

Anomalous photoinduced absorption of conjugated polymer/fullerene mixtures at low temperatures and high frequencies

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1. Introduction

Light induced charge transfer from conjugated polymers and their oligomers to different electron acceptors, e.g. fullerenes or tetracyano-*p*-quinodimethane (TCNQ) derivatives has been studied extensively [1–5]. From time-resolved photoinduced absorption (PIA) studies it is well known that the charge-transfer process from a conjugated polymer to C₆₀ or C₆₀ derivatives takes place on an ultrafast time scale (<100 fs) [2]. On the other hand, the back electron transfer is remarkably slow; lifetimes on the order of milliseconds can be observed for the charge separated states in such systems. This very efficient charge separation has been utilized in polymeric photovoltaic devices [6–9].

Photoexcitation of conjugated polymers in liquid solutions or solid state films across the π – π^* energy gap produces a metastable triplet state by intersystem crossing from the excited singlet manifold [10,11]. These triplet states were identified by their dipole allowed T₁–T₂ transition, which exhibit a red shift with increasing chain length [10]. The lifetimes of these triplet states are on the order of 10–100 ms. In composite films of these polymers mixed with electron accepting molecules the triplet–triplet absorption is quenched due to a prior charge transfer. Absorption detected magnetic resonance (ADMR) experiments on films of pristine poly[2-methoxy-(5-2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) have shown that the origin of the photoinduced absorption in the range between 1.1 and 1.6 eV is due to excited triplet states (spin 1), whereas mixed films of MEH-PPV and C₆₀ show in the same energetic region PIA

features due to charge separated states of spin 1/2 [12]. Light induced electron spin resonance (LESR) studies on mixed films of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and the C₆₀ derivative 1-(3-methoxycarbonyl)-propyl-1-1-phenyl-(6,6)C₆₁ (PCBM) showed two light induced ESR lines, Fig. 1 one with a *g*-factor of 2.0025 being due to the polymer radical cation and the other one with a *g*-factor 1.9995 originating from the fullerene radical anion [13]. LESR was not only used to identify light induced species in conjugated polymer fullerene mixtures but also their recombination kinetics at low temperatures were studied [14]. Below 40 K the recombination process is dominated by tunneling and lifetimes of several hours were observed in MDMO-PPV/PCBM mixtures [14]. In this work, near steady state (quasi cw) photoinduced absorption spectroscopy was applied to study solid-state films of MDMO-PPV/PCBM mixtures. Quasi-cw means that a mechanical chopper is used to modulate the intensity of the excitation light beam which allows modulation frequencies of maximum a few kilohertz'. Thus, this PIA technique is usually used to identify long-lived photoinduced species. It can also be used to estimate the lifetime of these photoinduced species or more precisely their lifetime distribution following the work of Ehrenfreund et al. [15].

According to the simple polaron picture the photoinduced absorption spectrum of conjugated polymer/fullerene mixtures exhibiting a light induced charge transfer should consist of three absorptions. Two of them are related to allowed polaronic transitions on the conjugated polymer donor cation radical and one to fullerene acceptor anion radical absorption. The fullerene anion absorption is usually very weak and often not observed on the side of overwhelming intensity of polymer polaron absorption. Spectra observed for conjugated polymer/fullerene mixtures have a low energy absorption (around 0.5 eV) and a second broad absorption around

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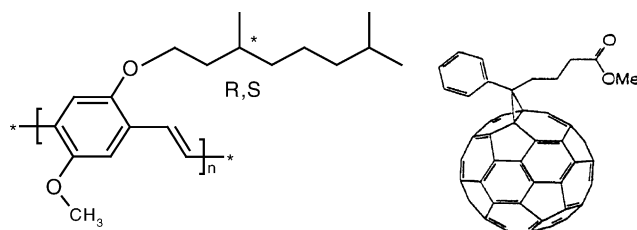


Fig. 1. Chemical structure of poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C₆₀ (PCBM).

~1.3–1.4 eV with a plateau up to the absorption band-edge. This high energy part of the PIA spectrum exhibits spectroscopic features that the simple polaron picture is not sufficient to describe in detail [16].

Photoinduced absorptions caused polaron pairs [17] are possible candidates for the observed high energy part of the PIA spectrum. These species have been found in conjugated polymers and conjugated polymers moderately doped with fullerenes in photoinduced absorption detected magnetic resonance (PADMR) experiments [18]. However, in earlier magnetic resonance experiments on samples investigated also in this work no polaron pair signature was found [19].

We report PIA experiments on thin films of MDMO-PPV/PCBM mixtures performed at low temperatures. By comparing PIA spectra recorded at very high modulation with the spectra recorded at low modulation frequencies polarons having different lifetimes can be separated and visualized. This analysis clearly shows that the PIA spectrum of conjugated polymers at energies around 1.3–1.4 eV (high energy peak) originates from spectral superposition of two distinctly different photoexcited species which are proposed to be intramolecular and intermolecular polarons.

2. Experimental

MDMO-PPV has been purchased from COVION Germany. PCBM was provided by J.C. Hummelen (University of Groningen, The Netherlands) and its synthesis has been described in Ref. [20]. Solutions for film preparation were made in the following way: first materials were separately dissolved using the same organic solvent (chlorobenzene). The polymer solution was stirred for several hours at elevated temperatures. The fullerene solution was first put into an ultra-sonic bath for ~15 min and then stirred for another hour at room temperature. As a last step both solutions were mixed to achieve a master solution holding a concentration of 3 mg/ml MDMO-PPV and 9 mg/ml PCBM. Films were prepared by spin-coating this solution on a cleaned glass substrate to obtain an optical density at 500 nm of approximately 0.5. For PIA studies in the VIS/NIR spectral region samples were mounted in a Oxford CF204 continuous flow cryostat which allowed measurements down to 16 K.

PIA spectra were taken using an Ar-ion laser at 476 nm as a pump (typically 30 mW operation without focussing) and experiments were performed at 16 K.

Using mechanical modulation of the pump beam, the changes in the white light (120 W tungsten-halogen lamp) probe beam transmission ($-\Delta T$) were detected after dispersion with a 0.3 m monochromator in the range from 0.55 to 2.1 eV with a Si-InGaAsSb sandwich detector and recorded phase sensitively with a dual-phase lock-in amplifier. In a second experiment the probe light transmission (T) was recorded. From this the PIA spectra ($-\Delta T/T \approx \Delta\alpha d$) are obtained after correction for the sample luminescence and normalization on the probe light transmission. The time response of the PIA setup was checked for different wavelengths to ensure that the observed spectra are not distorted by the measurement equipment.

3. Results

The photoinduced absorption spectrum (in-phase and out-of-phase) recorded at 330 Hz for MDMO-PPV/PCBM film is shown in Fig. 2a. The spectra with the positive/negative amplitude represent the in-phase/out-of-phase component, respectively. Both components have comparable amplitudes and show the same spectral dependence. In

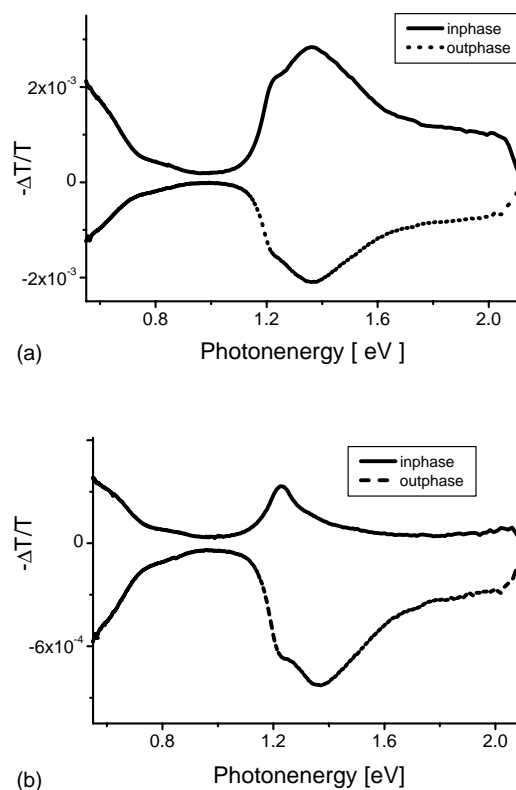


Fig. 2. (a) Photoinduced absorption spectra of MDMO-PPV/PCBM acquired at (a) 330 Hz and (b) 2970 Hz. In both spectra in-phase (solid line) and out-of-phase (dashed line) components are plotted.

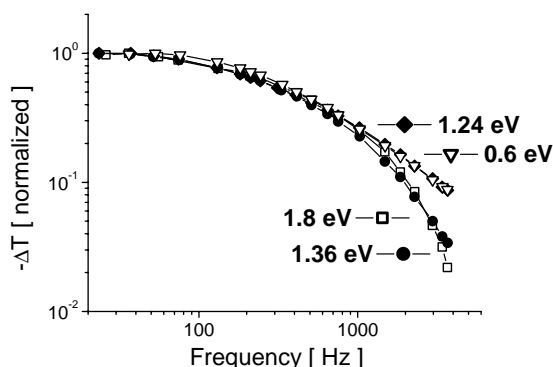


Fig. 3. Modulation frequency dependence of the PIA signal recorded at 0.6, 1.24, 1.36, 1.8 eV. Measurements were performed at 16 K normalized at the lowest recorded modulation frequency.

both spectra, peaks and shoulders have similar shapes and positions.

Increasing the excitation light modulation frequency to 2970 Hz the amplitudes of the spectra decrease by one order of magnitude and the shape of the in-phase component changes significantly, while the shape of the out-of-phase part remains the same (Fig. 2b). Instead of a broad PIA spectrum between 1.1 and 2.1 eV one fairly symmetric peak with smaller amplitude is found for the in-phase component at high modulation frequencies. The maximum of this peak is positioned at 1.24 eV. The PIA feature at low energies (0.55–0.9 eV) does not change position and shape upon changing the modulation frequency. Only its intensity is reduced at high modulation as compared to the low modulation frequency spectrum in Fig. 2a.

In Fig. 3, the frequency dependence of several features in the spectrum is plotted (0.6, 1.2, 1.36, 1.8 eV). For better comparison curves are normalized. Increasing the modulation frequency, the high energy PIA band relaxes faster than the low energy PIA bands indicating a longer living component at the high energy PIA band which can be overchopped more easily.

4. Discussion

Results presented above illustrate that the observed PIA spectrum is generated by species with different lifetimes (distribution of lifetimes). Fig. 3 shows that the frequency dependence recorded at 0.6 and 1.24 eV are very similar suggesting a common origin. Theory [21] predicts that the optical absorption spectrum of a positive polaron extended on one conjugated segment (intrachain polaron) should consist of two strong absorption bands (Fig. 4a). The gap energy E_g and the position of the levels P_1 and P_2 depend on the effective conjugation length of the chain segment the positive polaron is located on as well as on its electron–phonon coupling constant. It is well known that due to randomly introduced defects and morphological effects a distribution of effective conjugation lengths exist in a solid state con-

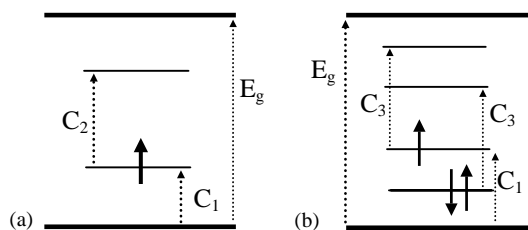


Fig. 4. (a) Allowed optical transitions in a localized (intramolecular) polaron and (b) delocalized (on two conjugated segments, intermolecular) polaron. Energetic positions of different levels are only schematic.

jugated polymer film. Therefore, two broadened absorption features are expected for the transitions C_1 and C_2 .

We suggest that the low energy (≈ 0.6 eV) and the symmetric high energy absorption around 1.24 eV observed at high modulation frequencies correspond to these two absorptions C_1 and C_2 . For the rest of the PIA spectrum (shown in Fig. 5 as difference between the high frequency modulated PIA and the low frequency modulated PIA) several possibilities can be considered. The energetic position of the remaining spectrum supports the idea that a polymer or fullerene triplet absorption [5] is present. However, as demonstrated by Wei et al. [12] in conjugated polymer/fullerene mixtures triplet excited states are quenched due to the photoinduced charge transfer. Also MDMO-PPV⁺/PCBM⁻ triplet pairs could cause additional absorption in the PIA spectrum but were not detected in magnetic resonance experiments for samples with high fullerene content [12]. Recently, the influence of interchain interactions on the optical response of a singly charged polaron has been addressed in a theoretical study. In the calculations co-facially aggregated dimers of two five-unit PPV oligomers separated by four angstrom have been considered [20]. Results show that the positive polaron is delocalized over both chains and that four polaron levels are present in the bandgap (interchain polarons). The optically allowed transitions within such a delocalized polaron are shown in Fig. 4b. Calculations show that transitions C_3 and C'_3 are expected at higher energies compared to the transition C_2 of the localized polaron. The idea of

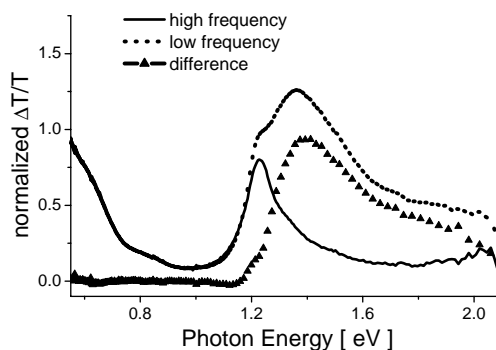


Fig. 5. Normalized (at 0.57 eV) PIA spectra recorded at high (solid line) and low (dashed line) modulation frequencies and the difference between the high and the low modulation frequency spectra (triangles).

delocalized polarons in conjugated polymer films is also supported by reports on photoinduced/charge induced absorption experiments of polythiophenes [21,22].

The experimental results presented above may be explained in the following way.

At low modulation frequencies the PIA-spectrum contains features of localized and delocalized polarons. Increasing the modulation frequency, long-living components of the spectra are suppressed and only species with a lifetime $\leq 1/(\text{modulation frequency})$ can be observed in the in-phase PIA spectrum. The PIA-spectrum at high modulation frequency shows only two dominant features. As discussed before two absorptions are expected for intrachain polarons. One may conclude that the part of the spectrum present in the spectrum acquired at 330 Hz but missing at 2970 Hz is related to delocalized interchain polarons (Fig. 5).

5. Summary

In the PIA spectrum of a MDMO-PPV/PCBM film two different photoexcited species were identified by comparing low and high frequency measurements. Theoretical calculations suggest that the observed species are intrachain and interchain polarons. It is interesting to note that under this explanation the lifetime of intrachain species is observed to be shorter as compared to the lifetime of interchain polarons. This could be related to the fact that interchain species can more easily migrate in the bulk to lower energy sites where they will be deeply trapped. The presented experiments also show that working at different modulation frequencies can help to distinguish different features in a photoinduced absorption spectrum.

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