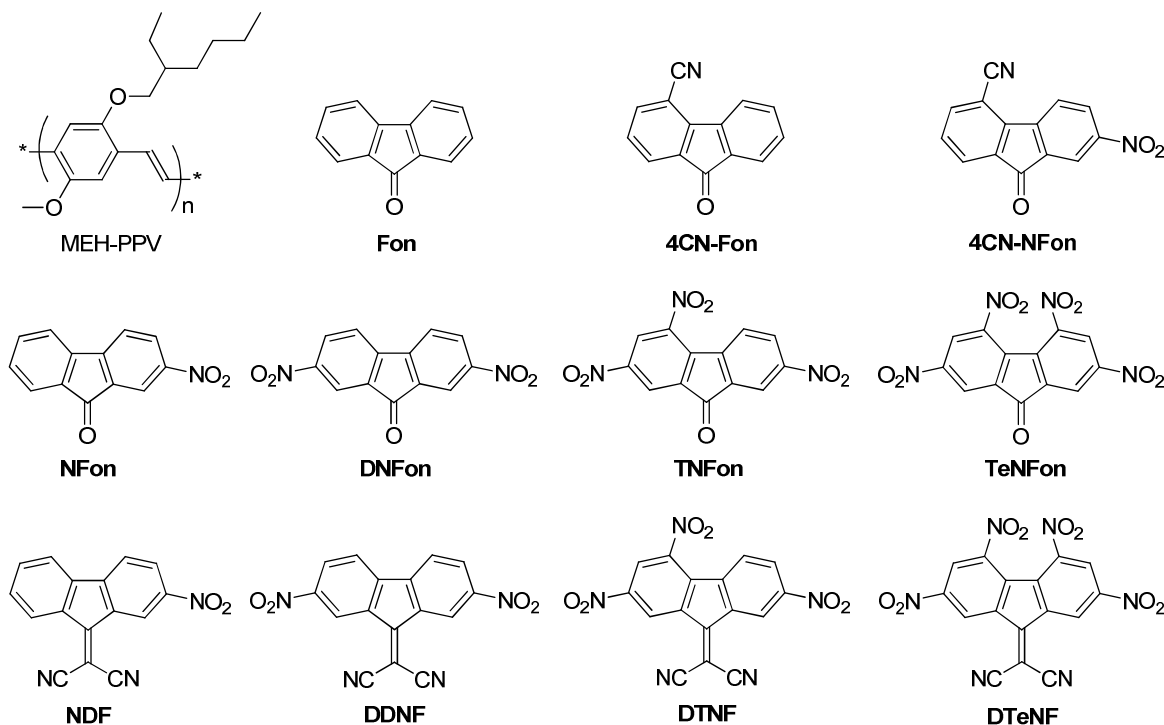
Ground-state CTCs have also been observed in conjugated polymer-fullerene blends¹⁶ although their absorption is extremely weak¹⁷⁻¹⁹, partially because CTCs are formed only near the donor-acceptor interface which volume share is minute. In contrast, in polymer-acceptor blends with pronounced

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2 ground-state charge transfer, a CTC is formed almost per each conjugated segment so that exciton
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4 diffusion and other concurrent processes (e.g., generation of triplets) do not affect the photophysics. As
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6 a result, optical excitation leads to immediate formation of a charge-separated state whose charge
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8 relaxation dynamics can be readily monitored.^{20,21} Furthermore, the new generation of low bandgap
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10 conjugated polymers for organic photovoltaics (OPV), which has already demonstrated the highest
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12 efficiencies in polymer solar cells,^{22,23} is built upon a push-pull donor-acceptor concept²⁴ which extends
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14 the light absorption into the red region of the solar spectrum. This is highly reminiscent of Mulliken-
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16 type CTC absorption, the difference in the charge-transfer state origin (i.e. covalently linked alternating
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18 electron donating and electron accepting monomer units in the polymer backbone *vs.* non-covalently
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20 bonded polymer and small-molecule acceptor) notwithstanding.

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26 Insofar, the effect of an acceptor EA on the charge recombination dynamics in conjugated polymer
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28 CTCs has only been studied for two commercially-available acceptors of different molecular
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30 structures.^{20,21} As a result, no functional dependences of the charge recombination rates as a function of
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32 acceptor EA could have emerged, in sharp contrast to the case of small-molecule CTCs in solutions.⁴⁻⁷
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34 This calls for a systematic study of charge recombination dynamics in conjugated polymer based CTCs
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36 where the acceptor EAs are varied in a controlled and predictable way with as small as possible
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38 alternations of the acceptor molecular structure.

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42 In this paper, we report on how the acceptor EA controls the charge recombination dynamics in
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44 CTCs between an archetypical conjugated polymer donor MEH-PPV (poly[2-methoxy-5-(2'-
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46 ethylhexyloxy)-1,4-phenylene vinylene])²⁵ and a family of small molecular acceptors (Figure 1). A
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48 series of fluorene acceptors with a range of EAs was designed, synthesized and characterized by cyclic
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50 voltammetry and Density Functional Theory calculations. The CTC excited state dynamics were
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52 studied via generation and recombination of photoinduced charges employing ultrafast visible-pump –
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54 IR-probe photo-induced absorption spectroscopy. We show that the recombination rate scales
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56 exponentially with the acceptor EA, similar to the earlier observations for small-molecule CTCs in
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2 solution.^{6, 26} Finally, the anisotropy dynamics suggest that separated charges in most of the blends
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4 remain highly spatially-localized, in sharp contrast to the case of the pristine polymer.
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35 **Figure 1.** Structures of the MEH-PPV polymer (upper left) and the studied series of fluorene electron
36 acceptors. Abbreviations of the latter are shown in bold.
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43 2. EXPERIMENTAL

44 2.1. Samples

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48 Fluorenone (**Fon**) and 2,7-dinitrofluorenone (**DN Fon**) have been purchased from Sigma-Aldrich and
49 used without further purification. Details of the synthesis of fluorene acceptors 2-nitrofluorenone
50 (**NFon**), 2,4,7-trinitrofluorenone (**TN Fon**), 2,4,5,7-tetranitrofluorenone (**TeNFon**), 2-nitro-9-
51 dicyanomethylenefluorene (**NDF**), 2,7-dinitro-9-dicyanomethylenefluorene (**DDNF**), 2,4,7-trinitro-9-
52 dicyanomethylenefluorene (**DTNF**), 2,4,5,7-tetranitro-9-dicyanomethylenefluorene (**DTeNF**)
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2 dicyanomethylene fluorene (**DTNF**), 2,4,5,7-tetranitro-9-dicyanomethylene fluorene (**DTeNF**), 4-
3 cyanofluorenone (**4CN-Fon**), and 2-nitro-5-cyanofluorenone (**4CN-NFon**) and their characterizations
4 are given in the Supporting Information (see “Synthesis of fluorene acceptors” section and Figs.S1-S16
5 for NMR spectra). Absorption spectra of the acceptors in chlorobenzene (Fig.S17) are situated in the
6 blue-UV region below 450 nm; no signs of aggregation at concentrations up to $2 \text{ g}\cdot\text{L}^{-1}$ were found.
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14 MEH-PPV was chosen as a donor since it is known to readily form a ground-state CTC with fluorene
15 electron acceptors.^{13, 27} MEH-PPV (Sigma-Aldrich, $M_n = 86000$, $M_w = 420000$) and fluorene acceptors
16 were dissolved separately in chlorobenzene at a concentration of $2 \text{ g}\cdot\text{L}^{-1}$. The solutions were placed
17 into an ultrasonic bath for 15 minutes at 22°C and then stirred with a magnetic stirrer for ~ 6 hours at
18 50°C . Their blends were prepared by mixing the solutions of MEH-PPV and an acceptor with a molar
19 ratio of 1:0.3 per polymer repeat unit. Further increase of the acceptor concentration in the blends led to
20 phase segregation with loss of sample optical quality.²⁸
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31 Films were prepared by drop casting of MEH-PPV/acceptor solution onto a $150 \mu\text{m}$ thick microscope
32 cover slide with subsequent drying for 8 hours in an air atmosphere at 22°C . The resulted optical
33 density of the samples did not exceed ~ 1.5 at their maxima. The solution of MEH-PPV with the highest
34 EA acceptor, **DTeNF**, exhibited strong phase segregation and CTC precipitation, and therefore was not
35 used in the optical experiments. All experiments were performed at ambient conditions; no sample
36 degradation was observed during the experiments.
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49 Electrochemical experiments were carried out using an Autolab PGSTAT-302N potentiostat-
50 galvanostat. Cyclic voltammetry (CV) measurements were performed in a three-electrode cell equipped
51 with a platinum disk ($d = 1.6 \text{ mm}$) as the working electrode, platinum wire as a counter electrode and a
52 non-aqueous Ag/Ag^+ reference electrode (0.01 M AgNO_3 and $0.1 \text{ M Bu}_4\text{NPF}_6$ in MeCN). Cyclic
53 voltammograms were recorded at room temperature in dry acetonitrile, deoxygenated by bubbling with
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argon gas, with 0.1 M Bu₄NPF₆ as supporting electrolyte, with ohmic drop compensation. The potentials were corrected with ferrocene/ferrocenium redox pair (Fc/Fc⁺) as an internal standard, which showed the potential of 0.090–0.100 V versus the used reference electrode in our conditions. LUMO energies (E_{LUMO}^{CV}) were estimated from the half-wave reduction potentials using the widely used relation introduced by Pommerehne *et al.*²⁹ (see also Ref. 30): E_{LUMO}^{CV} [eV] = $-(4.8 - E_{1/2}^{red})$, where -4.8 eV is the potential of Fc/Fc⁺ redox pair versus Fermi level. MEH-PPV HOMO and LUMO energies of -5.0 and -2.8 eV, respectively, were taken from the electrochemical data in Ref. 31.

2.3. Computational procedures

DFT computations of the geometries of the studied fluorene electron acceptors were carried out with the Gaussian 09³² package of programs by using Pople's 6-31G split valence basis set supplemented by d-polarization functions for heavy atoms and with diffusion functions on them. Becke's three-parameter hybrid exchange functional^{33,34} with the Lee–Yang–Parr gradient-corrected correlation functional (B3LYP)³⁵ were employed. The restricted Hartree-Fock formalism was used for calculations of neutral molecules whereas the unrestricted HF formalism was used for the calculation of radical anion states. No constraints were used and all structures were free to optimize in an acetonitrile solution using the polarizable continuum model (PCM).³⁶⁻⁴⁰ Thus, the geometries were optimized at the B3LYP/6-31+G(d) level of theory and the electronic structures were calculated at the same level of theory. From these calculations on the neutral molecules (in acetonitrile) we estimated the frontier orbital energy levels, E_{LUMO}^{DFT} and E_{HOMO}^{DFT} . Vertical electron affinities (EA_V^{DFT}) were computed as the difference between the total energies of the optimized neutral state E_{total}^{OptN} and the radical anion at the frozen geometry of the neutral, $E_{total}^{RA,F}$:

$$EA_V^{DFT} = E_{total}^{OptN} - E_{total}^{RA,F} \quad (1)$$

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Adiabatic electron affinities (EA_A^{DFT}) were calculated as the difference in total energies between the optimized geometries of the neutral E_{total}^{OptN} and radical anion $E_{total}^{RA,Opt}$ states, including zero point energies corrections ZPE^N and ZPE^{RA} for the two state, respectively:

$$EA_A^{DFT} = E_{total}^{OptN} - E_{total}^{RA,Opt} + ZPE^N - ZPE^{RA} \quad (2)$$

2.4. Ultrafast spectroscopy experiments

The dynamics of photogenerated charges in selected materials have been explored with a photoinduced absorption (PIA) technique, where allows monitoring the time evolution of photoinduced charges. The method is based on the fact that a charge (a hole) created on a polymer molecule induces absorption bands in the polymer optical gap in the IR range.⁴¹ These bands called low energy (LE) and high energy (HE) polaron bands⁴² are situated for the MEH-PPV polymer at ~ 3500 and ~ 10000 cm^{-1} , respectively.^{20,43} The LE band is more suitable as a reporter of charge concentration because it is not contaminated by other responses, like electro absorption, stimulated emission etc. which allows for a background free measurement.^{20, 44} In the PIA technique, two pulses are applied: the first one photogenerates the charges and the second one probes the charge concentration by monitoring induced absorption in the IR spectral region. For the aforementioned reasons, the probe wavelength was set at $2.94 \mu\text{m}$, i.e. near the LE polaron absorption peak (see Ref. 20 for the polaron absorption spectrum).

Briefly, the PIA experiments were performed with a home-built 1kHz Ti:Sapphire multipass amplifies laser system that pumps an IR optical parametrical oscillator (OPO) and a nonlinear optical parametrical amplifier (NOPA). The NOPA generated ~ 30 fs, ~ 3 nJ pulses in the visible range (500–750 nm). The power density at the sample position did not exceed 800 nJ/cm^2 to ensure a linear excitation regime and absence of bimolecular (non-geminate) recombination. The IR OPO was optimized to provide ~ 70 fs pulses at $\sim 3400 \text{ cm}^{-1}$ (near the center of the LE polaron absorption band). To realize polarization-sensitive measurements, the polarization of the IR probe beam was rotated by

45° with respect to the polarization of the visible pump beam. Parallel and perpendicular components of the probe beam were selected after the sample by grid-wire polarizers and detected by two InSb photodiodes. The photodiode signals were processed by lock-in amplifiers synchronized to a mechanical chopper (500 Hz) inserted into the visible pump beam. To obtain relative changes in the transmission ΔT , the differential pump-on, pump-off signal ΔI from the lock-ins were normalized to the intensity I of the IR beam transmitted through the sample:

$$\Delta T = \frac{\Delta I}{I} \quad (3)$$

To calculate the isotropic $\Delta T_{Iso}(t)$ and anisotropic $r(t)$ transients the standard expressions (4, 5)⁴⁵ were used:

$$\Delta T_{Iso}(t) = \frac{\Delta T_{\parallel}(t) + 2 \cdot \Delta T_{\perp}(t)}{3} \quad (4)$$

$$r(t) = \frac{\Delta T_{\parallel}(t) - \Delta T_{\perp}(t)}{3 \cdot \Delta T_{Iso}(t)} \quad (5)$$

where $\Delta T_{\perp}(t)$ and $\Delta T_{\parallel}(t)$ are relative transmission changes of the perpendicular and parallel components of the probe signal. All data were obtained under ambient conditions at room temperature.

3. RESULTS AND DISCUSSION

3.1. Fluorene acceptors design

The acceptor EA engineering was achieved by attaching a number of different electron-withdrawing functional groups to the fluorene core: from one to four nitro groups or/and cyano group at the benzene rings, as well as using carbonyl oxygen or dicyanomethylene groups at the C-9 bridged atom of the fluorene moiety (Figure 1). While the effect of introducing several electron withdrawing groups in the fluorene moiety is not exactly additive (especially in the case nitro groups introduced at different positions of the fluorene moiety), analysis of previous spectroscopic and electrochemical studies on

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2 different electron acceptors of the fluorene series allows for making such generalizations. The
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4 introduction of an NO₂ group in substituted fluorenes increases the EA of the fluorene molecule by
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6 ~0.2–0.3 eV while replacement of oxygen in the carbonyl group by the dicyanomethylene fragment
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8 increases the EA by ~0.35–0.45 eV.⁴⁶⁻⁵² Therefore, with the structural variations of a selected series of
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10 fluorene acceptors presented in Figure 1, the LUMO energy levels can be tuned by ~1.5 eV.
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13 14 15 16 3.2. Cyclic Voltammetry

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18 To estimate the LUMO energy levels of fluorene electron studied acceptors, their electrochemical
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20 reduction was studied by cyclic voltammetry (CV) in dry acetonitrile, with a common three electrode
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22 scheme using Fc/Fc⁺ as an internal reference. Most of the studied acceptors showed two (or even three)
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24 reversible redox waves in acetonitrile solution to form stable radical anion and dianion species (in CV
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26 timescale), respectively, except for the lowest EA acceptors **Fon**, **4CN-Fon** and **NFon**, which showed
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28 only the first redox wave to be reversible (Figure 2). An increase of the number of nitro groups results
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30 in progressive shift of redox potentials into the positive potential region, and further pronounced shifts
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32 are observed on replacement of O by C(CN)₂ groups. The first and second half-wave reduction
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34 potentials, $E_{1/2}^{red1}$ and $E_{1/2}^{red2}$, are collated in Table 1 and have been used to estimate the LUMO energy
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36 levels of acceptors (E_{CV}^{LUMO} , Table 1, Fig. 3), assuming an Fc potential of –4.8 eV versus Fermi level.
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38 The data for E_{CV}^{LUMO} presented in Table 1 indicate that for both series (fluorenones and 9-
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40 dicyanomethylenefluorenes) each nitro group incrementally decreases the LUMO energy of the
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42 acceptors by ~0.22–0.27 eV, except for the weakest acceptor, unsubstituted fluorenone **Fon**, in which
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44 case an insertion of first NO₂ group (**NFon**) results in a decrease of the LUMO energy by 0.34 eV.
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46 Replacement of oxygen by a dicyanomethylene group in acceptors decreases their LUMO energies by
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48 0.41–0.46 eV. These data are in good agreement with the observed linear relationships of first
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50 reduction potentials,⁵³ as well as with intramolecular charge transfer energies⁵⁴ in fluorene acceptors by
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Hammett-type correlations. The EAs of the studied acceptors estimated from the electrochemical experiments, were assigned as $EA^{CV} = -E_{LUMO}^{CV}$, in accordance with Koopman's theorem.

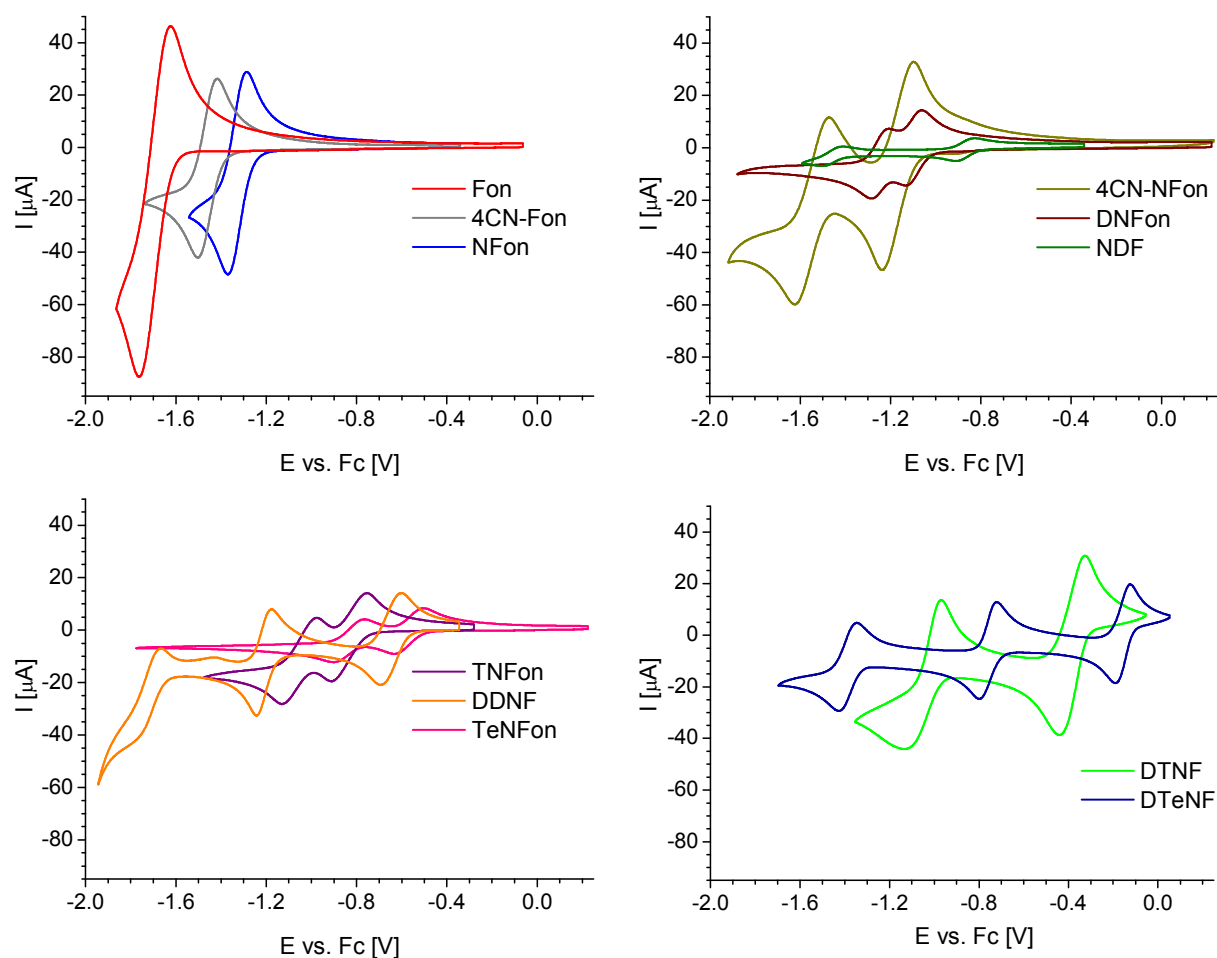


Figure 2. Cyclic voltammograms of fluorene acceptors in deoxygenated acetonitrile, supporting electrolyte 0.1 M Bu_4NPF_6 , scan rate 100 mV s^{-1} .

Table 1. Reduction CV potentials and calculated energy levels of fluorene acceptors

Compound	$E_{1/2}^{red1}$	$E_{1/2}^{red2}$	E_{LUMO}^{CV}	E_{LUMO}^{DFT}	E_{HOMO}^{DFT}	EA_V^{DFT}	EA_A^{DFT}
	[V] ^a	[V] ^a	[eV] ^b	[eV] ^c	[eV] ^c	[eV] ^d	[eV] ^e
Fon	-1.669	–	-3.131	-2.781	-6.534	2.891	3.140
4CN-Fon	-1.460	–	-3.340	-3.013	-6.847	3.120	3.379
4CN-NFon	-1.159	-1.516	-3.641	-3.555	-7.292	3.647	3.910
NFon	-1.328	–	-3.472	-3.372	-6.966	3.459	3.730
DNFon	-1.098	-1.245	-3.702	-3.749	-7.435	3.839	4.087
TNFon	-0.839	-1.054	-3.961	-4.045	-7.789	4.142	4.393
TeNFon	-0.564	-0.814	-4.236	-4.377	-8.136	4.478	4.725
NDF	-0.869	-1.456	-3.931	-3.768	-7.041	3.891	4.081
DDNF	-0.648	-1.210	-4.152	-4.045	-7.492	4.165	4.356
DTNF	-0.383	-1.050	-4.417	-4.302	-7.815	4.420	4.621
DTeNF	-0.157	-0.760	-4.643	-4.591	-8.074	4.710	4.869

^a The first and second reduction half-wave potentials in acetonitrile versus Fc/Fc⁺, calculated as averages of anodic and cathodic peak potentials from cyclic voltammetry. ^b LUMO energy levels from CV experiments: $E_{LUMO}^{CV} = 4.8 - E_{1/2}^{red1}$. ^c HOMO and LUMO energy levels from B3LYP/6-31+G(d) calculations in acetonitrile. ^d Vertical electron affinities of acceptors from B3LYP/6-31+G(d) calculations in acetonitrile (see eq. 1). ^e Adiabatic electron affinities of acceptors from B3LYP/6-31+G(d) calculations in acetonitrile (see eq. 2).

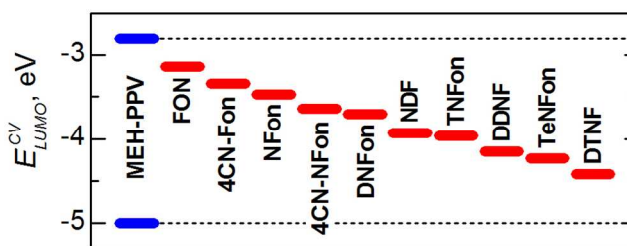


Figure 3. Positions of the LUMO energy levels (E_{LUMO}^{CV}) of fluorene electron acceptors from CV experiments (red blocks). MEH-PPV HOMO and LUMO energies (blue blocks) are also shown for comparison.

3.3. DFT Computational Studies

DFT computations have been performed at B3LYP/6-31+G(d) level of theory for both geometry optimizations and calculations of electronic structures of neutral acceptors and their radical anions. The effect of the solvent (acetonitrile) was incorporated using the polarizable continuum model (PCM) to match the results with CV measurements in this solvent. Kohn-Sham frontier orbital energies for neutral acceptors, E_{HOMO}^{DFT} and E_{LUMO}^{DFT} , are collated in Table 1 (more details on B3LYP/6-31+G(d) level of theory calculations are given in Supporting Information, Table S1). Orbital energy diagrams together with HOMO and LUMO orbital coefficients of the fluorene acceptors obtained from B3LYP/6-31+G(d) calculations in acetonitrile are given in the SI (Figure S18 and Table S2). It is evident that nitro groups incrementally decrease the LUMO energy levels for both fluorenone and 9-dicyanomethylene series of acceptors (Figure S18), and while their effect is not fully additive, the trend is clear and in general reproduces well the observations of CV experiments. Both nitro groups and dicyanomethylene fragment are substantially involved in LUMO delocalization, with a more pronounced effect for the NO₂ groups in positions 2,7- as compared to positions 4,5-. Cyano groups in the benzene ring are very weakly involved in the LUMO delocalization (Figure 4, Table S2). The lower degree of LUMO delocalization over the 4,5-nitrogroups is partially due to a steric effect. According to single crystal X-ray data for various fluorene acceptors and their CTC, this results in rotation of NO₂ around the C–N bond to form dihedral angles with the fluorene plane (in general, 30–50° and 3–10°, for nitrogroups in positions 4,5- and 2,7-, respectively).^{48-53, 55-60}

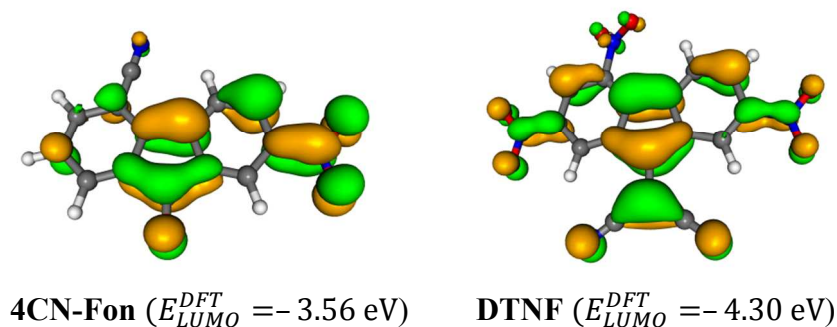


Figure 4. LUMO orbital coefficients for two representative fluorene acceptors from B3LYP/6-31+G(d) calculations in acetonitrile (for others, see Table S2)

In the DFT calculations, EAs are sometimes approximated by the LUMO energies ($EA = -E^{LUMO}$) in accordance with DFT-Koopman's theorem. In addition to such estimation, we also calculated vertical and adiabatic electron affinities, EA_V^{DFT} and EA_A^{DFT} (Table 1). Both vertical and adiabatic EA values are in excellent linear relationship with the computed E_{LUMO}^{DFT} energies, while better coincidence in absolute values is observed with the vertical ionization potentials, EA_V^{DFT} (average deviations of ca. – 0.1 eV, Figure 5 and SI, Figures S19 and S20). Comparison of the DFT data with CV experiments indicates that E_{LUMO}^{DFT} and EA_V^{DFT} show reasonably good linear correlations with the experimental E_{LUMO}^{CV} values obtained from the cyclic voltammetry experiments, while for EA_A^{DFT} the deviations are somewhat larger (Figure 5). In all the cases, the slopes are slightly higher than unity and increased positive deviations are observed for weaker acceptors **Fon** and **4CN-Fon**, implying an underestimation of the EA by the DFT calculations. Small deviations from linear dependence between the CV data and computational estimations of orbital energies are partially due to the known fact of overestimation of conjugation by hybrid functionals⁶¹⁻⁶⁵ affecting the computed LUMO energies as well as adiabatic EA values. Yet, reasonably good linear correlations between the experiments and the theory allow using computational methods in the design of fluorene acceptors with predictable EAs. Therefore, in the following we will use $-E_{LUMO}^{CV}$ as the acceptor EA.

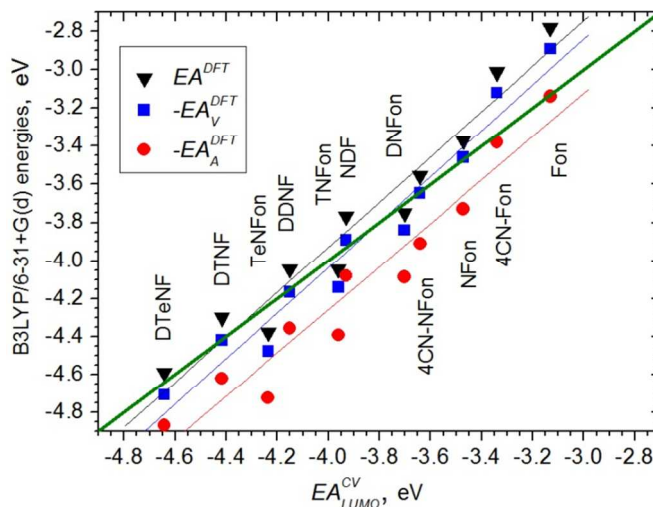


Figure 5. Comparison of experimental and calculated B3LYP/6-31+G(d) LUMO energy levels (ionization potentials) for the studied electron acceptors. Green line represents a bisection of equal energies between the axes (as such, the best quantitative coincidence with experimental data is for EA_A^{DFT} calculated values). Solid lines show linear fits to the respective data sets.

3.4. Steady-State Absorption

Figure 6a plots optical absorption spectra of the MEH-PPV:acceptor blends. For the sake of simplicity, the blends are named after the respective acceptor. With increase of the acceptor EA, i.e. with lowering of the effective HOMO–LUMO energy gap, the blends show characteristic signatures of a ground-state polymer:acceptor CTC previously identified for MEH-PPV:**TNFon** blends.^{8-11,13} First, an absorption tail begins to form in the polymer bandgap, i.e. at wavelengths longer than 600 nm (Figure 6b). Second, the absorption maximum is progressively shifted to the red (Figure 6a) for acceptors with EA higher than that of **4CN-NFon**. This indicates that the majority of the conjugated chains are involved in the CTC.¹³ For acceptors with high EA, an additional CTC absorption band is formed (most clearly seen for **TeNFon**), in accordance with the Mulliken model which predicts that the CTC absorption should be progressively red-shifted with increasing of the acceptor EA.

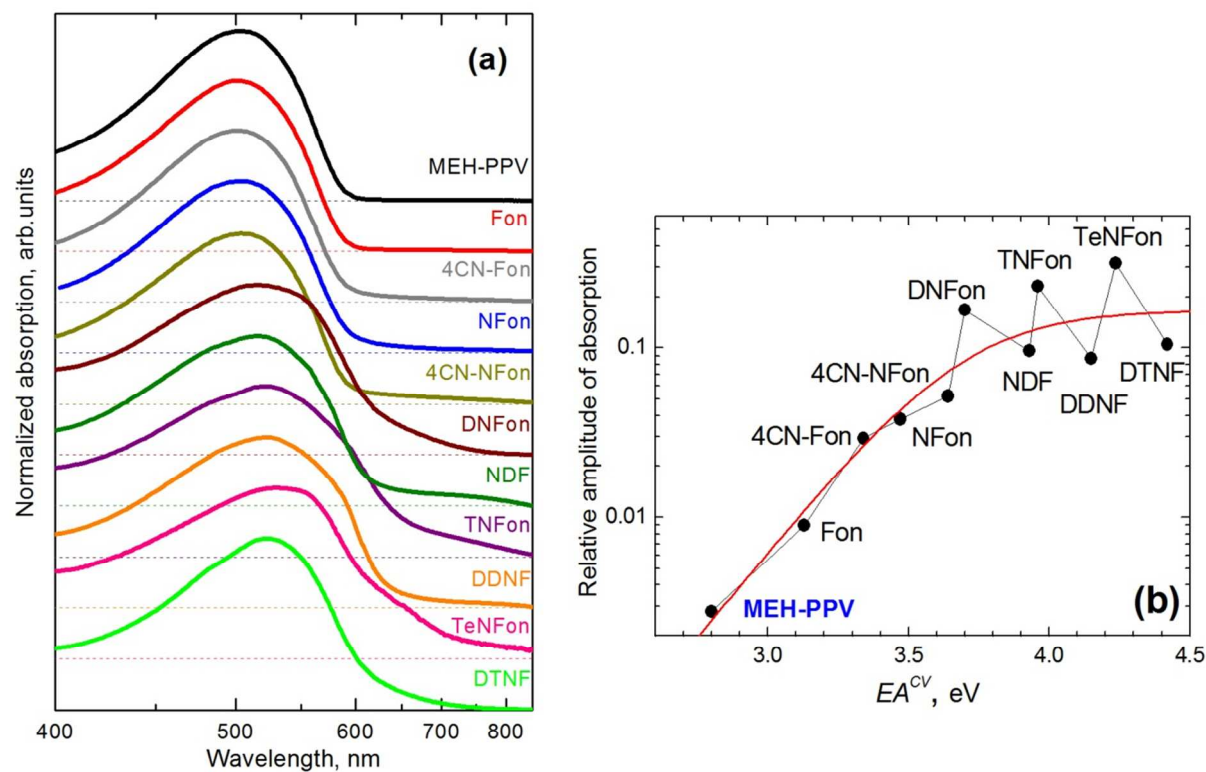


Figure 6. (a) Normalized absorption spectra for MEH-PPV:acceptor films. The spectra are shifted vertically for clarity; the acceptor EA increases from top to bottom. The spectrum of a pristine MEH-PPV film is also shown at the top for comparison. (b) Absorption at the red tail of the spectrum (650 nm; chosen arbitrarily) relatively to the maximum absorption as a function of acceptor EA. The red curve shows the fit to an *ad hoc* function $A(\exp(-b \cdot EA) + c)^{-1}$ to highlight the initial exponential growth followed by the saturation.

The absorption spectra in Figure 6a indicate that the polymer forms easily observable CTCs with the acceptors having an EA equal or higher than that for **DNFon**. For acceptors with a relatively low EA (**4CN-NFon**, **NFon**, **4CN-Fon** and **Fon**) the only CTC signature is a weak absorption in the polymer gap (Figure 6b) that increases exponentially with acceptor EA. Interestingly, the CTC absorption ceases to be a monotonic function of EA at the position of **DNFon**. As follows from Figure 6b, the fluorenone acceptors (i.e. with carbonyl oxygen at the C-9 bridged atom of the fluorene moiety, Figure

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2 1) form stronger absorbing CTCs than their dicyanomethylene-fluorene-derivatized counterparts with
3 comparable EAs (cf. for pairs **NDF/TNFon** and **DDNF/TeNFon**). Therefore, EA is not the only
4 variable that governs the CTC properties even for acceptors with similar molecular structure.
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10 11 3.5. Photoinduced Charge Generation and Recombination

12 While absorption data are indispensable in studying formation of the ground-state CTCs, they do not
13 provide any information on the excited-state dynamics, i.e. on the processes of charge separation and
14 recombination. For this, a visible-pump IR-probe arrangement²⁰ was used where the magnitude of PIA
15 signals in the region of LE polaron absorption (at 2.94 μm) monitors the concentration of photoinduced
16 charges on the polymer.
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25 Figure 7 shows isotropic PIA transients for all the MEH-PPV:acceptor blends recorded at an
26 excitation wavelength of 560 nm. This excitation wavelength was chosen at the lower-energy side of
27 the absorption spectra (Figure 6a) to minimize deposition of excessive excitation energy. As is clear
28 from Figure 7a, the initial charge photogeneration for all the samples is extremely fast and occurs
29 within the apparatus time resolution of ~ 100 fs, regardless of the acceptor. Therefore, we conclude that
30 the polaron generation in the blends occurs faster than 100 fs, and hence forward donor-to-acceptor
31 electron transfer is almost immediate upon optical excitation and does not depend on the driving force
32 for charge separation (acceptor EA). In contrast, the decaying parts of the transients are strongly
33 acceptor-dependent with the relaxation timescale changing from ~ 50 ps for **Fon** to ~ 1 ps for **DTNF**.
34 These timescales are attributed to the charge recombination (or back electron transfer from the acceptor
35 to the polymer) process.
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51 We briefly comment on the origin of the PIA signal from the film of pristine MEH-PPV. Ideally,
52 such excitation should be of entirely excitonic nature so that no polarons are produced. However, a
53 number of MEH-PPV excitons quickly dissociate into charge species which assignment was actively
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debated in the past (see for instance Ref. 66. Here we use the PIA signal from the pristine MEH-PPV film only as a reference for the charge recombination in the blends not affected by CTC formation.

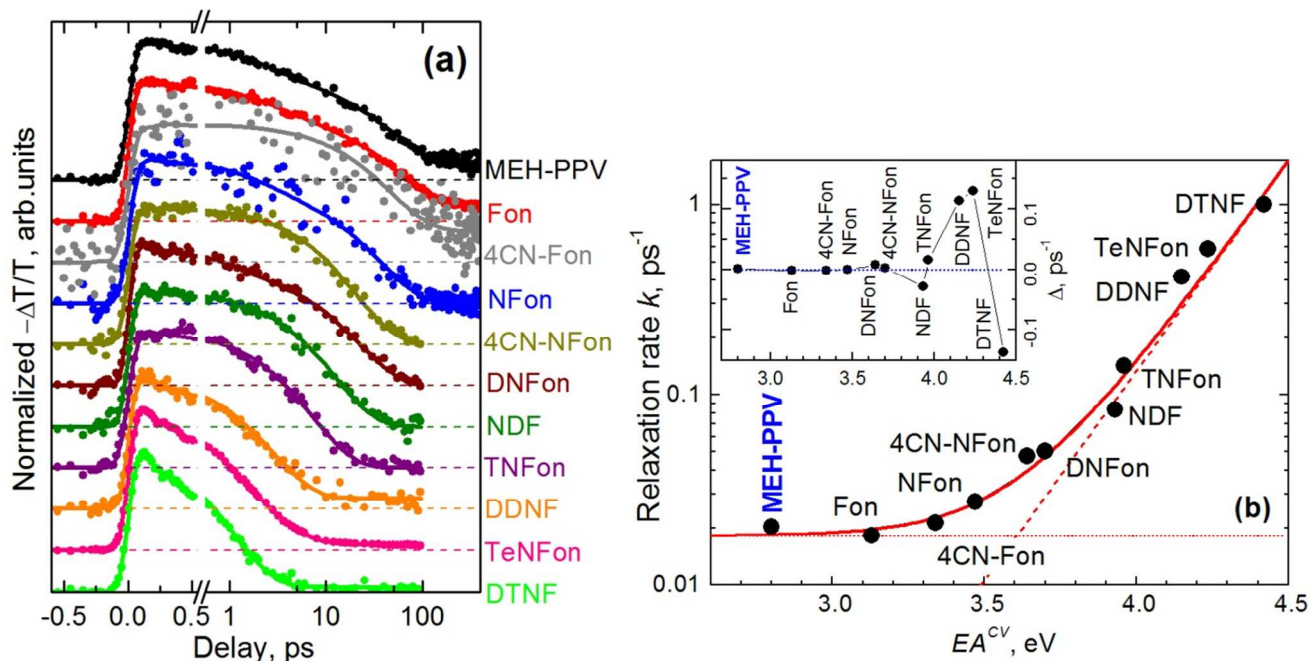


Figure 7. (a) Normalized isotropic PIA transients for the MEH-PPV:acceptor blends at an excitation wavelength of 560 nm and probe wavelength of 2.94 μm . Dots represent experimental data while solid curves show bi-exponential fits with the parameters listed in Table S3 in the Supporting Information. The transients are shifted vertically for clarity; the corresponding zero signal levels are shown by dashed lines. Note the logarithmic scaling of the delay axis after the break. The PIA signal from the pristine MEH-PPV film (black) is shown as a reference. (b) Charge recombination rate in blends of MEH-PPV:acceptor as a function of EA. The solid curve represents the best fit to the experimental data (dots) according to Eq.6. The dashed and dotted lines are asymptotes for the acceptor-to-polymer and intrapolymer recombination channels, respectively. The inset presents deviations of the experimental values from the best fit at the linear scale.

To quantify the dynamics, the transients were fitted by a bi-exponential function (Figure 7a, solid lines) with fit parameters presented in Table S3 (see Supporting Information). Two recombination rates most probably correspond to different donor-acceptor configurations or/and partial electron transfer. In any case, for the majority of the acceptors, the amplitude of the dominating exponential functions exceeds 90% and is always higher than 80%. We took the weighted average of the two time constants as the characteristic time of the charge recombination.

Figure 7b summarizes the relation between the charge recombination rate, k , and the acceptor EA. The intermolecular recombination rate mostly follows the exponential trend with some deviations for low-EA acceptors. This deviation originates from a second, intrapolymer (i.e. between units of the same and/or different polymer chains) channel of charge recombination that is characteristic for pristine MEH-PPV. The charge recombination rate that accounts for the both donor-acceptor and intrapolymer channels is therefore expressed as follows:

$$k = k_{ET} \cdot \left[\exp\left(\frac{EA}{\Delta E}\right) - 1 \right] + k_0, \quad (6)$$

where k_{ET} is the proportionality coefficient, ΔE is a characteristic energy, and k_0 is the rate of the intrapolymer charge recombination. The fit to the experimental data resulted in the following values:

$$k_{ET} = 2.1 \cdot 10^{-10} \text{ ps}^{-1}, \quad \Delta E = 0.2 \text{ eV}, \quad \text{and} \quad k_0 = 0.018 \text{ ps}^{-1}.$$

The linear dependence of the logarithm of the charge recombination rate, $\ln(k)$, on EA has been observed in many small-molecule ground-state CTCs, both in solution^{6,7} and solid phase.^{26,67} The obtained value of $\Delta E^{-1} = 5 \text{ eV}^{-1}$ of the slope of the exponential factor is also similar to previous studies of small-molecule CTCs. For instance, Gould *et al.*⁶ reported the slope value of $\sim 5 \text{ eV}^{-1}$ in a series of CTCs formed between cyanoaromatic acceptors and methyl-substituted benzene donors. Hubig *et al.* found^{7,26} the slope to vary from 2 eV^{-1} in benzene–methylviologen mixtures up to 3.6 eV^{-1} in CTCs between large aromatics and TCNB (tetracyanobenzene) acceptor.

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2 In the Marcus model,⁶⁸ an increase of the charge recombination rate with increasing EA (the driving
3 force) corresponds to the so-called inverted regime.⁶⁹⁻⁷¹ Various interpretations of the Marcus model
4 were proposed to obtain a linear dependence of the experimentally observed $\ln(k)$ on EA for charge
5 recombination in various small-molecule CTCs. As follows from the Marcus equation,⁶⁸ such linear
6 dependence of $\ln(k)$ appears when the reorganization energy becomes much larger than the driving
7 force for charge recombination. As the latter is always higher than 0.5 eV for the examined CTCs, this
8 leads in our case to unreasonably high reorganization energy, by a factor of 5 higher than imposed by
9 kT . On the other hand, the linear EA dependence of $\ln(k)$ can be assigned to the energy gap law for
10 radiationless transitions in polyatomic molecules as was explained for small-molecule CTCs adsorbed
11 on porous glass at different temperatures.⁶⁷ These are quantum transitions between (nearly)
12 degenerated vibrational levels that belong to the ground and excited electronic states of the molecule⁷²
13 (that is a photoexcited CTC in our case). Note that these transitions are not thermally activated as the
14 classic Marcus model implies (for detailed discussion of the inverted Marcus and the energy gap
15 models, see Refs.^{69,70}). Therefore, we suggest that in the conjugated polymer CTCs the charge
16 recombination mechanism is very similar to that observed earlier in small-molecule CTCs.
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37 The data in Figure 7a suggest that the acceptor EA is the prime factor that governs charge
38 recombination rate for the CTCs used herein. Nonetheless, the fluorenone acceptors are characterized
39 by slightly higher relaxation rates than the dicyanomethylenefluorene ones of similar EAs (compare,
40 for instance, pairs of **NDF/TNFon** and **DDNF/TeNFon**). This shows that other CTC parameters such
41 as the molecular orbital overlap, the donor-acceptor distances, packing motif etc. that enter the pre-
42 exponential factor in Eq. 6, are also important.
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51 From Figure 7b one can readily establish the EA (which is, in the first approximation, directly linked
52 to the driving force for charge recombination) where the donor-acceptor recombination channel begins
53 to dominate over the intrapolymer one (~50 ps for pristine MEH-PPV). This energy can be estimated
54 by equalizing the rates of donor-acceptor and intrapolymer charge transfer, i.e. as the abscissa of the
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crossing point between the dashed and dotted lines in Figure 6b, which results in ~ 3.6 eV. Figure 8 presents PIA anisotropy transients for the MEH-PPV:acceptor blends. The initial anisotropy value of ~ 0.3 is virtually independent of the acceptor. This means that the transient dipoles of photoexcitation (i.e. blend absorption) and probe (i.e. polaron absorption) remain unaffected by CTC formation. The long-time behavior strongly depends on the acceptor: for **DNFon** and acceptors with higher EA the transient anisotropy does not change appreciably from its initial value. In contrast, for the acceptors with lower EA (**Fon**, **NFon**, and **4CN-NFon**), the anisotropy decreases with time in a similar fashion as for MEH-PPV, although to a lower extent. The anisotropy dynamics are ascribed to polaron migration on the polymer: as the polaron samples polymer segments with various orientations, the memory of the initial direction of the polaron transition dipole moment is more and more lost. Therefore, we conclude that the polarons are more mobile in the blends with acceptors of low EA, while they are more localized in the blends with the acceptors of higher EA. The border line, as found above in the isotropic PIA and steady-state spectroscopy data, is drawn at EA of the **DNFon** acceptor.

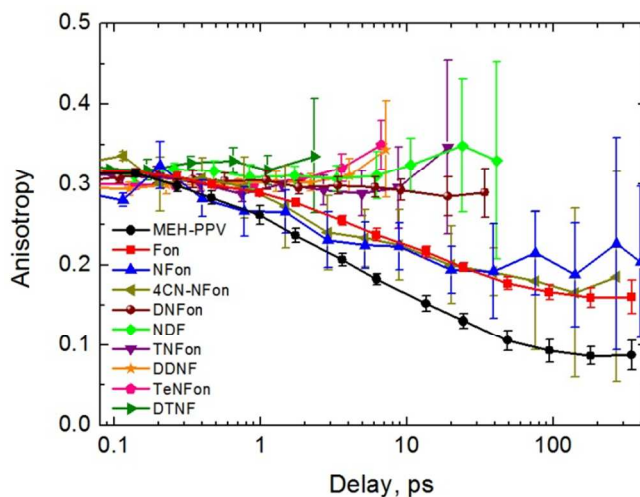


Figure 8. PIA anisotropy transients for the MEH-PPV:acceptor blends at an excitation wavelength of 560 nm and probe wavelength of 2.94 μm . The transients are delay-limited because of deteriorating signal-to-noise ratio due to short lifetimes in the blends with high-EA acceptors.

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2 Based on our optical experiments, we propose the following model of charge dynamics in polymer-
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4 acceptor blends with ground-state CTCs (Figure 9). For low-EA acceptors, namely **Fon**, **NFon**, and
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6 **4CN-NFon**, the CTC concentration in the polymer phase is relatively low while the majority of
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8 acceptor molecules form their own phase (Figure 9a). As a consequence, a part of the photoexcitations
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10 that are characteristic of pristine polymer is mobile, but another part – those of CTCs – is localized.
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12 The fraction of the former decreases for acceptors with high EA which results in the red-wing
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14 absorption (Figure 6a), accelerated recombination rate (Figure 7), and lowered anisotropy values
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16 (Figure 8). Acceptors with high EA form CTCs that are more dispersed in the conjugated polymer
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18 (Figure 9b; see also discussion on the absorption spectra, Figure 6) so that a polymer photoexcitation
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20 always occur near an acceptor molecule that immediately receives the photoexcited electron. Such
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22 complexation, in turn, planarizes MEH-PPV segments thereby increasing the conjugation length within
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24 these fragments of the polymer backbone (and consequently delocalization of the photoexcitation) that
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26 in turn facilitates an efficient charge separation processes. As a consequence, the polaron stays in the
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28 vicinity of its birth place which results in a time-independent anisotropy. Note that in this case the
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30 intrapolymer recombination channel (the second term in Eq. 6) becomes irrelevant and therefore the
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32 recombination rates approach the exponential behavior (Figure 7b). Most probably, the previously
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34 observed self-organization of the polymer chains in crystalline domains due to the CTC formation¹⁴
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36 adds another dimension to this scenario; a more detailed investigation on this issue is underway.
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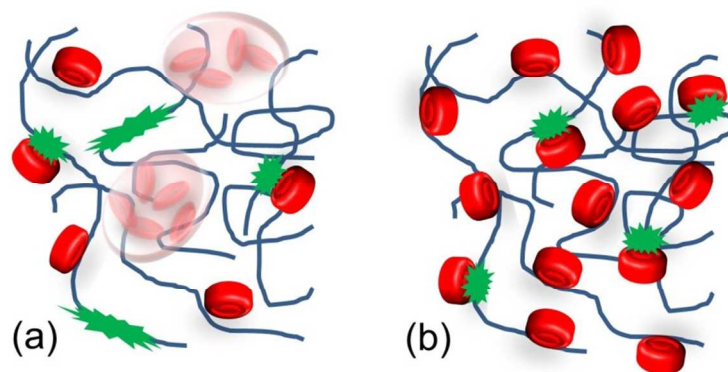


Figure 9. Impression of the MEH-PPV:acceptor blend charge dynamics for acceptors with low (a) and high (b) EAs. Very few of low-EA acceptors form CTCs (red pucks) with polymer chains (blue) while most of acceptors aggregate in their own phase (shaded in light red). This results in mobile (extended green) and more localized (green) photoexcitations. In contrast, almost all high-EA acceptors form CTCs with polymer chains resulting in localized excitations only.

4. CONCLUSIONS

The ground-state CTCs formed between the MEH-PPV conjugated polymer donor and a series of fluorene electron acceptors with varying electron affinity have been studied using a combined platform of synthetic chemistry, DFT calculations, and time-resolved spectroscopy. The acceptor EAs were engineered by attaching a variety of electron withdrawing functional groups (cyano, nitro, and carbonyl) to the fluorene core to systematically modify the LUMO–HOMO energies of the acceptors. Both energies were calculated using a DFT method at the B3LYP/6-31+G(d) level of theory and compared with measurements of acceptor’s electrochemical reduction potential obtained from cyclic voltammetry. The experimental and theoretical values demonstrated excellent agreement.

The formation of the ground-state CTCs in polymer-acceptor blends has been identified by optical absorption spectroscopy through the appearance of an additional absorption in the polymer bandgap.

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2 Visible-IR PIA spectroscopy has been further employed to study excited-state charge separation and
3 recombination dynamics. In all the blends, charge photogeneration is extremely fast (<100 fs), while
4 charge recombination shows noticeably different dynamics ranging from 1 to 50 ps. The acceptor-to-
5 polymer recombination rates exhibit an exponential scaling with the acceptor EA with parameters that
6 are similar to those reported earlier for small-molecule CTCs. Transient anisotropy data have indicated
7 that in the CTCs with acceptors of relatively high EA, the mutual orientation of photoexcited and
8 polaron transient dipole moments is retained, whereas in the low EA acceptors the two dipole moments
9 become less correlated.
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21 The experimental data have been discussed in terms of a charge dynamics model where the low EA
22 acceptors form relatively sparse CTCs with the polymer chain and most of the acceptor molecules stay
23 phase-separated from the polymer. In contrast, the high EA acceptors are thought to be rather dispersed
24 in the polymer due to pronounced CTC formation. As a result, in the first case photoexcitations are
25 fractionated between delocalized polymeric and more localized CTCs ones while in the second case
26 photoexcitations are localized around the point of their creation.
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35 The effect on the acceptor EA on the charge recombination dynamics has clear implications for
36 organic solar cells. The charge-transfer state with the hole at the donor and the electron at the acceptor,
37 both near the interface, has been recognized as a key intermediate state on the route from photon
38 absorption to free charges in various donor-acceptor combinations.^{27,31,42,73} Our results demonstrate that
39 acceptors with a higher EA (i.e. those providing a stronger driving force for charge separation) result in
40 an exponentially increased recombination rate from the CTC state which leads to reduction of the long-
41 lived separated charges. These two opposite trends should be carefully balanced in designing the novel
42 organic bulk heterojunctions.
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2 ASSOCIATED CONTENT
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5 **Supporting Information**
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8 Synthesis and characterization of studied fluorene acceptors with respective ¹H and ¹³C NMR
9 spectra, UV-visible absorption spectra of the acceptors, DFT calculations for fluorene acceptors and
10 correlations between computational DFT data and CV experiments, fitting parameters for the ultrafast
11 spectroscopy data.
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19 This material is available free of charge via the Internet at <http://pubs.acs.org>.
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43 **Notes**
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46 The authors declare no competing financial interest.
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49 **Author Contributions**
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53 The manuscript was written through contributions of all authors. All authors have given approval to the
54 final version of the manuscript.
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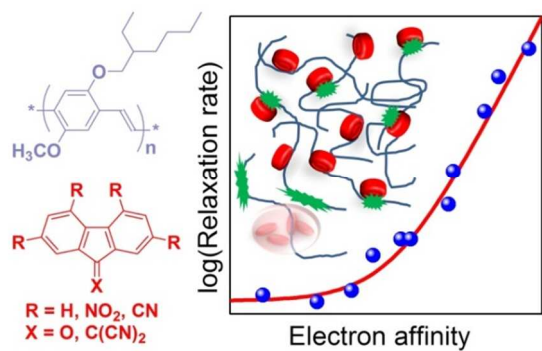
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