Association function of conjugated polymer charge-transfer complex[†]

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Received 4th January 2010, Accepted 4th March 2010 First published as an Advance Article on the web 15th April 2010 DOI: 10.1039/b927324g

The donor-acceptor ground-state charge-transfer complex (CTC) formed in solution between a conjugated polymer, poly[methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene-vinylene] (MEH-PPV), and a low-molecular-weight organic acceptor, 2,4,7-trinitrofluorenone (TNF), is studied by optical absorption and Raman spectroscopy. The CTC absorption as a function of TNF content shows a threshold increase that is in conflict with the model commonly used for optical characterization of low-molecular-weight CTCs. The shift of MEH-PPV characteristic Raman band at 1585 cm⁻¹ also exhibits a threshold dependence upon TNF addition. We assign the threshold in both the absorption and Raman data to the CTC concentration. To describe the threshold in the terms of the common model, we extend it by introducing an association function instead of a constant. The association function of acceptor concentration has been calculated to be $K_a \sim 1.5-3 \text{ M}^{-1}$ below the threshold, to increase steeply up to $K_a \sim 6-7.5 \text{ M}^{-1}$ just after the threshold, and then to grow gradually up to $K_a \sim 40 \text{ M}^{-1}$. The CTC molar absorption coefficient has been found to be $\varepsilon_{\text{CTC}} = (12.7 \pm 0.6) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 635 nm. We explain the threshold as a result of the positive feedback: the CTC formation induces planarizaton of conjugated polymer segments that in turn facilitates further CTC formation.

Introduction

Blends of conjugated polymers with low-molecular-weight acceptors are actively studied as promising materials for organic solar cells and photodetectors. In the past, it was commonly believed that conjugated polymer donors and organic acceptors do not form charge-transfer complexes (CTC) in their electronic ground state because of the observed additivity of optical absorption and vibrational spectra of the blends studied.^{1,2} However, recent studies on a number of donor-acceptor blends, with the donor being a conjugated polymer or oligomer, have shown the presence of chargetransfer absorption^{3,4}—a characteristic signature of a Mulliken CTC. In blends of one of the most studied conjugated polymers, poly[methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), with some low-molecular-weight organic acceptors, the presence of ground-state charge-transfer was also confirmed by vibrational spectroscopy: the characteristic vibrational bands of both the donor and acceptor are shifted in the blends.⁵ Moreover, even in the most studied blends of conjugated polymers and fullerenes a weak CTC absorption band has recently been identified.^{6,7}

The CTC formation can noticeably change the photophysics in the donor–acceptor blend. Indeed, the pathway from excitons to free charges, which is crucial for the solar cell performance, includes the CTC states as key intermediates.^{7–10} On the other hand, the CTC formation can influence the donor-acceptor phase separation¹¹ and hence change the blend morphology. The latter is of paramount importance for efficient bulk-heterojunction solar cells.¹² In addition, the Raman data indicate that the conjugated polymer chains involved in the CTC become more planar.⁵

The CTC formation between low-molecular-weight compounds in solution is commonly studied by optical absorption spectroscopy, providing the CTC association constant, molar absorption coefficient, and stoichiometry from the concentration dependencies of charge-transfer absorption. These parameters were not reported earlier for conjugated polymer CTCs.

In this work, we address the problem of determining the parameters of conjugated polymer CTCs in solution by using MEH-PPV/TNF (TNF = 2,4,7-trinitrofluorenone) blends as a model. In these blends, the CTC absorption is readily observable, and its intensity is comparable with the polymer main absorption band.^{3,13} We have found that in solution both the MEH-PPV/TNF CTC's absorption and the frequency of the strongest MEH-PPV Raman band at ≈ 1585 cm⁻¹ demonstrate a threshold change with increasing acceptor content. As a result, we conclude that MEH-PPV/TNF CTC cannot be described by any association constant, and we have to introduce a CTC association function and calculate it from the experimental data. We explain the threshold behavior by peculiarities of the CTC formation between the conjugated polymer and low-molecular-weight acceptors.

Model for CTC association constant

In this section, we describe the model commonly used to characterize CTCs in solution. The CTC association constant of a donor-acceptor complex with stoichiometry

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[†] Electronic supplementary information (ESI) available: Absorption and Raman spectra. See DOI: 10.1039/b927324g

1: N = MEH-PPV : TNF,*i.e.* the number of acceptors per donor, is defined as

$$K_{a} = \begin{cases} \frac{C_{CTC}^{M}}{(C_{A}^{M} - NC_{CTC}^{M})(C_{D}^{M} - C_{CTC}^{M})}, & N \ge 1\\ \frac{C_{CTC}^{M}}{(C_{A}^{M} - C_{CTC}^{M})(C_{D}^{M} - \frac{1}{N}C_{CTC}^{M})}, & N \le 1 \end{cases}$$
(1)

where C_A^M and C_D^M are the acceptor and the donor molar concentrations before the CTC is formed in the blend, respectively; and C_{CTC}^M is the equilibrium CTC molar concentration.

In blends of low-molecular-weight compounds, the CTC association constant K_a , molar absorption coefficient ε_{CTC} , and stoichiometry N are usually determined from CTC optical absorption. The CTC absorption coefficient α_{CTC} is measured as a function of the donor and acceptor concentrations in the blend, and then the CTC parameters K_a , and ε_{CTC} are obtained as fitting parameters of the experimental data.^{14,15} From eqn (1) and the relation $C_{CTC} = \alpha_{CTC}/\varepsilon_{CTC}$ one can obtain α_{CTC}

The Raman spectra were measured in solutions in the back reflection geometry. Experimental details are given in ref. 5.

Results and discussion

CTC absorption

Fig. 1 demonstrates absorption spectra of MEH-PPV/TNF blends for different acceptor molar fractions $x = C_A^M/(C_D^M + C_A^M)$ in solutions ($C^0 = 2.5$ g l⁻¹) and in films prepared from the same solutions. The scattering background in optical density for MEH-PPV/TNF films at x < 0.3 was shown to be low.^{11,18} A wide absorption band appearing in the MEH-PPV bandgap upon addition of TNF both in films and solutions is a characteristic of the ground state MEH-PPV/TNF CTC.⁵ Insets in Fig. 1a and b show the CTC absorption in solutions and films at 635 nm as a function of molar fraction *x*, correspondingly. At this wavelength, the CTC absorbance is

$$\alpha_{\rm CTC}(C_{\rm A}^{\rm M}, C_{\rm D}^{\rm M}) = \frac{\varepsilon_{\rm CTC}}{2} \begin{cases} C_{\rm A}^{\rm M} + NC_{\rm D}^{\rm M} + \frac{N}{K_{\rm a}} - \sqrt{\left(C_{\rm A}^{\rm M} + NC_{\rm D}^{\rm M} + \frac{N}{K_{\rm a}}\right)^2 - 4NC_{\rm A}^{\rm M}C_{\rm D}^{\rm M}}, \ N \le 1 \\ \frac{C_{\rm A}^{\rm M}}{N} + C_{\rm D}^{\rm M} + \frac{1}{K_{\rm a}N} - \sqrt{\left(\frac{C_{\rm A}^{\rm M}}{N} + C_{\rm D}^{\rm M} + \frac{1}{K_{\rm a}N}\right)^2 - 4\frac{C_{\rm A}^{\rm M}C_{\rm D}^{\rm M}}{N}, \ N \ge 1 \end{cases}$$
(2)

Note that the K_a and $\varepsilon_{\rm CTC}$ are commonly determined, not from eqn (2), but by using approximated methods such as Benesi–Hildebrand¹⁶ or similar ones, that allow a linear fit of the spectral data for $C_A^{\rm M} \gg C_D^{\rm M}$ or $C_A^{\rm M} \ll C_D^{\rm M}$. These approximated methods can result in incorrect values K_a and $\varepsilon_{\rm CTC}$.¹⁷ Because of this, eqn (1) and (2) will be used to study MEH-PPV/TNF CTC. To find the K_a and $\varepsilon_{\rm CTC}$, one needs to measure the $\alpha_{\rm CTC}$ as a function of $C_D^{\rm M}$ and $C_A^{\rm M}$ and then to fit the data with eqn (2) using K_a and $\varepsilon_{\rm CTC}$ as fitting parameters. As will be shown below, the described model referred to as the common model cannot describe our experimental data. To reconcile our data with the common model, we have to use an association function in it instead of association constant.

Experimental

MEH-PPV (Sigma-Aldrich, $M_n = 86\,000$, $M_w = 420\,000$) and TNF were dissolved separately in chlorobenzene at initial concentrations C_A^0 and C_D^0 in the range 1.5–4 g l⁻¹. These quite high concentrations were used to observe the threshold in CTC absorption. The concentrations were equal for each series of samples and will be denoted as $C^0 = C_A^0 = C_D^0$. Blends were prepared by mixing the solutions of MEH-PPV and TNF with their molar ratio from 1:0.1 to 1:8 per polymer unit. Films were prepared on glass substrates by spin casting at 1500 rpm. Absorption spectra of MEH-PPV/TNF blends were recorded by using a fiber-coupled spectrometer (Avantes). The solution spectra were measured in a quartz cuvette with a 100 µm thick solution layer.

Raman spectra were recorded using a double monochromator DFS52 (LOMO) equipped with a thermoelectrically cooled photomultiplier (R2949, Hamamatsu). The external cavity diode laser emitting at 670 nm was used as an excitation source.



Fig. 1 Absorption spectra of MEH-PPV/TNF blends in solutions (a) and films (b). Insets show the absorption coefficient in solutions (a) and normalized optical density (OD) in films (b) *vs.* molar fraction at 635 nm (indicated by arrows at the *x*-axes). The dashed curve in panel (a), inset is calculated from eqn (2) for $K_a = 6.5 \text{ M}^{-1}$, $\varepsilon_{\text{CTC}} = 12000 \text{ M}^{-1} \text{ cm}^{-1}$ and N = 1. The initial concentration was $C^0 = 2.5 \text{ g} \text{ l}^{-1}$.

high, and the polymer absorbance is nearly absent. The shift of polymer absorption band is about 15 nm upon CTC formation; therefore, this shift cannot modify absorption measured at 635 nm (see ESI, Fig. 1S[†]).

As follows from Fig. 1, the CTC absorption depends on x in a strongly different way in solutions and films. The absorption increases gradually with increasing x in films, whereas it shows a steep increase at a certain $x \approx 0.25$ in solutions. This x will be referred to as the threshold molar fraction x_t (Fig. 1a, inset).

To compare the common model given by eqn (2) with our absorption experimental data, we transform the variables in eqn (2) from (C_D^M, C_A^M) to (C^0, x) by using the following equations:

$$C_{\rm A}^{\rm M} = \frac{C_{\rm D}^{\rm M0} C_{\rm A}^{\rm M0} x}{C_{\rm D}^{\rm M0} x + C_{\rm A}^{\rm M0} (1-x)}, \ C_{\rm D}^{\rm M} = \frac{C_{\rm D}^{\rm M0} C_{\rm A}^{\rm M0} (1-x)}{C_{\rm D}^{\rm M0} x + C_{\rm A}^{\rm M0} (1-x)},$$
(3)

where $C_{\rm D}^{\rm M0}$ and $C_{\rm A}^{\rm M0}$ are the molar donor and acceptor concentration of the initial MEH-PPV and TNF solutions, respectively. After this transformation, the CTC absorption coefficient for blends with the same initial concentrations C^0 will be a one-dimensional function $\alpha_{\rm CTC}(x)$:



Fig. 2 Frequency of the strongest Raman band of MEH-PPV (circles) *vs.* acceptor molar fraction. The dotted line is the calculated maximum of a weighted superposition of the CTC and pristine MEH-PPV Raman bands. As follows from the Raman data for the MEH-PPV band at 966 cm⁻¹, at least 50% of MEH-PPV chains are involved in the CTC at x = 0.5 ($C^0 = 2.5$ g l⁻¹).⁵ According to these data, the CTC band parameters were estimated from the Raman band at ≈ 1580 cm⁻¹ for x = 0.5 ($C^0 = 2.5$ g l⁻¹), and the weights were determined by the CTC concentration calculated for N = 0.2 and $K_a = 60$ M⁻¹ from eqn (2).

$$\alpha_{\rm CTC}(x) = \frac{\varepsilon_{\rm CTC}}{2} \begin{cases} \frac{C_{\rm D}^{\rm M0}(x(1-N)+N)}{xm+1} + \frac{N}{K_{\rm a}} - \sqrt{\left(\frac{C_{\rm D}^{\rm M0}(x(1-N)+N)}{xm+1} + \frac{N}{K_{\rm a}}\right)^2 - 4N\left(\frac{C_{\rm D}^{\rm M0}}{xm+1}\right)^2 (1-x)x}, \ N \le 1 \\ \frac{C_{\rm D}^{\rm M0}(xN^*+1)}{xm+1} + \frac{1}{K_{\rm a}N} - \sqrt{\left(\frac{C_{\rm D}^{\rm M0}(xN^*+1)}{xm+1} + \frac{1}{K_{\rm a}N}\right)^2 - 4\frac{1}{N}\left(\frac{C_{\rm D}^{\rm M0}}{xm+1}\right)^2 (1-x)x}, \ N \ge 1 \end{cases}$$
(4)

where $m = C_{\rm D}^{\rm M0}/C_{\rm A}^{\rm M0} - 1$ and $N^* = (1 - N)/N$. The model function $\alpha_{\rm CTC}(x)$ is convex for any $K_{\rm a}$, $\varepsilon_{\rm CTC}$, and N, *i.e.*, its second derivative is always negative (Fig. 1a, inset). On the contrary, the experimental $\alpha_{\rm CTC}(x)$ is concave at $x_{\rm t}$, *i.e.*, its second derivative is positive (Fig. 1a, inset). It should be emphasized that any variations of model parameters $K_{\rm a}$, $\varepsilon_{\rm CTC}$ and N cannot change the sign of the second derivative of the model. Consequently, the common model with any values of $K_{\rm a}$, $\varepsilon_{\rm CTC}$, and N does not describe our experimental data.

Raman spectroscopy data

The strongest MEH-PPV Raman band at $\approx 1585 \text{ cm}^{-1}$ corresponding to the symmetric stretching vibration of the phenyl ring downshifts in MEH-PPV/TNF blends that indicates decreasing the π -electron density at the conjugated polymer segments corresponding to CTC formation.⁵ Fig. 2 demonstrates the Raman frequency as a function of acceptor molar content in MEH-PPV/TNF solutions (the corresponding Raman spectra are presented in the ESI, Fig. 2S†). The curve in Fig. 2 shows a threshold at $x_t \approx 0.22$ similar to that observed in the absorption (Fig. 1a). In contrast to the solutions, the Raman frequency in MEH-PPV/TNF films depends smoothly on acceptor content without any threshold.⁵

We assign the observed Raman frequency dependence in Fig. 2 mainly to the CTC concentration. As the CTC absorption at 670 nm is much higher than that of the pristine MEH-PPV, a contribution of the resonant Raman effect into the shape of the curve in Fig. 2 is possible. However, this resonant effect cannot result in the observed curve shape, as discussed below.

To illustrate the role of the resonant Raman effect, suppose that on the contrary the C_{CTC} grows gradually with increasing TNF content without any threshold. In that case the nonresonant Raman frequency would smoothly downshift from $\approx 1585 \text{ cm}^{-1}$ (pristine MEH-PPV) following the CTC concentration. The dotted curve in Fig. 2 is the calculated maximum of a superposition of the CTC and pristine MEH-PPV Raman bands with their weights determined by the CTC concentration, *i.e.*, without any resonant effect. The latter enhances the CTC contribution to the Raman band compared with the pristine polymer, and the resulting curve in Fig. 2 can be only higher than the dotted one. Moreover, if we assume that the CTC extinction ε_{CTC} has a threshold increase at $x \approx x_{t}$, then a corresponding feature could appear above the dotted curve. The higher CTC content, i.e., the more conjugated segments are involved in the CTC, the less the contribution of the resonant effect to the measured Raman frequency should be observed. As a result, the dotted curve in Fig. 2 must approach the experimental one with any contribution of the resonant effect.

Nevertheless, the experimental data in Fig. 2 are below the model at $x < x_t$ that contradicts with the assumption about a smooth C_{CTC} dependence on the acceptor content. Therefore, we conclude that the threshold in the Raman data in Fig. 2 should be assigned to the threshold in CTC concentration.

Origin of the threshold

Both the absorption and Raman data show the very similar threshold-like dependences on the acceptor content. If the

CTC absorption is the product $C_{CTC}\varepsilon_{CTC}$, the Raman data are related mainly to C_{CTC} . Therefore, it is natural to assign the threshold in absorption to the C_{CTC} . Note that aggregation effects could hardly contribute to the $\alpha_{CTC}(x)$ (Fig. 1a, inset). Indeed, the shapes of absorption spectra of pristine MEH-PPV are very similar at strongly different concentrations, and it is transparent at 635 nm even at the highest concentration (see ESI, Fig. 3S†); hence, only the CTC absorbs at 635 nm. Moreover, the CTC concentration is far less than that of either donor or acceptor, and it is expected to be in the range 10^{-5} – 10^{-3} M⁻¹ (see below).

Eqn (2) is based on the Beer-Lambert-Bouguer law, the relationship $\alpha_{\text{CTC}} = C_{\text{CTC}} \varepsilon_{\text{CTC}}$, and the K_a definition [eqn (1)]. As none of these equations has any features that could result in a threshold behavior, the common model cannot describe the observed threshold in the CTC absorption. However, it could be extended to explain our experimental data if we assume that one or several of the CTC parameters (C_{CTC} , ε_{CTC} , N) are not constants but functions of the donor and acceptor concentration. The steep increase observed in α_{CTC} at x_t could be assigned to some dependence of the CTC parameters on x and C^0 . As the Raman data are not directly linked to the ε_{CTC} , we conclude that the K_a should depend on x and C^0 to give the threshold both in the absorption and Raman data. To calculate the K_a (x,C⁰), we need to determine the ε_{CTC} . In the following section, we calculate the $\varepsilon_{\rm CTC}$ and show that it does not depend on x and C^0 . The possible CTC stoichiometry dependence on x will be discussed as well.

CTC extinction

As the shapes of the spectra of CTC in films and solutions at $x > x_t$ are very similar (Fig. 1 and ESI, Fig. 4S[†]), we suggest that the optical characteristics of CTC in films and solutions at $x > x_t$ are also similar, and hence the dependences $\varepsilon_{\text{CTC}}(x, C^0)$ at fixed C^0 are expected to be the same. Then, if the steep change in the $\alpha_{\text{CTC}}(x)$ observed at x_t would contribute to the $\varepsilon_{\text{CTC}}(x)$, this change would be observed both in films and solutions. However, the CTC absorption in films changes gradually with x without any threshold (Fig. 1b, inset). Consequently, the $\varepsilon_{\text{CTC}}(x)$ in solutions is also expected not to have any sharp feature and not to contribute to the threshold in the $\alpha_{\text{CTC}}(x)$.

To support this hypothesis, the $\varepsilon_{\rm CTC}$ in solution was calculated for two sets of MEH-PPV/TNF blends with different initial donor and acceptor concentrations: $C^0 = 4$ and 2.5 g l⁻¹. The calculation was performed under the following assumptions: (i) the ratio between the CTC and polymer absorptions is the same in solution and film (Fig. 4S†):

$$\frac{\varepsilon_{\rm p}^{\rm s}}{\varepsilon_{\rm CTC}} = \frac{\varepsilon_{\rm p}^{\rm f}}{\varepsilon_{\rm CTC}^{\rm f}} \tag{5}$$

where ε_p^f and ε_p^S are the polymer molar absorption coefficients in film and solution, respectively; ε_{CTC}^f and ε_{CTC} are the CTC ones; (ii) all acceptor molecules are involved into the CTC in films at low acceptor concentration (x < 0.3)⁵ and hence Table 1 CTC extinction in solution at 635 nm

	CTC molar absorption coefficient, $\epsilon_{\rm CTC}/10^3 \text{ M}^{-1} \text{ cm}^{-1}$	
Molar fraction, x	$C^0 = 2.5 \text{ g } \mathrm{l}^{-1}$	$C^0 = 4 \text{ g } 1^{-1}$
0.13	12.2 ± 0.3	n/a
0.17	12.6 ± 0.4	n/a
0.23	13.2 ± 0.4	11.7 ± 0.8
0.25	13.3 ± 0.3	n/a
0.26	13.1 ± 0.4	n/a
0.27	13.0 ± 0.4	n/a
0.29	11.7 ± 0.4	11.9 ± 0.9
0.33	n/a	11.7 ± 0.7

 $C_{\text{CTC}}^{\text{f}} = C_{\text{A}}^{\text{f}}$. As a result, K_{a} tends to infinity in films at x < 0.3 [see eqn (1)] and

$$\varepsilon_{\rm CTC}^{\rm f} = \frac{\alpha_{\rm CTC}^{\rm M}}{C_{\rm A}^{\rm f}} \tag{6}$$

Combining eqn (5) and (6), and using the relationship $\alpha_{\text{CTC}} = C_{\text{CTC}} \varepsilon_{\text{CTC}}$, we obtain the CTC molar absorption coefficient in solution ε_{CTC} :

$$\varepsilon_{\rm CTC} = \frac{\alpha_{\rm CTC}^{\rm f} \varepsilon_{\rm p}^{\rm s} C_{\rm p}^{\rm f}}{\alpha_{\rm p}^{\rm f} C_{\rm A}^{\rm f}} = \frac{\alpha_{\rm CTC}^{\rm f} \varepsilon_{\rm p}^{\rm s}}{\alpha_{\rm p}^{\rm f} \nu},\tag{7}$$

where ν is the acceptor : donor molar ratio $\nu = x/(1 - x)$. Table 1 presents $\varepsilon_{\rm CTC}$ values calculated according to eqn (7). The values of $\varepsilon_{\rm CTC}$ in Table 1 are very close for all the x and for the two different initial concentrations. In fact, the observed variations in the value of $\varepsilon_{\rm CTC}$ cannot be responsible for the threshold-like feature observed. Averaging $\varepsilon_{\rm CTC}$ over x < 0.3 according to assumption (ii) results in the CTC molar absorption coefficient $\varepsilon_{\rm CTC} = (12.7 \pm 0.6) \times 10^3 \,{\rm M}^{-1} \,{\rm cm}^1$ at 635 nm.

CTC stoichiometry

To find out the CTC stoichiometry, Job's method is usually used.¹⁵ However, because of the threshold behavior of $\alpha_{\text{CTC}}(x)$, the Job or related methods cannot be used. Therefore, we have to make some reasonable assumptions about the CTC stoichiometry.

In a conjugated macromolecule, π -electrons are delocalized over a number of polymer units. If the acceptor molecular orbitals overlap with those of one or a few polymer units to form the CTC, the electron density from other units of the polymer chain can be transferred to the acceptor molecule.⁵ This means that the number of the polymer units involved in the CTC can be noticeably larger than the number of polymer units forming the direct contact, i.e., donor-acceptor molecular orbital overlapping. Note that another acceptor molecule can form the direct contact with the same conjugated segment.⁵ Moreover, if two conjugated segments belonging to the same or different macromolecules are close to each other, one acceptor molecule could involve them in the CTC resulting in a sandwich-like donor-acceptor-donor CTC.⁵ As a result, a conjugated polymer can form CTCs of variable donor : acceptor stoichiometry. The stoichiometry can be defined as the number of acceptor molecules N involved in the CTC per polymer unit.

The CTC stoichiometry in MEH-PPV/TNF films can vary in the range $0.1 \le N \le 0.5$, *i.e.*, there are at least two polymer units per one TNF molecule.⁵ As shown above, the shapes of the spectra of CTC are very similar in films and solutions at $x > x_t$. This allows us to assume that the charge-transfer interaction between MEH-PPV and TNF is similar in solutions and films at least at $x > x_t$, and therefore the CTC stoichiometry is the same in both. If the CTC stoichiometry averaged over all the CTCs in the sample would change with x, the corresponding change in ε_{CTC} would be observed. In the first approximation, the ε_{CTC} is expected to be proportional to the number of acceptor molecules involved into CTC per polymer repeat unit. Since the ε_{CTC} is nearly constant both at $x \leq x_{\text{t}}$ and $x > x_t$, the same stoichiometry at any x is expected. Thus, we suggest the CTC stoichiometry does not contribute to the threshold-like behavior of the CTC absorption $\alpha_{CTC}(x)$.

Interpretation of the threshold

The absorption and Raman data on MEH-PPV/TNF solutions show a threshold dependence on the TNF content. In contrast, no threshold is observed in films. Therefore, the threshold is associated with the peculiarities of CTC formation in solution, and we have assigned it to the CTC concentration. Below, we propose an explanation of the threshold.

The CTC formation induces changes in the polymer conformation.⁵ Indeed, the intensity of MEH-PPV Raman band at 966 cm^{-1} assigned to the out-of-plane CH bending vibration of the vinylene group decreases in the blend upon TNF addition.⁵ This vibration is forbidden in the Raman spectrum for the planar configuration of the polymer chains.¹⁹ Accordingly, the conjugated polymer segments become more planar upon CTC formation.⁵ As was suggested earlier, two conjugated segments can be involved in the CTC in which an acceptor molecule is sandwiched between conjugated segments.⁵ It is natural to suggest that the planarization facilitates π -orbital overlapping between the conjugated chains involved in the CTC and nearby acceptor molecules (Fig. 3). In addition, the planarized segments in the CTC have a longer conjugated length²⁰ and, hence, a higher HOMO energy. According to Mulliken model, the higher the HOMO energy, the higher the $K_{\rm a}$. Therefore, one can expect a higher probability that another CTC will be formed nearby, i.e., at this or adjacent segment. As a result, the CTC formation is characterized by a positive feedback: the higher the CTC concentration, the higher the probability of further CTC formation. This feedback can result in a threshold in the CTC concentration, and it is analogous to the one in polymer gels where the next cross-link



Fig. 3 Illustration of planarization of polymer chain as a result of the CTC formation. Black curves are polymer chains, solid rectangles are TNF molecules involved into CTC, and the open ones are free TNF.

is formed near the previous one.²¹ At low molar fraction $x < x_t$, the CTC concentration is too low to launch the efficient feedback. At $x \ge x_t$, the feedback turns on and the CTC concentration steeply increases, which results in the threshold in both the absorption and Raman spectra.

CTC association function

As follows from the above discussion, the observed threshold dependence $\alpha_{\text{CTC}}(x, C^0)$ should be assigned to $K_a(x, C^0)$. Therefore, the latter is not a constant and will be referred to as the association function of x and C^0 . We have calculated the $K_a(x, C^0)$ for various C^0 by using the definition of the association constant given by eqn (1), the experimentally obtained CTC concentration $C_{\text{CTC}}(x, C^0) = \alpha_{\text{CTC}}(x, C^0) / \varepsilon_{\text{CTC}}$, and the maximum stoichiometry N = 0.5.

To analyze the CTC characteristics, the two variables were used above: initial concentration C^0 and molar fraction x. These variables directly stem from the preparation method of the blends. However, according to the definition of K_a , the donor and acceptor concentration in the blend, *i.e.*, C_A and C_D , are more natural variables. Fig. 4 shows the calculated association function K_a (C_A , C_D) for a number of initial concentrations C^0 . As mentioned above, the CTCs can be formed with stoichiometry N < 0.5, but the distribution of CTCs on different N is not known. As a result, the calculated K_a (C_A, C_D) for the maximum stoichiometry N = 0.5 gives the lower estimate of C_a as follows from eqn (1).

As Fig. 4 shows, at $C_A < 0.8 \text{ g l}^{-1}$ the association function is in the range $K_a \sim 1.5-3 \text{ M}^{-1}$. According to the above explanation, the acceptor concentration is too low to turn on the feedback. For all the C^0 , the K_a shows a threshold at $C_A \sim 0.8 \text{ g l}^{-1}$ increasing up to $K_a \sim 6-7.5 \text{ M}^{-1}$ for all the C_D studied; therefore, the feedback turns on. Note that the overall experimental error in K_a is about 20%. While this error is quite large, it is considerably lower than the difference in K_a before and after the threshold. Upon increasing the acceptor concentration after the threshold, the K_a proceeds to grow monotonically. The maximum value of the association function was measured to be $K_a \sim 45 \text{ M}^{-1}$ for $C^0 = 4 \text{ g l}^{-1}$. Therefore, the association function value can vary by more than one order of magnitude with the acceptor content.



Fig. 4 CTC association function for different initial concentrations indicated in the figure.

Conclusion

The formation of intermolecular ground-state charge-transfer complex (CTC) in solution between conjugated polymer MEH-PPV and organic acceptor TNF has been studied by using optical absorption and Raman spectroscopy. CTC formation in conjugated polymers appears to be a more complex process compared with low-molecular-weight donor-acceptor blends. The common model used to characterize low-molecularweight CTCs of Mulliken type in terms of association constant, CTC extinction, and stoichiometry cannot describe our optical absorption data. Specifically, the CTC concentration shows a threshold increase with the acceptor content that is in conflict with the common model. The CTC molar absorption coefficient was found, and it does not depend on the donor/ acceptor concentration. To describe the MEH-PPV/TNF CTC formation, we have extended the common model by replacing the association constant with a function of the donor and acceptor concentration. This association function has been calculated from the experimental data, and its value can vary by more than one order of magnitude with the acceptor content. The threshold observed both in the absorption and Raman data has been related to the peculiarities of charge-transfer interaction between conjugated segments of the polymer and low-molecular-weight acceptors in solution. We explain the threshold as a result of the positive feedback: the CTC formation induces planarizaton of conjugated polymer segments that in turn facilitates further CTC formation.

Acknowledgements

This work is partially supported by the program "Scientific and educational personnel of innovative Russia" (contract #02.740.11.5155). We thank M. Bendikov for discussion and critical reading of the manuscript.

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