Chapter 5

Ultrafast Dynamics in Charge-Transfer Complexes of Conjugated Polymers

In this chapter, the charge photogeneration and early recombination in charge-transfer complexes (CTCs) of an archetypical conjugated polymer (MEH-PPV) and strong low-molecular-weight acceptors are studied by ultrafast visible-pump – IR-probe spectroscopy. A MEH-PPV/PCBM blend was studied in parallel as a “reference” photovoltaic material. After excitation of the CTC band, an immediate (<100 fs) electron transfer is observed from the polymer chain to the acceptor with the same yield as in the MEH-PPV/PCBM blend. The forward charge transfer in the CTCs is followed by an efficient (~95%) and fast (<30 ps) geminate recombination. Polarization sensitive experiments demonstrate high (~0.3) values of transient anisotropy for the CTCs polaron band. In contrast, in the MEH-PPV/PCBM blend the dipole moment orientation of the charge-induced transition is less correlated with the polarization of the excitation photon. According to our data, photogeneration and recombination of charges in the CTCs take place within a single pair of a polymer conjugation segment and an acceptor while in the MEH-PPV/PCBM blend exciton migration precedes the separation of charges. The interpretation of the ultrafast experiments is supported by photocurrent measurements on the corresponding MEH-PPV/acceptor photodiodes.

4 The current chapter is based on the following publications:


5.1. Introduction

The process of charge photogeneration in conjugated polymer based materials has been actively studied in the last two decades because of its key importance for organic solar cells and photodetectors.\textsuperscript{1-3} Charge generation is extremely efficient in polymer-fullerene blends\textsuperscript{4, 5} which are usually considered as a simple mixture of two compounds without noticeable charge-transfer interaction in the electronic ground state.\textsuperscript{1} At the same time, the formation of a weak ground-state charge-transfer complex (CTC) has recently been identified in a number of blends of conjugated polymers with low-molecular weight organic acceptors.\textsuperscript{6, 7} The donor-acceptor CTCs show high stability\textsuperscript{8} and an extended photosensitivity in the red and near IR ranges due to the presence of a CTC absorption band in the optical gap of the polymer.\textsuperscript{6, 9, 10} Therefore, polymer materials with a weak ground-state charge transfer offer a potential way to develop low-bandgap materials for plastic photovoltaics. Interestingly, evidence of the formation of a very weak CTC in blends of conjugated polymers with the soluble fullerene derivative PCBM has recently been reported,\textsuperscript{11-13} which attracts additional interest to polymer-based CTCs as a model system.

Previous photophysics studies on various low-molecular\textsuperscript{9, 10} and polymer based\textsuperscript{13} CTCs demonstrated that in these materials charge photogeneration and recombination differ considerably from donor-acceptor blends without ground-state charge transfer (Fig.5-1a). As the CTC influences the material properties in a number of ways, one can envisage several reasons for such a difference. First, the CTC photoexcitation formally corresponds to immediate electron transfer from the donor to the acceptor\textsuperscript{14, 15} implying that charge separation begins at the very moment of photon absorption. This is in sharp contrast with the bulk-heterojunction concept of conventional donor-acceptor mixture,\textsuperscript{3, 16} in which an exciton photoexcited either at the donor or acceptor needs to diffuse to the donor-acceptor interface where the charge separation occurs. Second, the donor-acceptor coupling in the CTC might have a negative effect on photon-to-charge conversion. Donor-acceptor interaction facilitates not only an efficient charge separation but also a geminate recombination\textsuperscript{17, 18}, hereby reducing availability of charge carriers at long times. Finally, the interaction between the donor and acceptor in CTCs could influence the morphology of the blend\textsuperscript{19} which, for instance, in polymer-
fullerene blends, is of paramount importance for efficient charge photogeneration\textsuperscript{20} and transport.\textsuperscript{21, 22} Specifically, CTC can facilitate donor-acceptor intermixing\textsuperscript{19} counteracting phase-separation usually observed in donor-acceptor blends without charge-transfer interaction.\textsuperscript{22} Being hardly distinguishable in cw photocurrent experiments\textsuperscript{6, 13}, most of these effects can be dissected from photoexcitation dynamics at the 0.1-100 ps time scale.

One of the most efficient ways of studying the initial dynamics of photogenerated charges in conjugated polymers is photoinduced absorption (PIA) spectroscopy\textsuperscript{23} that nowadays features sub-100-fs time resolution\textsuperscript{24}. In a PIA experiment, the time evolution of characteristic absorption bands associated with the photoinduced charges is directly monitored. In PPV-type polymers, these bands include the so-called high-energy (HE) band at ~1.1 $\mu$m\textsuperscript{18, 25, 26}, the low-energy (LE) band around 3.5 $\mu$m\textsuperscript{27, 28}, and the IR active vibrations (IRAV) band around 8-10 $\mu$m\textsuperscript{24, 29}. The LE band is the most suitable one for optical detection of induced charges because, on one hand, the LE band is not contaminated by presence of stimulated emission, electroabsorption, triplet-state excitation, or ground-state bleaching\textsuperscript{30, 31} as the widely exploited HE band might be. On the other hand, unlike the IRAV band, it lacks absorption originating from the ground-state vibrational modes of the polymer, thereby allowing for background-free

\textbf{Figure 5-1.} a) Schematic of frontier molecular orbitals in CTC. Arrows show optical excitation and electron-transfer pathway. b) Chemical structures of CTC acceptors (DNAQ, TNF), donor polymer MEH-PPV, and reference acceptor PCBM.
measurements. Another attractive property of the LE band stems from the fact that the orientation of the LE transition dipole is strongly correlated with the orientation of the electronic (exciton) absorption dipole of the polymer chain, similar to the HE band. Therefore, polarization-sensitive PIA experiments can provide valuable information on charge and energy transfer among conjugated segments of the polymer. This venue has been exploited only cursorily so far, even for the HE polaron band.

The current chapter will be devoted to the early-time photophysics of polymer-acceptor blends with a pronounced ground-state CTC formation. The CTCs between a MEH-PPV polymer and two acceptors (TNF and DNAQ) with different electron affinities have been used as a model system. PIA spectroscopy on the LE band allowed us to follow the transient absorption changes caused by positive charges on the polymer chains with 100 fs time resolution. After excitation of the CTCs in the visible, an immediate (<100 fs) appearance of the LE band was observed which is associated with ultrafast formation of charges on the polymer. Although the charge photogeneration in CTCs shows a yield comparable to that in MEH-PPV/PCBM blend, it is followed by an efficient and fast (<30 ps) geminate recombination. As a result of the recombination, the concentration of long-lived charges in the CTCs appears to be one order of magnitude lower than in a MEH-PPV/PCBM blend. According to the polarization-sensitive experiments, photogeneration and recombination of charges in the CTCs occur within a parent donor-acceptor pair in contrast to the MEH-PPV/PCBM blend where ultrafast energy transfer takes place prior to charge generation. The results of the ultrafast optical experiments are in good agreement with external quantum efficiency measurements of photon-to-current conversion, observed in the corresponding MEH-PPV/acceptor photodiodes.

5.2. Experimental

As model CTCs we studied binary mixtures of poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) with 2,4,7-trinitrofluorenene (TNF) or 1,5-dinitroantraquinone (DNAQ) (Fig.5-1b). The MEH-PPV/TNF and MEH-PPV/DNAQ blends were prepared by dissolving each component separately in chlorobenzene with a concentration of 1 g/L. The solutions were mixed with
weight ratio of MEH-PPV:TNF or MEH-PPV:DNAQ of 1:0.3 to maximize the CTC concentration in the films. Up to this ratio, almost all acceptor is involved in the CTC with no signs of separate acceptor phase formation as follows from difference scanning calorimetry data and Rayleigh scattering data of CTCs with different acceptor concentrations.

Films were prepared by drop-casting on 180-µm thick fused silica microscope cover slides (UQG-Optics). The reference blend of MEH-PPV and the soluble C₆₀ derivative (6,6)-phenyl-C₆₁-butyric-acid (PCBM) with 40% of fullerene content (by weight) was prepared following the same procedure. Optical densities at the excitation wavelength of the samples were kept below 0.6 to ensure homogeneous excitation along the beam propagation direction. All experiments were performed in ambient conditions as no sample degradation during measurements was observed.

Time- and spectrally-resolved PIA experiments were performed at two setups optimized for either wide-range IR tunability or high time resolution. The first system was based on a commercially-available Ti:Sapphire regenerative amplifier (Hurricane, Spectra-Physics) and two optical parametric amplifiers (TOPAS, Light Conversion) operating in the visible (500-700 nm) and IR (1.2-20 µm) regions. The output of the former was used as a pump while the latter provided the tunable IR probe. The polarizations of the pump and probe beams were always parallel. The cross-correlation width for any wavelength combination did not exceed 400 fs.

The second laser system featured a substantially higher time resolution (<100 fs) and a better signal-to-noise ratio at the expense of IR tunability. The output of a home-build 1 kHz Ti:Sapphire multipass amplifier pumped a noncollinear optical parametric amplifier (NOPA) and a 3-stages IR OPO. The NOPA followed by a BK7 prism compressor, produced 30 fs, 40 nJ excitation pulses tunable over the visible range (500-700 nm). The IR OPO was specially designed to generate short (<70 fs, 350 cm⁻¹ FWHM) transform-limited pulses centered at the LE charge-associated band of MEH-PPV at 3 µm. The polarization of the IR probe beam was rotated by 45° with respect to the polarization of the visible pump beam. After the sample, the probe component parallel or perpendicular to the pump was selected by a wire-grid polarizer (1:100 extinction) and detected by a liquid-nitrogen-cooled InSb photodiode.
In both setups, the visible pump beam was focused into a factor of 2 wider spot than the IR beam to minimize the spatial inhomogeneity of excitation in the probed region. The density of absorbed photons in the sample did not exceed $10^{18} \text{ cm}^{-3}$ which is one order of magnitude lower than typically required for exciton-exciton annihilation to affect the dynamics.\(^{37}\) (However it is in average $\sim10^3$ times higher than sun illumination). The IR signal was processed by a lock-in amplifier referenced to a mechanical chopper in the pump beam, and normalized to the averaged power of the transmitted light $I$ to obtain the relative change in transmission:

$$\Delta T = \frac{\Delta I}{I}$$

where $\Delta I$ is the difference between the probe beam powers with the pump open/closed. In the polarization-sensitive measurements, the isotropic (population) signal $\Delta T_{\text{Iso}}(t)$ and the induced anisotropy $r(t)$ were calculated\(^{38}\) using the following expressions:

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

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

where $\Delta T_{\parallel}$ and $\Delta T_{\perp}$ are the relative transmission changes for the parallel and perpendicular components of the probe, respectively. Note that upon derivation of Eqs.2 and 3, a random three-dimensional distribution of chromophores is assumed. However, anisotropic polymer chain packing was reported in similar blends for directions across and along the film\(^{39, 40}\). Although this can potentially lead to a slight crosstalk between the isotropic and anisotropic signals, the range of possible anisotropy values from 0.4 (parallel dipole moments) to -0.2 (orthogonal dipole moments) is not affected\(^{38}\). A detailed account of data processing and global fitting analysis can be found in Appendix 5-6.

In the cw PIA experiments, the sample was excited at the wavelength of 532 nm by the second harmonic of a cw Nd:YAG laser with an intensity of 60 mW/cm\(^2\). For the near-IR measurements a combination of a tungsten-halogen lamp, a
monochromator coupled to a Si or cooled InGaAs photodetector, and a lock-in amplifier at 75 Hz modulation frequency was employed. For longer IR wavelengths, an FTIR spectrometer (Infralum FT-801) was used with the successive 32 sec acquisition of spectra with and without cw illumination. In the latter measurements, a sample was drop-cast on a IR transparent BaF$_2$ substrate.

For the photocurrent measurements, sandwich-type samples were prepared on ITO-covered glass substrates. A PEDOT:PSS layer was spin-cast onto the ITO-side. After that, an active layer was spin-cast (1000 rpm) on top of the PEDOT:PSS layer from MEH-PPV/acceptor 5 g/L chlorobenzene solution. The active layer absorbed less than 50% of the incident light (the thickness did not exceed 50 nm) so that the internal filtering effect can be neglected. Then aluminum contacts were thermally deposited onto the active layer. Photodiodes were illuminated through the substrate by a spectrally-dispersed tungsten-halogen lamp, and the preamplified photocurrent was measured by a lock-in amplifier at a 75 Hz modulation frequency.

5.3. Results and discussion

Figure 5-2 presents linear absorption spectra of pristine MEH-PPV, MEH-PPV/DNAQ and MEH-PPV/TNF CTCs, and the MEH-PPV/PCBM blend as a reference. The mixing of the polymer with TNF and DNAQ results in substantial changes of the absorption spectra. First, the absorption edge shifts beyond 600 nm and, second, an absorption wing is formed at about 650 nm and stretches to the near IR region. Since pristine MEH-PPV, TNF and DNAQ are transparent in this region, the absorption that emerged in the red was attributed to the CTC bands$^6,33$. The enhancement of the red absorption correlates with the acceptor affinities, indicating a stronger charge-transfer interaction in MEH-PPV/TNF than in MEH-PPV/DNAQ. As a result, MEH-PPV/DNAQ and MEH-PPV/TNF CTCs provide a wider absorption range that extends to the red/near-IR spectral region compared to the MEH-PPV/PCBM blend. Similarly to MEH-PPV/PCBM mixture$^1$, the fluorescence in the CTCs was quenched by at least three orders of magnitude compared to pristine polymer. No subsidiary fluorescence bands corresponding to the CTC radiative relaxation$^{41,42}$ were observed in the 600-1800 nm spectral region.
To identify optical signatures of the charged states in CTCs, we compared the transient PIA CTC spectra to the well-studied charge-associated bands in the MEH-PPV/C\textsubscript{60} blends. For that, the excitation pulses with a \textasciitilde 15 nm FWHM bandwidth were centered at a wavelength of 650 nm. This wavelength matches the red flank of the CTC absorption band (Fig.5-2) thereby causing direct charge separation between the CTC acceptor and donor. In addition, the pristine MEH-PPV polymer is transparent at 650 nm and, therefore, its direct response (if any, \textit{vide infra}) is excluded.

Figure 5-3 depicts the time-resolved PIA spectrum of MEH-PPV/DNAQ CTC recorded at 1 ps delay between the pump and probe pulses (circles). For comparison, the cw PIA spectrum of a MEH-PPV/C\textsubscript{60} blend recorded at the excitation wavelength of 532 nm is also shown as a solid curve. Both spectra exhibit similar features: a broad absorption band at \textasciitilde 3 \mu m and several narrower bands at \textasciitilde 10 \mu m and \textasciitilde 7 \mu m (not well resolved in the CTC spectrum due to finite time-bandwidth product of the ultrashort pulses). All these PIA bands are known to be characteristic signatures of positive charges on the MEH-PPV chains\textsuperscript{27, 30, 31}. The bands at 1000-1600 cm\textsuperscript{-1} are associated with modifications of IR active
Figure 5-3. Transient PIA spectrum of MEH-PPV/DNAQ CTC at 1 ps (open circles) and 50 ps (closed triangles) after the 660 nm excitation. For comparison, the cw PIA spectrum of the MEH-PPV/C_{60} 1:0.1 blend excited at 532 nm is shown by the black curve. The dotted line depicts the transmission spectrum of unexcited MEH-PPV/DNAQ. IRAV, LE, and HE stand for IR active vibrations, low-energy and high-energy polaron PIA bands, respectively.

vibrational modes while the band at 3000 cm\(^{-1}\) is assigned to the LE polaron\(^{30}\). Only the cw PIA measurements were extended to observe the HE polaron band at \(\sim 1 \mu\text{m}\). The measured time evolution up to 1 ns was similar for both IRAV and LE bands which points to their identical origin, namely, the formation of the surplus charge on the polymer chain. As was discussed in the Introduction, despite the readily avoidable CH-stretch lines at \(\sim 3.3 \mu\text{m}\), the LE band is free from background absorption (Fig.5-3, dashed curve), which warrants accurate differential absorption and anisotropy measurements. In addition, the width of the LE band allows probing with short IR pulses which enhances the temporal resolution. With this in mind, our attention will be further focused at the LE polaron band as an optical probe for charged states at the MEH-PPV.

In general, the amplitude of the PIA signal is sensitive to the concentration of charges in the polymer and the absorption cross-section (or extinction coefficient). The relaxation of the charged state, environment rearrangement, or other structural processes may lead to a change in the LE transition cross-section. Any sensitivity of the LE transition to relaxation of the charged state should be
manifested in the spectral dynamics of the LE transition band. However, the spectra observed in the time interval from 0.5 to 50 ps are identical within the experimental accuracy (Fig.5-3). Moreover, the CTC PIA spectra follow exactly the cw PIA spectrum of MEH-PPV/C\textsubscript{60} blend, indicating a similar origin of the signals both on the picosecond and millisecond time scales. The similarity of PIA spectra at such different times strongly suggests that the frequencies of charge-associated transition, and most probably their cross sections, do not experience any substantial change with the time. This allows us to assume temporal changes in the magnitude of the transition dipole moment to be relatively small. In other words, we regard the transient dynamics of the LE absorption band as mainly originating from the temporal evolution of charge population but not the transition cross-section. Note also that identity of the transient spectra at short and long delays rules out a possible spectral modification of the LE band due to heating of the focal volume by dissipated energy of the pump pulse.

Figure 5-4 compares the time evolution of the LE PIA band in MEH-PPV/TNF, MEH-PPV/DNAQ CTCs, and MEH-PPV/PCBM blend probed at 3300 cm\textsuperscript{-1}. As before, the CTCs were excited at the wavelength of 650 nm while the MEH-
PPV/PCBM blend was excited near the polymer absorption maximum at 540 nm to minimize the effect of a direct PCBM excitation in the red region. The LE band in the MEH-PPV/PCBM blend displays a slow decay with time constants of 3.5 ps (22%), 30 ps (30%) and >1 ns (48%). These parameters were obtained by global multi-exponential fitting of the parallel and orthogonal polarization transients as well as the anisotropy convoluted with the instrument response function (see Table 5-1, and appendix 5-6 for model). In contrast, the PIA decay in the CTCs occurs mainly within the first 30 ps. Although the weights and the time constants of the fast components are slightly different for both CTCs, the decrease of PIA during the first 30 ps is much more prominent than in the MEH-PPV/PCBM blend.

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<tr>
<th>acceptor</th>
<th>Isotropic component</th>
<th>Anisotropy</th>
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<tbody>
<tr>
<td>TNF</td>
<td>$A_1$ ($T_1$)</td>
<td>$A_2$ ($T_2$)</td>
</tr>
<tr>
<td>DNAQ</td>
<td>0.31 (0.3 ps)</td>
<td>0.43 (5.8 ps)</td>
</tr>
<tr>
<td>PCBM</td>
<td>0.22 (3.5 ps)</td>
<td>0.31 (30 ps)</td>
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Table 5-1. Parameters of the tri-exponential fit $\sum A_i \exp(-t/T_i) (i = 1,2,3)$ of isotropic PIA transients and bi-exponential fit $r_0 \sum a_i \exp(-t/\tau_i) (i = 1,2)$ of transient anisotropy. The sum of amplitudes and were normalized to unity. A constant offset with the anisotropy value of was added to the MEH-PPV/DNAQ and MEH-PPV/TNF CTCs data to account for the anisotropy rise at long delays (Fig.5-5).

If we assume that the charge-associated absorption cross-section does not change in time, the LE PIA band reflects the density of the charged species at the MEH-PPV, and therefore, PIA decay represents the process of charge recombination. The limited PIA decay in the MEH-PPV/PCBM blend is indicative of slow recombination of the photogenerated charges. The obtained 50% efficiency of geminate recombination is in good agreement with the average dissociation probability of bound electron-hole pairs of 42% deduced from the cw photocurrent experiments on PPV:PCBM photovoltaic cells under open-circuit conditions. At the same time, the PIA signal from the CTCs decays remarkably faster, pointing to a rapid decrease of charge density in time. Most likely, the shift of electron density
to the acceptor during the excitation in the CTCs is followed by back electron transfer to the donor, i.e. CTC relaxation to the ground state. We can speculate that the three different time scales of 0.3 ps, 4-5 ps, and 20-30 ps with comparable amplitudes (Table 5-1) reflect a broad distribution of the relaxation rates which originates from a morphology-related diversity of CTC strengths; however, this hypothesis requires further verification. The observed recombination results in a long-time survival probability of the separated charges in CTCs of around 3\% (MEH-PPV/TNF) and 8\% (MEH-PPV/DNAQ) which is approximately a factor of 10 lower than in MEH-PPV/PCBM blend.

Figure 5-4b presents the PIA evolution at short time delays after excitation. The PIA of MEH-PPV/PCBM blend does not display any fast decay during first 1 ps, either because of the lack of recombination dynamics or because the charge recombination is compensated for by dissociation of a few long-lived excitons on a subpicosecond time scale. With the experimental time resolution of 100 fs there is no difference in the signal risetime between the CTCs and MEH-PPV/PCBM blends. Similarly to previous studies on IRAV\textsuperscript{24} and HE polaron bands\textsuperscript{26}, the rise of the LE polaron absorption is excellently described by a convolution of the exponentially-decaying signal and the apparatus function (Fig.5-4b, solid lines). Therefore, charge generation after excitation occurs much faster than 100 fs, in all materials. For the MEH-PPV/PCBM blend, this is consistent with the previously measured electron transfer time of 45 fs in MDMO-PPV/PCBM\textsuperscript{45}. In general, charge transfer between the donor and acceptor sites might not be the only mechanism of charge generation in the case of MEH-PPV/PCBM blend. In pristine polymers, other processes like charge separation on defects or generation of “spatially indirect” excitons\textsuperscript{46} are alternative scenarios for charge generation. However, the efficiency of such processes in pristine polymers does not exceed 10\%\textsuperscript{27,24}, and becomes negligibly low in blends with high PCBM concentration (as used in the current study).

Despite being incredibly fast, the charge separation in CTCs might still be preceded by some intermediate stages similar, for instance, to the exciton transport in MEH-PPV/PCBM blends. The lifetime of such processes should not exceed 50 fs because they did not result in any noticeable retardation of the isotropic PIA transients (Fig.5-4b). To address this point in detail, we performed transient
anisotropy measurements that can be sensitive to the degree of localization of the charge photogeneration.

Figure 5-5 presents transient anisotropy decays observed in the MEH-PPV/PCBM blend excited at 540 nm and in the CTCs excited at 650 nm. In the reference MEH-PPV/PCBM blend, the anisotropy value amounts to mere $r_0 = 0.18$ (the red diamonds) at 150 fs delay. This is consistent with the loss of polarization memory during exciton migration to the polymer/fullerene interface before charge separation occurs. Being mostly intermolecular, the exciton migration inevitably destroys the memory of the polarization of initial excitation due to the random orientations of dipole moments. The derived value of the initial anisotropy is also similar to one obtained from stimulated emission of DOO-PPV films because the polaron inherits the anisotropy of the parent exciton. The further decrease of anisotropy at a 0.5 ps time scale can be explained by either continuing deformation of the polymer chain after the excitation or/and polaron migration within the stacked polymer domain, as was recently concluded from pump-probe photocurrent experiments. These processes result in an anisotropy decrease by half within the first picosecond after excitation. The subsequent slow anisotropy decay (~50 ps) can be assigned to migration of the holes in the polymer because by this time all other processes such as the energy diffusion and charge

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**Figure 5-5.** Transient anisotropy decay of the LE polaron band in MEH-PPV/DNAQ (circles) and MEH-PPV/TNF (triangles) CTCs after 650 nm excitation, and in MEH-PPV/PCBM (diamonds) blend excited at 540 nm. Solid curves are fits to data with parameters given in Table 5-1. Note the logarithmic scale of the delay axis.
generation as well as polymer backbone deformation have mostly been completed.
Thus the most probable reason for the charge-associated transition to change
its orientation is polaron hopping from one polymer segment to another one which
has a different orientation of the dipole moment.

Although, to the best of our knowledge, the transient optical anisotropy of the
polarons in the MEH-PPV/PCBM blends has never been reported before, its main
characteristics corroborate the accepted picture of the exciton and charge dynamics
in MEH-PPV/PCBM blends. Note that the anisotropy signal does not depend on
charge concentration or absorption cross-section as these two are reduced in the
numerator and denominator of Eq.5-3. Also note that anisotropy experiments seem
to be a more sensitive probe of charge transport than the isotropic pump-probe
transients (Fig.5-4) as most of the features apparent in the anisotropy remain
hidden in the isotropic response. In particular, the 0.5 ps time scale on which the
anisotropy decreases by a half, is not seen at all in the isotropic transients. This also
emphasizes the importance of contrasting the isotropic and anisotropic PIA
signals.

The anisotropy in the CTCs (Fig.5-5, green circles and blue triangles) is
persistently higher than in the MEH-PPV/PCBM blend. For instance, it begins at a
value of $r_0 \approx 0.3$ (vs. $r_0 = 0.18$ in the MEH-PPV/PCBM blend) which is close to
maximum possible value of 0.4. Note that the anisotropy transients for CTCs
indicate no component with a decay time comparable to the temporal resolution.
We have previously concluded from the isotropic dynamics that charges on the
polymer chain are generated immediately after the excitation, and, therefore, no
intermediate “dark” state where the polarization direction could have been
scrambled is involved in the charge dynamics. Therefore, a finite angle between
the transition dipole moments of the fundamental and the LE polaron transitions is
the most obvious and plausible explanation for the lower-than-0.4 initial
anisotropy. The initial anisotropy value of $r_0 \approx 0.3$ can be recalculated into an
(average) angle of $\sim 20^\circ$ between the dipole moments of fundamental and LE
transitions. Alternatively, the initial anisotropy value of 0.3 could result from
delocalization of the CTC excitations over several conjugated segments in the
presence of high molecular order. The high initial anisotropy value also indicates
that the charge separation is confined within the initially-excited CTC pair. This is
in accord with Mulliken’s model of the photoexcited CTC that predicts direct
separation of charges between the donor and acceptor upon photoexcitation of the CTC band signifying that energy migration does not play an as important role in CTCs as it does in MEH-PPV/PCBM.

The slight (~20%) decrease of the anisotropy after 0.7 ps observed in the MEH-PPV/TNF CTC only (not in the MEH-PPV/DNAQ CTC) is less prominent than the 50% drop in MEH-PPV/PCBM blend (for exact values, see Table 5-1). Therefore, this anisotropy decay in the MEH-PPV/TNF CTC is assigned to continuing deformation of the polymer chain that keeps adapting itself to the excess excitation energy. This is also in line with the absence of a similar decay for the MEH-PPV/DNAQ CTC where the excitation energy excess is lower due to higher energy of the CTC absorption.

Another striking feature in the anisotropy dynamics is the delayed rise that begins at ~10 ps and reaches the highest possible value of 0.4 at ~100 ps delay. This anisotropy increase cannot be explained within a single CTC ensemble model as it would imply that the memory for the initial polarization is regained after having been lost. This leads us to the conclusion that there are at least two sub-ensembles amongst the excited CTCs. Most of the induced charges have the initial LE transition anisotropy of $r_0 = 0.3$ and 90-95% of them recombine in first 50 ps, while some of charges (about 5-10%) live infinitely long (at our experimental time scale) and have a constant anisotropy value of $r'_0 = 0.4$. As the contribution of the former sub-ensemble diminishes in time due to the charge recombination, the latter one becomes more noticeable and finally takes over. Therefore, the transient anisotropy dynamics in CTCs can be explained by the interplay between responses of the short- and long-lived sub-ensembles.

The precise origin of the long-lived sub-ensemble can not be determined solely from the presented spectroscopic experiments. One possible interpretation, based on the previous Raman scattering studies, might be that polymer chains upon the CTC formation straighten and form more ordered domains. This leads, first, to a better correlation in the dipole moment orientation of fundamental and LE electronic transitions, and, second, to a steady anisotropy value while the polaron migrates in the polymer domain. The hypothesis of domain formation and higher intermolecular order in CTCs could be tested by grazing angle x-ray diffraction measurements. Another explanation can be the presence of impurities of stronger (highly nitrated) acceptor in the film.
Figure 5-6. The peak values of the isotropic PIA transients as a function of the excitation wavelength for MEH-PPV/DNAQ (circles), MEH-PPV/TNF (triangles) CTCs and MEH-PPV/PCBM blend (diamonds). The energies of the absorbed light are shown as dashed, dash-dotted, and solid curves, respectively. For direct comparison, the curves were normalized to the absorption maxima at ~510 nm, and the PIA data were rescaled with the same factors. The energy flux of the incident light in all measurements was equal to 15 \mu J/cm^2.

Figure 5-6 presents the peak values of the isotropic PIA signals (symbols) as a function of the excitation wavelength while the respective energies of the absorbed light are shown as solid curves. The latter were scaled to the identical values at absorption maxima at about 510 nm, and the former were renormalized using the same scaling factors to ensure direct comparison between the efficiencies of the photon-to-charge conversion in CTCs and MEH-PPV/PCBM. The amplitudes of the peak PIA signals from all samples are similar for excitation around 550 nm which indicates comparable yield of photon-to-charge conversion within the experimental accuracy. This signifies that the initial charge generation is as efficient in CTCs as in the MEH-PPV/PCBM blend, where it is close to unity. In all cases, the peak values of the PIA and, therefore, densities of generated charges follow reasonably well the wavelength dependence of light energy absorbed by the sample. Consequently, for the excitation wavelengths above 580 nm, CTCs provide even more charges than MEH-PPV/PCBM. This improved photosensitivity of CTCs originates from the formation of charge-transfer band in the red and near-IR spectral region.
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Figure 5-7. Isotropic PIA of the LE band in MEH-PPV/DNAQ (circles) and MEH-PPV/TNF (triangles) CTCs excited at 540 nm. Solid curves represent multi-exponential fits to data. All data are normalized to their maximum value.

All time-resolved measurements on CTCs were also repeated with the excitation wavelength of 540 nm, i.e. near the absorption maximum of the pristine MEH-PPV (Fig.5-2). Obtained PIA and anisotropy transients were similar to those depicted in Figs.5-4 and 5-5. The only slight difference is that for the MEH-PPV/DNAQ and MEH-PPV/TNF CTCs the concentration of long-lived charges excited at 540 nm is somewhat higher than that at 650 nm. This can indicate that the hot CTC excitons have a slightly higher probability to dissociate into separated long-live charges. The similarity of PIA kinetics in the CTC at both the excitation wavelengths indicates that the charge-transfer transition is always involved in the CTC excitation. Therefore, CTC states can be a key intermediate stages in the process of charge photogeneration in polymer/acceptor blends. It also confirms the previous observation that for the donor-to-acceptor ratios used, most of the polymer chains are involved in CTCs formation 33, 34.

To make a connection between the early stages of photogeneration and the concentration of long-lived mobile charges in the studied materials, we performed cw photocurrent experiments on corresponding photodiodes with MEH-PPV/acceptor ratios close to those used in the ultrafast experiments. The photocurrents spectra are presented in Fig.5-8 in terms of external quantum efficiency (EQE), i.e. the probability of an incident photon to generate a pair of
charge carriers at the device electrodes. The photocurrent spectra correlate well with the respective absorption spectra. For instance, in MEH-PPV/TNF and MEH-PPV/DNAQ, the CTC contributes to the photocurrent in the optical gap of MEH-PPV, i.e. for wavelengths longer than 570 nm. Note that in the MEH-PPV/PCBM blends, the photocurrent in this range is determined by the PCBM absorption.

Figure 5-8. Photocurrent action spectra of MEH-PPV/DNAQ (dashed curve) and MEH-PPV/TNF (dash-dotted curve), and MEH-PPV/PCBM blend (solid curve) photodiodes. The donor:acceptor concentrations are by weight 1:0.3, 1:0.38, and 1:0.4, respectively. EQE stands for external quantum efficiency.

Qualitatively, the EQE in the CTCs is at least one order of magnitude lower compared to the reference MEH-PPV/PCBM blend. Based on the ultrafast spectroscopy measurements, we attribute such low EQE to efficient charge recombination and poor charge mobility in the CTC but not to ineffective photon-to-charge conversion. The fact that the EQE in the MEH-PPV/DNAQ CTC is higher than that in the MEH-PPV/TNF (Fig.5-8), is consistent with the less pronounced geminate recombination in the former (consult Fig.5-4a). However, the geminate recombination alone does not suffice to account for the observed two-orders-of-magnitude differences in the EQEs of the CTCs and MEH-PPV/PCBM as the concentration of long-lived charges differs only by a factor of ~10 (Fig.5-4a). Most likely, an additional decrease of photocurrent is caused by low charge mobility, which is supported by the anisotropy measurements. This conclusion is supported by previous studies on the PVK:TNF CTC as well as our photocurrent measurements.
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data for different MEH-PPV:acceptor ratios. In fact, increase of the acceptor content in the MEH-PPV/DNAQ and MEH-PPV/TNF blends beyond 1:0.3 does not considerably change the EQE as it does in the case of the MEH-PPV/PCBM blends due to a dramatic enhancement of charge mobility. Thus, although the initial photon-to-charge conversion in the CTC is as efficient as in PCBM, the fast geminate recombination and low electron mobility do not allow for an efficient charge collection at the device electrodes.

Finally, we discuss potential reasons for the high yield of charge recombination in the CTCs and possible ways to prevent it. The pronounced recombination can arise not only from the donor-acceptor interaction but also from the specifics of the morphology of the material. At the used 1:0.3 donor:acceptor ratio, CTCs show almost completely homogeneous mixing of the compounds with no evidence of separated phases. According to the Onsager theory, the confinement of photogenerated charges within the parent donor-acceptor pair enhances the recombination probability. Similar effects have previously been observed in other donor-acceptor materials where a low-molecular weight donor and acceptor were aggregated, or where a donor chromophore and a fullerene were linked covalently. On the other hand, efficient generation of long-lived charges was observed in donor-acceptor blends with charge-transfer interactions but without complete mixing of the donor and acceptor phases. These examples suggest that the recombination efficiency in polymer/acceptor blends might correlate with the absence of donor-acceptor phase separation and acceptor electron mobility rather than with the CTC formation. CTC forms a homogeneous ‘new’ material and additional acceptor is needed to provide a gradient for charge separation. If this is the case, the recombination of charges in CTC might be reduced by providing the charge carriers an efficient escape route from the parent CTC, for instance, by using an additional acceptor with high electron mobility (see Chapter 6).

5.4. Conclusions

In this chapter, ultrafast polarization sensitive VIS–IR spectroscopy has been used to study the photophysics of conjugated polymer-based CTCs and MEH-PPV/PCBM blend. The excitation of the CTC absorption band results in ultrafast (<100 fs) charge generation in CTCs with a yield similar to that in the MEH-
PPV/PCBM blend. An efficient (~95 %) and fast (<30 ps) geminate charge recombination follows in CTCs while in the MEH-PPV/PCBM blend it does not exceed 50%. The induced anisotropy decay in MEH-PPV/PCBM blend is consistent with intermolecular energy and charge transfer processes that take place at 0.1 and 30 ps time scales, respectively. The efficient charge and energy transfer in the MEH-PPV/PCBM blend are in sharp contrast with CTCs where processes of photoexcitation, charge separation and recombination appear to be localized within a single donor-acceptor pair. This together with the efficient recombination channels is accountable for the low EQE observed in the corresponding CTC based photodiodes. Results presented in the current chapter showed that advantages of CTCs can eventually be combined with efficient photon-to-current conversion only if the generated charges are removed from the CTC within 5 ps after the photoexcitation. Such a process will be presented in the Chapter 6.

5.5. Appendix. Data Fitting and Analysis

The data of the polarization-selective pump-probe experiments were fitted with the following generic model. The PIA signal amplitude was considered to be proportional to the overall concentration of charges \( N \) (which also accounts for possible variation in the IR absorption cross-section).

The concentration was partitioned between two sub-ensembles \( N' \) and \( N'' \)

\[
N(t) = N'(t) + N''(t)
\]  
(5-A1)

Time evolution of the first sub-ensemble was modeled as a sum of exponential decays to represent the charge concentration and anisotropy, respectively:

\[
N'(t) = A_1 \cdot \exp\left(-\frac{t}{T_1}\right) + A_2 \cdot \exp\left(-\frac{t}{T_2}\right) + A_3 \cdot \exp\left(-\frac{t}{T_3}\right)
\]  
(5-A2)

\[
R'(t) = r_0 \left[ a_1 \exp\left(-\frac{t}{\tau_1}\right) + (1-a_1) \exp\left(-\frac{t}{\tau_2}\right) \right]
\]  
(5-A3)
where \( T_i \) stands for the population relaxation time of the component with the amplitude \( A_i \) (\( A_3 = 1 - A_1 - A_2 \)), \( \tau_i \) is the anisotropy decay time weighted with the amplitude \( a_i \), and \( r_0 \) is the initial anisotropy value.

The second ensemble was considered long-lived (at the time scale of our experiment) and possessing a constant anisotropy

\[
N''(t) = A''_0
\]

\[
R''(t) = r''_0
\]

The amplitudes of the parallel \( \Delta T_{II}(t) \) and perpendicular \( \Delta T_{\perp}(t) \) polarization transients can now be expressed as:

\[
\Delta T_{II}(t) = A \cdot \left\{ N'(t) \cdot [1 + 2R'(t)] + N''(t) \cdot [1 + 2R''(t)] \right\}
\]

\[
\Delta T_{\perp}(t) = A \cdot \left\{ N'(t) \cdot [1 - R'(t)] + N''(t) \cdot [1 - R''(t)] \right\}
\]

where \( A \) is a normalization coefficient.

Making use of Eqs.5-2 and 5-3, one can derive the following expressions for the isotropic signal and transient anisotropy:

\[
\Delta T_{Iso}(t) = \frac{\Delta T_{II}(t) + 2 \cdot \Delta T_{\perp}(t)}{3} = A \cdot \left[ N'(t) + N''(t) \right]
\]

\[
r(t) = \frac{\Delta T_{II}(t) - \Delta T_{\perp}(t)}{3 \cdot \Delta T_{Iso}(t)} = \frac{N'(t) \cdot R'(t) + N''(t) \cdot R''(t)}{N'(t) + N''(t)}
\]

As can be seen from Eq.5-A8, the isotropic transient is free of contamination by reorientational dynamics, i.e. directly proportional to the charge concentration. In contrast, the anisotropy calculated according to Eq.5-3, is presented by a mixture of purely reorientational and concentration-related contributions. This reflects the fact that the anisotropy is not an additive quantity and therefore can not be analyzed as such. However, if one of the sub-ensembles dominates (for instance, \( N'(t) >> N''(t) \)), the concentration contribution drops out:

\[
r(t) = R'(t)
\]

Nevertheless, under the circumstances the anisotropy dynamics should be analyzed only together with the population kinetics.
Following this route, we fitted simultaneously the transients measured with parallel and perpendicular polarization, and the anisotropy transients. For that, the expressions given by Eqs.5-A6 and 5-A7 were convoluted with the instrument response function (a Gaussian with a 100 fs FWHM). We found that inclusion of anisotropy into the fitting routine enhances greatly the accuracy at long times, i.e. where the PIA signals are relatively weak. The results of such a global fit procedure are presented in Table 5-1, figures 5-5 and 5-5. The anisotropy values at long times presented in Fig.5-5, are averaged over 5 adjacent points.

5.6. References

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