Charge transfer dynamics in advanced conjugated systems
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Chapter 2

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

This chapter is devoted to ground and excited state charge transfer in charge transfer complexes in films formed from a semiconducting polymer, MEH-PPV (poly[2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylene vinylene]) blended with a variety of fluorene electron acceptors. The electron affinity (EA) of the fluorene acceptors is systematically varied over ~1.5 eV by attachment of various electron withdrawing groups to the fluorene core. Steady-state absorption and Raman spectroscopies are used to investigate the formation of the ground state charge transfer complexes. The charge transfer dynamics are studied using an ultrafast visible-pump – IR-probe photoinduced absorption experiments. We demonstrate that the acceptor EA is the key – but not the only – parameter that governs charge recombination rates which scale exponentially with the EA. From the time-resolved data we deduced a model that describes the blend morphology for acceptors with low and high EAs. The results presented herein have a clear implication for organic photovoltaics as increasing the acceptor EA increases the driving forces for efficient exciton dissociation but inevitably increases the rate of charge recombination.

The current chapter is based on the following publication:
2.1. 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 (ET) 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 to acceptor charge transfer in the CTC ground state is mainly controlled by the difference between the donor ionization potential and the acceptor 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.\(^3\)

In recent years, a novel kind of Mulliken-type CTCs involving conjugated polymers as donors has been identified in a variety of polymer-acceptor blends.\(^4\,-\,^8\) A number of unusual properties makes the polymer-based CTCs especially fascinating in comparison to their small-molecule counterparts. Planarization of the polymer chains\(^9\) and formation of crystalline domains\(^10\) 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 a number of the repeating units of the polymer is transferred to an acceptor molecule.\(^9\,\,11\) Furthermore, the polymer-based CTCs can be beneficial for organic solar cells because their absorption range extends up to 1 \(\mu\)m (i.e. deeply into the polymer band gap\(^12\)) and the polymer photooxidation stability is also drastically increased due to CTC formation.\(^13\,\,14\)

Ground-state CTCs have also been observed in conjugated polymer-fullerene blends\(^15\) although their absorption is extremely weak.\(^16\,-\,18\) These observations have changed the long-standing paradigm\(^19\) in organic photovoltaics (OPVs) that ET occurs only in the excited state of a donor:acceptor system while the ground-state charge transfer is irrelevant.\(^20\) Nowadays the charge transfer (CT) state with the hole at the donor and the electron at the acceptor, both near the interface, is recognized as a key intermediate state on the route from photon absorption to creation of free charges in various donor:acceptor combinations.\(^21\,\,22\) Furthermore, the new generation of low band gap conjugated polymers for OPV, which has already demonstrated the highest efficiencies in polymer solar cells,\(^23\,\,24\) is built upon a push-pull donor:acceptor concept (i.e. covalently linked alternating
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electron donating and electron accepting monomer units in the polymer backbone\textsuperscript{25} which extends the light absorption into the red region of the solar spectrum. This is highly reminiscent of Mulliken-type CTC absorption which is readily detected visually as a film color change.\textsuperscript{7,8}

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 ET, i.e. charge recombination, occurs within a finite time span.\textsuperscript{26,27} The early studies on dynamics of small-molecule CTCs in solutions\textsuperscript{28,29} 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.\textsuperscript{28} In contrast, the effect of an acceptor EA on the charge recombination dynamics in films has only been studied for a couple of acceptors\textsuperscript{4,30,31} despite the fact that charge migration in films substantially changes the photophysics, contrary to small-molecule CTCs in solution.\textsuperscript{32} Furthermore, in films of conjugated polymers, the very formation of the CTCs alters the film morphology which could indirectly (via the acceptor EA) affect the dynamics of photoinduced charges.

In this chapter, we address the issue of how the acceptor EA controls the charge recombination dynamics in CTCs between an archetypical conjugated polymer donor MEH-PPV (poly[2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylene vinylene])\textsuperscript{33} and a family of small molecular acceptors (Figure 2.1). A series of fluorene acceptors with a range of EAs was synthesized and characterized by cyclic voltammetry at School of Chemistry of Bangor University, United Kingdom, by the group of I. F. Perepichka.\textsuperscript{34} The formation of the ground-state CTCs in the blends was identified by optical absorption and the frequency shift of the polymer Raman band, while the CTC excited state dynamics were studied via generation and recombination of photoinduced charges employing ultrafast visible-pump – IR-probe photoinduced absorption (PIA) spectroscopy. We show that the recombination rate scales exponentially with the acceptor EA, in full accordance with the earlier observations for small-molecule CTCs in solution.\textsuperscript{28, 35} Finally, the anisotropy dynamics suggest that separated charges in most of the blends remain spatially highly localized, in sharp contrast to the case of the pristine polymer.
Figure 2.1. Structures of MEH-PPV polymer (upper left) and studied series of fluorene electron acceptors. Abbreviations of the latter are shown in bold.

2. 2. Experimental section

2.2.1. Samples

Fluorenone (Fon) and 2,7-dinitrofluorenone (DNFon) have been purchased from Sigma-Aldrich and used without further purification. Details of the synthesis of fluorene acceptors 2-nitrofluorenone (NFon), 2,4,7-trinitrofluorenone (TNFon), 2,4,5,7-tetrinitrofluorenone (TeNFon), 2-nitro-9-dicyanomethylenefluorene (NDF), 2,7-dinitro-9-dicyanomethylenefluorene (DDNF), 2,4,7-trinitro-9-dicyanomethylenefluorene (DTNF), 4-cyanofluorenone (4CN-Fon), and 2-nitro-5-cyanofluorenone (4CN-NFon) and their characterizations are given in Ref. 34.

Regioregular MEH-PPV was chosen as a donor since it is known to readily form a ground-state CTC with fluorene electron acceptors.\textsuperscript{9, 21} MEH-PPV (Sigma-Aldrich, $M_n = 86,000$, $M_w = 420,000$) and fluorene acceptors were dissolved
separately in chlorobenzene at a concentration of 2 g\cdot L\(^{-1}\). The solutions were placed into an ultrasonic bath for 15 minutes at 22 °C and then stirred with a magnetic stirrer for ~6 hours at 50 °C. Their blends were prepared by mixing the solutions of MEH-PPV and an acceptor with a molar ratio of 1:0.3 per polymer repeat unit. Further increase of the acceptor concentration in the blends led to phase segregation with loss of sample optical quality.\(^{36}\)

Films were prepared by drop casting of MEH-PPV:acceptor solution onto a 150 µm thick microscope cover slide followed by tilting the slide until the droplet of ca. 50 µL volume was distributed over the available surface of 22×22 mm. The film formed after evaporation of the solvent and was allowed to dry for 8 hours in an air atmosphere at 22 °C. All experiments were performed at ambient conditions; no sample degradation was observed during the experiments.

MEH-PPV HOMO and LUMO energies of -5.0 and -2.8 eV, respectively, were taken from the electrochemical data in Ref. 19. Fluorene acceptor’s reduction cyclic voltammetry potentials and calculated energy levels were obtained by group of I. Perepichka (School of Chemistry, Bangor University, UK) as described in Ref. 34.

2.2.2. Optical absorption and Raman spectroscopy

Absorption spectra of the blends were recorded with a Perkin-Elmer Lambda 900 spectrometer.

The Raman experiments were performed in a 180° backscattering configuration, using a triple-grating micro-Raman spectrometer (T64000, Jobin Yvon), consisting of a double-grating monochromator (acting as a spectral filter) and a polychromator which disperses the scattered light onto a liquid-nitrogen cooled charge coupled device (CCD) detector. The frequency resolution was better than 2 cm\(^{-1}\) for the frequency region considered. A krypton laser with 676.4 nm excitation wavelength to minimize the fluorescent background was focused onto the samples using a 50× microscope objective. The excitation intensity on the samples was about 1 µW/µm\(^2\).

In Raman data, the background was subtracted after its approximation by a quadratic polynomial function. The 1580 cm\(^{-1}\) Raman band of MEH-PPV was then fitted with a Gaussian function in the a 1565-1595 cm\(^{-1}\) range to determine position of its maximum with a typical 0.1 cm\(^{-1}\) accuracy according to Ref. 37.

2.2.3. Ultrafast spectroscopy experiments
The dynamics of photogenerated charges in selected materials have been explored with a PIA technique, which 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. These bands, called low energy (LE) and high energy (HE) polaron bands, are situated for the studied systems at ~3500 and ~10000 cm\(^{-1}\), respectively. 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. 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.

The PIA experiments were performed with a home-built 1kHz Ti:Sapphire multipass amplifier 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. The IR OPO was optimized to provide ~70 fs pulses at ~3400 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 \(\Delta T\), the differential pump-on, pump-off signal \(\Delta I\) from the lock-ins were normalized to the intensity \(I\) of the IR beam transmitted through the sample:

\[
\Delta T = \frac{\Delta I}{I}
\]

To calculate the isotropic \(\Delta T_{ISO}(t)\) and anisotropic \(r(t)\) transients the standard expressions:

\[
\Delta T_{ISO}(t) = \frac{\Delta T_{||}(t) + 2 \cdot \Delta T_{\perp}(t)}{3},
\]

and
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\[ r(t) = \frac{\Delta T_{\|}(t) - \Delta T_{\perp}(t)}{3 \cdot \Delta T_{\text{iso}}(t)} \]  

were used. Here \( \Delta T_{\perp}(t) \) and \( \Delta T_{\|}(t) \) are the relative transmission changes of the perpendicular and parallel components of the probe signal. All data were obtained under ambient conditions.

2.3. Results and discussion

2.3.1. 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 2.1). The introduction of a NO\(_2\) group in substituted fluorenes increases the EA of the fluorene molecule by \(~0.2\)–\(0.3\) eV, while replacement of oxygen in the carbonyl group by the dicyanomethylene fragment increases the EA by \(~0.35\)–\(0.45\) eV.\(^{42-48}\) Therefore, with the structural variations of the selected series of fluorene acceptors presented in Figure 2.1, the LUMO energy levels can be tuned by \(~1.5\) eV, see Figure 2.2. Table 2.1 contains the values of the reduction cycling voltammetry potentials (\(E_{\text{LUMO}}^{\text{CV}}\)) obtained by the group of I. Perepichka (School of Chemistry, Bangor University, UK).

![Figure 2.2](image)

*Figure 2.2. Positions of the LUMO energy levels (\(E_{\text{LUMO}}^{\text{CV}}\)) of fluorene electron acceptors from cyclic voltammetry experiments (red blocks). MEH-PPV HOMO and LUMO energies (blue blocks) obtained from Ref. 19 and are also shown for comparison.*
Table 2.1. Reduction cyclic voltammetry potentials of the fluorene acceptors depicted in Figure 2.1

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{LUMO}}^{\text{CV}}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fon</td>
<td>-3.131</td>
</tr>
<tr>
<td>4CN-Fon</td>
<td>-3.340</td>
</tr>
<tr>
<td>NFon</td>
<td>-3.472</td>
</tr>
<tr>
<td>4CN-NFon</td>
<td>-3.641</td>
</tr>
<tr>
<td>DN Fon</td>
<td>-3.702</td>
</tr>
<tr>
<td>NDF</td>
<td>-3.931</td>
</tr>
<tr>
<td>TN Fon</td>
<td>-3.961</td>
</tr>
<tr>
<td>DDNF</td>
<td>-4.152</td>
</tr>
<tr>
<td>TeNFon</td>
<td>-4.236</td>
</tr>
<tr>
<td>DTNF</td>
<td>-4.417</td>
</tr>
</tbody>
</table>

Due to the fact that the EA are sometimes approximated as the negative of the LUMO energies ($EA = -E_{\text{LUMO}}$) in accordance with generalized DFT-Koopman’s theorem, we used $-E_{\text{LUMO}}^{\text{CV}}$ as the acceptor EA:

$$EA^{\text{CV}} = -E_{\text{LUMO}}^{\text{CV}}$$  (4)

For more detailed explanations see the Ref. 34.

2.3.2. Steady-state absorption

Figure 2.3a shows optical absorption spectra of the MEH-PPV:acceptor blends. For the sake of simplicity, the blends are named after their respective acceptor. With increase of the acceptor EA, i.e. with decreasing effective HOMO–LUMO energy
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gap, the blends show characteristic signatures of a ground-state polymer:acceptor CTC previously identified for MEH-PPV:TNFon blends. First, an absorption tail begins to form in the polymer band gap, i.e. at wavelengths longer than 600 nm (Fig. 2.3b). Second, the absorption maximum is progressively shifted to the red (Fig. 2.3a) for acceptors with EA higher than that of 4CN-NFon. This indicates that the majority of the conjugated chains are involved in CTC formation. With an increase of the acceptor 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 acceptor EA.

Figure 2.3. (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 650 nm 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 2.3a 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 (Fig. 2.3b) 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 2.3b, the fluorenone acceptors (i.e. with carbonyl oxygen at the C-9 bridged atom of the fluorene moiety, Figure 2.1) form stronger absorbing CTCs than their dicyanomethylenefluorene-derivatized counterparts with comparable EAs (cf. for pairs NDF/TNFon and DDNE/TeNFon). Therefore, EA is not the only variable that governs the CTC properties even for acceptors with similar molecular structure.

2.3.3. Raman spectroscopy

Raman spectroscopy provides a reliable means to identify the ground-state charge-transfer,
49 which changes the electron density at the donor-acceptor chemical bonds involved in the CTC interactions and therefore results in a shift in the vibrational frequencies. In MEH-PPV:TNFon CTC, the MEH-PPV Raman band at 1582 cm\(^{-1}\) that corresponds to the valence vibrations of conjugated carbon bonds (the symmetric stretching vibration of the phenyl ring) is especially useful due to its pronounced spectral downshift.\(^9\) This frequency downshift is an evidence of partial transfer of the \(\pi\)-electron density from the polymer to the acceptor.\(^{50-51}\)

Figure 2.4a shows the position of the Raman band, while Fig. 2.4b shows the band’s maximum as a function the effective LUMO-HOMO gap. The MEH-PPV band at 1582 cm\(^{-1}\) downshifts up to \(~5\) cm\(^{-1}\) with increasing the acceptor EA.

The Mulliken model for ground-state CTCs predicts that the amount of ground-state charge transfer is controlled by the energy gap between the acceptor LUMO and the donor HOMO energies. Therefore, decreasing the effective EA should result in electron density decreasing at the polymer and, therefore, in a spectral downshift of the polymer Raman band. This is roughly in agreement with the Raman data in Fig. 2.4, however, with several deviations. Thus, the dependence is not smooth but rather stepwise. For the effective EA lower than 3.7 eV, the Raman band in the blends with Fon, 4CN-Fon, and 4CN-NFon peaks at the same frequency as that of the pristine polymer (~1582 cm\(^{-1}\)), or even upshifted by \(~2\) cm\(^{-1}\) in the blends with NFon (Fig. 2.4).
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Figure 2.4. (a) The 1582 cm\(^{-1}\) Raman line of MEH-PPV in 1:0.3 volume ratio MEH-PPV:acceptor blends. Dots represent the data points and Gaussian fits in 1565 cm\(^{-1}\) - 1595 cm\(^{-1}\) region for it, respectively. Black vertical line shows the maximum of Raman band for pristine MEH-PPV. The spectra are vertically shifted for convenience. (b) Maxima of the polymer band (~1582 cm\(^{-1}\) for the neat polymer) as a function of the effective LUMO-HOMO gap. The red line is a guide to the eye.

In contrast, for acceptors with the effective EA lower than 3.8 eV the Raman band demonstrates an ~5 cm\(^{-1}\) downshift, which does not show any systematic variation with the acceptor chemical structure, however it looks to be related to the overall shift for higher EA. Importantly, for these relatively strong acceptors the Raman band slightly downshifts as a whole assuming that the majority of the conjugated polymer chains (or segments) are involved in the CTCs.

The stepwise dependence in Fig. 2.4b is in line with the concentration threshold character of CTC formation observed in MEH-PPV:TNF\(_{\text{on}}\) solutions\(^{52-53}\). This stepwise behavior was explained as a collective phenomenon with a positive feedback driven by neighbor effects.\(^{54}\) Briefly, formation of a CTC on the polymer
chain results in an increased probability of new CTC formation near the existing one. Most likely, the same scenario governs the CTC formation in blends of MEH-PPV with the other fluorene acceptors and results in the stepwise dependencies of the CTC properties on the acceptor LUMO energy. As follows from the Raman data, the efficient CTC formation requires a threshold driving force determined by the EA<sub>CV</sub> of ~3.7 eV.

From the Raman and optical absorption data on the blends, one can conclude that the EA is one of the key factors controlling the ground-state charge transfer and CTC absorption in polymer:acceptor blends. Raman data do not show any CTC signatures for the four relatively weak acceptors: Fon, 4CN-Fon, NFon, and 4CN-NFon. As it was shown in Sec. 2.3.2, in the blends with these acceptors, no clear CTC features were observed in the absorption spectra either.

### 2.3.4. Photoinduced charge generation and recombination

While absorption data are indispensable in studying formation of the ground-state CTCs, they do not provide any information on the excited-state dynamics, i.e. on the processes of charge separation and recombination. For this, a visible-pump IR-probe arrangement<sup>31</sup> was used where the magnitude of PIA signals in the region of LE polaron absorption monitors the concentration of photoinduced charges on the polymer.

Figure 2.5a shows isotropic PIA transients for all the MEH-PPV:acceptor blends recorded at an excitation wavelength of 560 nm. This excitation wavelength was chosen at the lower-energy side of the absorption spectra (Figure 2.3a) to minimize deposition of excessive excitation energy.

As is clear from Figure 2.5a, the initial charge photogeneration for all the samples is extremely fast and occurs within the apparatus time resolution of ~100 fs, regardless of the acceptor. Therefore, we conclude that the polaron generation in the polymer occurs faster than 100 fs, and hence forward donor-to-acceptor ET is almost immediate upon optical excitation. In contrast, the decaying parts of the transients are strongly acceptor-dependent with the relaxation timescale changing from ~100 ps for MEH-PPV to ~1 ps for DTNF. These timescales are attributed to the charge recombination (or back ET from the acceptor to the polymer) process.
We briefly comment on the origin of the PIA signal from the film of pristine MEH-PPV. Ideally, such excitation should be of entirely excitonic nature so that no polarons are produced. However, a number of MEH-PPV excitons quickly dissociate into charge species which assignment was actively debated in the past (see for instance Ref. 54). 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.

To quantify the dynamics, the transients were fitted by a bi-exponential function (Figure 2.5a, solid lines) with fit parameters presented in Table 2.2.
Table 2.2. The fitting parameters of pristine MEH-PPV and MEH-PPV:acceptors transient spectra at 560 nm.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Isotropic decay</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T1 (A1)</td>
<td>T2 (A2)</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>50ps (0.65)</td>
<td>3ps (0.25)</td>
</tr>
<tr>
<td>Fon</td>
<td>55ps (0.65)</td>
<td>3ps (0.2)</td>
</tr>
<tr>
<td>4CN-Fon</td>
<td>47ps (0.78)</td>
<td>-</td>
</tr>
<tr>
<td>NFon</td>
<td>27ps (1)</td>
<td>-</td>
</tr>
<tr>
<td>4CN-NFon</td>
<td>21ps (1)</td>
<td>-</td>
</tr>
<tr>
<td>DNFon</td>
<td>20.5ps (0.82)</td>
<td>1ps (0.18)</td>
</tr>
<tr>
<td>NDF</td>
<td>12.3ps (1)</td>
<td>-</td>
</tr>
<tr>
<td>TNFon</td>
<td>7ps (1)</td>
<td>-</td>
</tr>
<tr>
<td>DDNF</td>
<td>2.7ps (0.6)</td>
<td>0.7ps (0.35)</td>
</tr>
<tr>
<td>TeNFon</td>
<td>1.7ps (0.98)</td>
<td>65ps (0.02)</td>
</tr>
<tr>
<td>DTNF</td>
<td>1ps (0.98)</td>
<td>-</td>
</tr>
<tr>
<td>DTeNF</td>
<td>0.4ps (0.92)</td>
<td>23ps (0.08)</td>
</tr>
</tbody>
</table>

To analyze the isotropic signal we have used the following bi-exponential fitting function:

\[ \Delta T_{ISO} = A_0 + A_1 \exp \left( -\frac{t}{T_1} \right) + A_2 \exp \left( -\frac{t}{T_2} \right) \]  

where \( A_i \) and \( T_i \) are the amplitudes and the time constants respectively, \( i \) - number of fitting exponents. The sum of amplitudes \( A_i \) and exponential baseline is normalized to 1. The two recombination rates most probably correspond to different donor/acceptor configurations or/and partial ET states. In any case, for the majority of the acceptors, the amplitude of the dominating exponential functions exceeds 90% (and is always higher than 80%), pointing at an almost mono-exponential relaxation. Therefore, the time constant of the dominating decay process was taken as the characteristic time for the back ET.

Figure 2.5b 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 back ET that is characteristic for neat MEH-PPV. The relaxation rate that accounts for the both intermolecular and intrapolymer channels is therefore expressed as follows:

\[
k = k_{ET} \cdot \exp \left( \frac{E_A}{\Delta E} \right) - 1 + k_0.
\]

where \( k_{ET} \) is the proportionality coefficient, \( \Delta E \) is a characteristic energy, and \( k_0 \) is the rate of the intrapolymer back ET. The fit to the experimental data resulted in the following values: \( k_{ET} = 4.1 \cdot 10^{-10} \text{ ps}^{-1} \), \( \Delta E = 0.2 \text{ eV} \), and \( k_0 = 0.018 \text{ ps}^{-1} \).

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\(^{28,29} \) and solid phase.\(^{35,55} \) 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 \textit{et al.}\(^{28} \) 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 \textit{et al.}\(^{29,35} \) found the slope to vary from 2 \text{ eV}^{-1} in benzene–methylviologen mixtures up to 3.6 \text{ eV}^{-1} in CTCs between large aromatics and TCNB (tetracyanobenzene) acceptor.

In the Marcus model,\(^{56} \) an increase of the charge recombination rate with increasing EA (the driving force) corresponds to the so-called inverted regime.\(^{57-59} \) Various interpretations of the Marcus model were proposed to obtain a linear dependence of the experimentally observed \( \ln(k) \) on EA for charge recombination in various small-molecule CTCs. As follows from the Marcus equation,\(^{56} \) such linear dependence of \( \ln(k) \) appears when the reorganization energy becomes much larger than the driving force for charge recombination. As the latter is always higher than 0.5 eV for the examined CTCs, this leads in our case to unreasonably high reorganization energy, by a factor of 5 higher than imposed by \( kT \). On the other hand, the linear EA dependence of \( \ln(k) \) can be assigned to the energy gap law for radiationless transitions in polyatomic molecules as was explained for small-molecule CTCs adsorbed on porous glass at different temperatures.\(^{55} \) These are quantum transitions between (nearly) degenerated vibrational levels that belong to the ground and excited electronic states of the molecule\(^{60} \) (that is a photoexcited CTC in our case). Note that these transitions are not thermally
activated as the classic Marcus model implies (for detailed discussion of the inverted Marcus and the energy gap models, see Refs. 57, 58). Therefore, we suggest that in the conjugated polymer CTCs the charge recombination mechanism is very similar to that observed earlier in small-molecule CTCs.

The data in Figure 2.5a suggest that the acceptor EA is the prime factor that governs charge recombination. Nonetheless, the fluorenone acceptors are characterized by slightly higher relaxation rates than the dicyanomethylenfluorene ones of similar EA (compare, for instance, pairs of NDF/TNFon and DDNF/TeNFon). This shows that other CTC parameters such as the molecular orbital overlap, the donor-acceptor distances, packing motif etc. that enter the pre-exponential factor in Eq. 6, are also important.

From Figure 2.5b one can readily establish the EA for which the intermolecular recombination channel due to back ET begins to dominate over the intrapolymer one (~50 ps for pristine MEH-PPV). This energy can be estimated by equalizing the rates of intermolecular and intrapolymer charge transfer, i.e. as the abscissa of the crossing point between the dashed and dotted lines in Figure 2.6b, which results in ~3.8 eV.

Figure 2.6 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 excitation (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 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 the DNFon acceptor.
Figure 2.6. PIA anisotropy transients for the MEH-PPV:acceptor blends. The transients are delay-limited because of deteriorating signal-to-noise ratio due to short lifetimes in the blends with high-EA acceptors.

2.3.5. Ground-state CTCs: influence on blends morphology

Based on the optical experiments, we propose the following model of morphology in polymer:acceptor blends with ground-state CTCs (Figure 2.7). For low-EA acceptors, namely Fon, NFon, and 4CN-NFon, the CTC concentration in the polymer phase is relatively low while the majority of acceptor molecules form their own phase (Figure 2.7a). As a consequence, a part of the photoexcitations that are characteristic of neat polymer is mobile, but another part – those of CTCs – is localized. The fraction of the former decreases with increasing acceptor EA which results in the red-wing absorption (Figure 2.3a), Raman shift (Figure 2.4a), accelerated back ET rate (Figure 2.5), and lowered anisotropy values (Figure 2.6). Acceptors with high EA form CTCs that are more dispersed in the conjugated polymer (Figure 2.7b; see also discussion on the absorption spectra, Figure 2.3) so that a polymer exciton is always generated near an acceptor molecule that immediately receives the photoexcited electron. Such complexation, in turn, planarizes MEH-PPV segments thereby increasing the conjugation length within these fragments of the polymer backbone (and consequently exciton delocalization) that facilitates trapping of all excitons through an efficient charge
transfer processes. As a consequence, the polaron stays in the vicinity of its birth place which results in a time-independent anisotropy. Note that the second, intrapolymer relaxation channel (the second term in Eq. 6) does not need to be involved and therefore the relaxation rates approach the asymptotic exponential behavior (Figure 2.5b). Probably, the previously observed self-organization of the polymer chains in crystalline domains due to the CTC formation\textsuperscript{10} adds another dimension to this scenario; a more detailed study on this point is underway.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2_7.png}
\caption{Impression of the MEH-PPV:acceptor blend morphology for acceptors with low (a) and high (b) EAs. For low-EA acceptors, very few of them form CTCs (red pucks) with polymer chains (blue) while most of acceptors aggregate in their own phase (shadowed in light red). This results in mobile (extended green) and more localized (green) excitations. For high-EA acceptors, almost all of them form CTCs with polymer chains resulting in localized excitations only.}
\end{figure}

\subsection*{2.4. Conclusions}

The ground-state CTCs formed between the MEH-PPV conjugated polymer donor and a series of fluorene electron acceptors with varying EA have been studied using an optical 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 EA of the acceptors.

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. Raman spectroscopy on the strongest MEH-PPV band at 1582 cm\textsuperscript{-1} has confirmed these findings. Visible-IR PIA
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Spectroscopy has been further employed to study excited-state charge separation and recombination dynamics. In all blends, charge photogeneration is extremely fast (<100 fs), while charge recombination shows noticeably different dynamics ranging from 1 to 50 ps. The acceptor-to-polymer recombination rates exhibit an exponential scaling with the acceptor EA with parameters that are similar to those reported earlier for small-molecule CTCs. Transient anisotropy data have indicated that in the CTCs with acceptors of relatively high EA, the mutual orientation of exciton and polaron transient dipole moments is retained, whereas in the low-EA acceptors the two dipole moments become less correlated.

The experimental data have been discussed in terms of a morphology model where the low-EA acceptors form relatively sparse CTCs with the polymer chain and most of the acceptor molecules stay phase-separated from the polymer. In contrast, the high-EA acceptors are thought to be rather dispersed in the polymer due to pronounced CTC formation. As a result, in the first case photoexcitations are fractioned between delocalized polymeric and more localized CTCs ones while in the second case excitations are localized around the point of their creation.

The effect on the acceptor EA on the charge transfer dynamics is directly linked to the field of organic photovoltaics. In polymer:fullerene and other phase-separated donor:acceptor blends, CTCs are formed only at the donor to acceptor interface so that photon absorption triggers photophysics at the domain boundaries of the phase-separated donor and acceptor domains. It is only at later times that the exciton diffusion delivers the excitations to the interfacial CTCs to form the charge-separated states. In such blends, the interfacial CTCs hardly contribute to optical absorption due to their relative scarcity and, in polymer-fullerene blends, due to their weakness. In contrast, in polymer:acceptor blends with pronounced ground-state charge transfer, as studied here, a CTC is formed per each conjugated segment so that exciton diffusion and other concurrent processes (e.g., generation of triplets) are excluded from the photophysics. As a result, optical excitation leads to immediate formation of a charge-separated state, and the charge relaxation dynamics can be monitored directly without contamination from competing photophysical processes.
2.5. References

1. Mulliken, R. S., Structures of Complexes Formed by Halogen Molecules with Aromatic and with Oxygenated Solvents. Journal of the American Chemical Society 1950, 72, 600-608.
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Chapter 2