Pis'ma v ZhETF, vol. 81, iss. 9, pp. 583 – 586 © 2005 May 10

Weak intermolecular charge transfer in the ground state of a π-conjugated polymer chain

D. Yu. Paraschuk[1)], S. G. Elizarov, A. N. Khodarev, A. N. Shchegolikhin[+], S. A. Arnautov[*], E. M. Nechvolodova[*]

International Laser Center, Moscow State University, 119992 Moscow, Russia

[+]Emanuel Institute of Biochemical Physics RAS, 119991 Moscow, Russia

[*]Semenov Institute of Chemical Physics RAS, 119991 Moscow, Russia

Submitted 2 March 2005
Resubmitted 25 March 2005

We show that a π-conjugated polymer chain can demonstrate weak intermolecular charge transfer in the electronic ground state. Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene]/2,4,7-trinitrofluorenone (MEH-PPV/TNF) donor-acceptor films have been studied by optical absorption, Raman, infrared spectroscopy, and differential scanning calorimetry. The factors influencing weak intermolecular charge transfer in π-conjugated chains are discussed.

PACS: 82.35.Cd, 78.30.Jw, 78.40.Me

1. Introduction. As is well known for small aromatic conjugated molecules, they can easily form intermolecular charge-transfer (CT) complexes in the electronic ground state with a molecule having higher electron affinity (see, e.g. [1, 2]). Such CT complexes were widely studied in the 50–60 s and their properties were successfully interpreted in the framework of the Mulliken model of weak CT interaction suggesting mixing of the ground-state wavefunctions [3]. These CT complexes usually have characteristic optical absorption in the visible range corresponding to a CT band. As was recently shown, relatively large π-conjugated molecules such as fullerenes or phthalocyanines can also form a ground-state CT complex [4, 5]. Non-conjugated polymers demonstrate CT interaction in the electronic ground state as well, e.g. polyvinylcarbazole CT complexes have been thoroughly studied since the 70 s [6, 7]. Intramolecular CT complexes of a conjugated polymer have been reported recently for polythiophene [8], where weak CT occurs from a polymer unit cell to the covalently bonded acceptor molecule.

At the same time, to our best knowledge, there are no reliable evidences in literature reporting noticeable intermolecular CT interaction of a π-conjugated polymer chain in the electronic ground state although a number of types of donor-acceptor blends and bilayers of π-conjugated polymers with low-molecular (e.g., [9, 10]) and high-molecular [11 – 14] acceptors including fullerenes [15, 16] and nanotubes [17] have been studied. It was demonstrated that donor-acceptor blends of conjugated polymers and organic electronic acceptors, e.g. MEH-PPV/C_{60} [15], MEH-PPV/ tetracyanoquinodimethane (TCNQ) [9], do not usually demonstrate ground-state CT. Despite early studies of poly(3-octylthiophene)/C_{60} films showed non-additive features in the optical absorption spectrum [18, 19], their vibrational IR spectra did not show any signs of non-additivity [20]. Note that non-additivity in the optical absorption spectrum of a donor-acceptor blend could result from other reasons, e.g. acceptor (donor) aggregation. At the same time, vibrational spectroscopy data could give strong evidences of CT complex formation since CT interaction should result in frequency shifts of the donor (acceptor) vibrational bands which are the most sensitive to redistribution in the π-electron density.

In our recent studies MEH-PPV blended with low-molecular organic acceptors, TNF or 1,5-dinitroantraquinone (DNAQ), we have observed that both the optical and IR transmission spectra of the blends are non-additive [21]. This could indicate CT interaction in the electronic ground state, if the origin of the non-additivity would be established. In fact, phase separation typical for donor-acceptor blends can increase light scattering giving an observable effect of non-additivity. In this Letter we show conclusive evidences for intermolecular CT interaction between a π-conjugated polymer chain and a low-molecular organic acceptor. We have studied MEH-PPV/TNF blends (Fig.1) and show that a CT absorption band appears in the optical absorption spectra and several vibrational donor (acceptor) bands demonstrate frequency shifts both in Raman and IR spectra. Further evidence follows from differential scanning calorimetry

1)e-mail: paras@polys.phys.msu.su

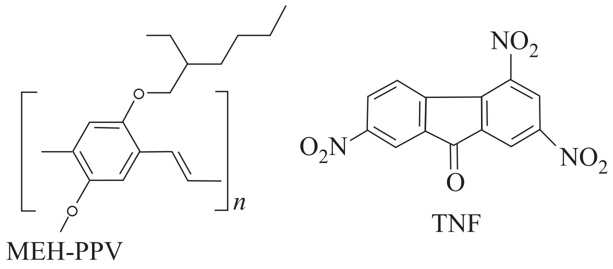

Fig.1. Structural formula for of MEH-PPV and TNF

(DSC) data. These observations we interpret as a result of partial ground-state CT in the donor-acceptor pair, i.e. CT interaction.

2. Experimental. Drop-cast films of pristine MEH-PPV (Sigma-Aldrich, MW=125.000) and its blends with TNF (Fig. 1) were prepared from different solvents (chorobenzene, toluene, cyclohexanone) with MEH-PPV concentration in the range of 0.5–2 g/l and by varying the molar ratio of the acceptor per polymer unit chain in the range of 0.1–1. Films on glass substrates and free-standing films were studied. All the measurements were done in ambient conditions.

The optical absorption spectra were recorded using a spectrophotometer (Hitachi 300). 1:1 MEH-PPV/acceptor blends had higher optical scattering than pristine MEH-PPV films. To evaluate the contribution of scattering losses in the optical transmission spectra, we measured the film transmission in narrow and wide (0.25 sr) solid angles at a few laser wavelengths (633, 810, 946 nm) [22]. IR transmission spectra of free-standing films of the blends and Raman spectra of the same films slightly packed in a "cavity" sample holder were recorded with $2\,cm^{-1}$ resolution using a Perkin-Elmer FTIR (Model 1720-X) spectrophotometer furnished with a NIR-FT Raman attachment. The back-scattering geometry and a liquid nitrogen cooled InGaAs detector were used for acquiring Raman spectra at excitation wavelength 1064 nm. DSC data were taken at 10 K/min heating rate by using a Perkin-Elmer Series 7 DSC analyser calibrated by indium and zinc melting standards.

3. Experimental results. MEH-PPV/TNF films have essentially difference in their color from that of pristine polymer. The absorption spectra of the MEH-PPV/TNF films are shifted to the red and have extended absorption tails extending down beyond 1.5 eV as compared to pristine MEH-PPV (Fig.2). Although addition of the acceptor results in noticeable increase of the scattering losses (Fig.2), they gives the major contribution to the measured optical density only for energies below 1.5 eV. Since TNF absorbs light mainly in the ultraviolet spectral range, the observed optical absorption below

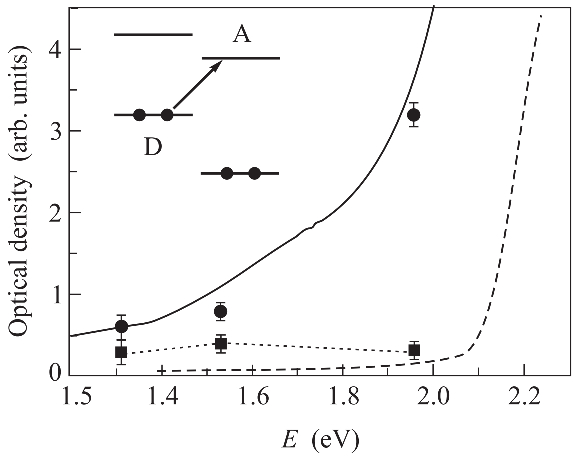

Fig.2. Absorption spectra of 1:1 MEH-PPV/TNF (solid) and pristine MEH-PPV (dashed) drop-cast films prepared from chlorobenzene. Points show the sum of absorption and scattering (circles) and only the scattering (squares) contributing to the measured optical density of the 1:1 MEH-PPV/TNF film by using technique described in [22]. The absorption and scattering data for the MEH-PPV/TNF molar ratio within the range 0.1-1 fall between those of pristine MEH-PPV and 1:1 MEH-PPV/TNF. Inset illustrates the donor and acceptor energy levels, the arrow indicates the CT complex absorption corresponding to the electron transfer from the highest occupied orbital (HUMO) of the donor (D) to the lowest unoccupied orbital (LUMO) of the acceptor (A)

the absorption edge of pristine MEH-PPV (Fig.2) could be a consequence of noticeable ground state interaction of MEH-PPV chains with the TNF molecules resulting from CT complex formation (Fig.2, inset). Increasing the optical scattering in MEH-PPV/TNF blends compared to pristine MEH-PPV films could result from a part of TNF molecules which are not involved in CT interaction. In fact, TNF crystallites are seen in 1:1 MEH-PPV/TNF blends using an optical microscope. Note that appearance of a red shift and of an extended tail in the MEH-PPV spectrum could be induced by two other effects: aggregation of polymer chains [23] and/or presence of relatively long conjugated chains. However, since the absorption tails observed for the blends were too intense and red shifted, it is difficult to suppose that either could result from blending of non-interacting components.

Partial CT in the electronic ground state is expected to induce shifts in the vibrational frequencies of both the donor and acceptor [1]. Indeed, as Fig.3 shows, Raman bands of MEH-PPV at ~ 1550 and $\sim 1580\,cm^{-1}$, corresponding to carbon-carbon (CC) stretching of the phenyl ring, are 3–$4\,cm^{-1}$ red shifted in the 1:1 MEH-PPV/TNF blend. The observed red shifts support our assumption about partial CT from MEH-PPV to TNF in the electronic ground state. As compared with our

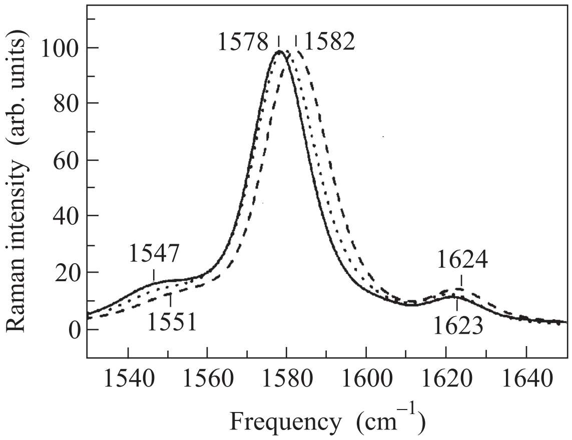

Fig.3. Raman spectra of pristine MEH-PPV (dashed), 1:0.2 MEH-PPV/TNF (dotted), 1:1 MEH-PPV/TNF(solid) free-standing films in the region of the strongest Raman band of MEH-PPV

case, doping of conjugated polymers, as has been reported for p-doped PPV [24, 25] corresponds to full CT and is capable of lowering the Raman frequencies of phenyl ring CC stretching modes which are strongly coupled with delocalized π-electrons by up to a few tens of wavenumbers.

Furthermore, we have found that a number of other Raman and IR bands in the MEH- PPV/TNF blends are not just a superposition of the corresponding spectra of pristine MEH-PPV and TNF. Here we discuss frequency shifts relevant only to TNF carbonyl C=O vibration at the vicinity of $\sim 1730\,\mathrm{cm}^{-1}$ observed both in IR and Raman spectra (Fig.4). The noticeable red shift of the C=O band in TNF for a few wavenumbers we explain by an increase of the electron density in the conjugated system of TNF resulting from partial ground-state CT. As is well documented for substituted fluorenones [26], introduction of electronegative substituents into a fluorenone molecule tends to increase the C=O frequency and the increase can amount up to $\sim 25\,\mathrm{cm}^{-1}$ raising within the series from aminofluorenone to TNF. The observed red shifts of the C=O frequency in MEH-PPV/TNF imply that electronegative action of nitro substituents could be partly compensated by extra electron density donated by MEH-PPV.

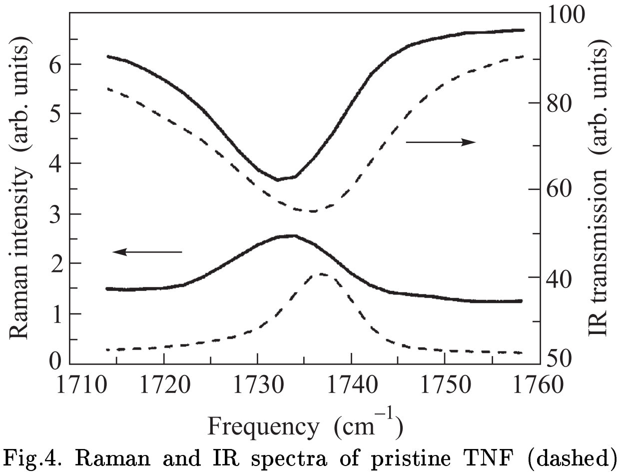

Fig.4. Raman and IR spectra of pristine TNF (dashed) and 1:1 MEH-PPV/TNF (solid) free-standing films in the region of the TNF C=O stretch vibration. The spectra are offset vertically for clarity

Thus, our vibrational studies indicate noticeable mixing of the ground state electronic wave functions of MEH-PPV and TNF providing partial CT from the donor to the acceptor. The observed a few wavenumbers shifts of vibrational bands in the MEH-PPV/acceptor blends indicate relatively weak CT interaction typical of Mulliken CT complexes.

If a CT complex is formed, it can give an observable effect in the DSC traces [27]. We have found that a strong endotherm peak corresponding to the melting point of the crystalline TNF phase essentially decreased in 1:1 MEH-PPV/TNF films and fully disappeared in 1:0.2 MEH-PPV/TNF films (Fig.5). Thus, there is no evidence of the presence of the crystalline acceptor phase in the 1:0.2 MEH-PPV/TNF film and therefore almost all the acceptor molecules are involved in some type of interaction with MEH-PPV. We interpret these observations as a direct consequence of intermolecular CT interaction between MEH-PPV and TNF.

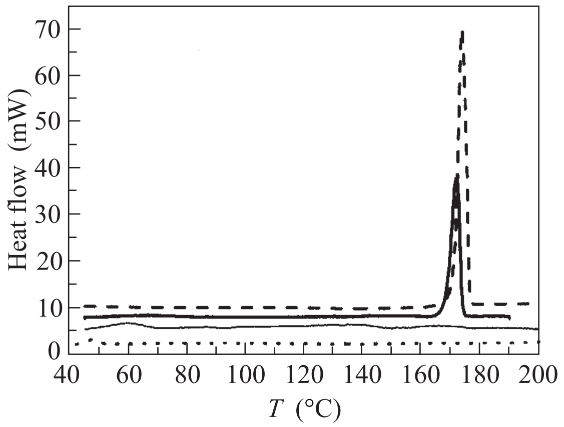

Fig.5. DSC traces for neat TNF (dashed line), 1:1 MEH-PPV/TNF film (bold solid line), 1:0.2 MEH-PPV/TNF film (thin solid line) and pristine MEH-PPV polymer (dotted line). All curves are normalized to equal sample weight and are offset vertically for clarity

4. Discussion. As mentioned above, despite a number of donor-acceptor blends of conjugated polymers have been studied by now, weak CT from a π-conjugated polymer chain in its electronic ground state has not been observed. At the same time, from the very beginning of the field of π-conjugated polymers, they are well known to be easily doped by elements and inorganic compounds [28]. Apparently, this doping corresponds to full CT. It is unclear why weak ground-state CT is not easy to observe in π-conjugated polymers. We discuss here main factors influencing weak CT from a π-conjugated chain. The important parameter controlling donor-acceptor intermolecular CT is the difference between the donor ionization potential and the acceptor electron affinity (EA) [1]. The EA of TNF is about 2.2 eV [29], which is within the range of EAs of acceptors studied in blends with MEH-PPV in Ref. [9]. Therefore, the magnitude of EA alone does not determine the ground-state CT in π-conjugated chains. On the other hand, according to Mulliken's model [1], intermolecular CT in the electronic ground state depends on the overlapping of the HOMO donor and the LUMO acceptor wavefunctions. Since the wavefunction at an extended conjugated chain (donor) is strongly delocalized, noticeable overlapping of the donor and acceptor wavefunctions necessitates delocalization of the acceptor wavefunction as well. This could explain why such a strong acceptor as TCNQ does not lead to ground-state CT in MEH-PPV/TCNQ blends [9]. However, ground-state CT was not observed for the acceptors both longer and shorter than TNF as well [9]. One can suggest that the TNF molecular orbital pattern provides better overlapping with corresponding MEH-PPV molecular orbitals. Note that another acceptor DNAQ, which has the EA and length similar to those of TNF, seems to provide weak ground-state CT in MEH-PPV/DNAQ blends as well. In these films the CT band was less intensive and the frequency shifts in vibrational spectra were weaker [21] than in MEH-PPV/TNF films.

5. Conclusions. Thus, we have given conclusive evidences that a π-conjugated polymer can participate in intermolecular ground-state CT interaction. MEH-PPV/TNF films show optical absorption spectra extending down to the near IR spectral range, while the vibrational spectra of the blends exhibit shifts of some characteristic vibrational bands belonging to both the donor and the acceptor. In addition, DSC studies of MEH-PPV/TNF films indicate that the content of the crystalline TNF phase in the blend is essentially decreased. These observations have been interpreted as a result of CT interaction between MEH-PPV and TNF in their electronic ground state. Our data are in consistent with the Mulliken model of intermolecular CT complexes suggesting noticeable mixing of the donor and acceptor wavefunctions.

This research was supported by European Office of Aerospace Research and Development via the International Science and Technology Center (project 2666P) and by Russian Foundation for Basic Research (# 04-02-16658).

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