

Photoinduced charge transfer between tetracyano-anthraquino-dimethane derivatives and conjugated polymers

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ABSTRACT

The photo-induced charge transfer between tetracyano-anthraquino-dimethane (TCAQ) derivatives and poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene) MDMO-PPV was studied by means of photoinduced absorption (PIA) spectroscopy in the VIS and IR spectral region and lightinduced electron spin resonance (LESR) spectroscopy. Three different TCAQ derivatives with alkyl-side chains for increased solubility compared to TCAQ and one of them attached to a C₆₀ molecule serve as strong electron acceptors. The photoinduced absorption in the VIS near-IR range shows a broad plateau around 1.8 eV followed by two peaks at 1.35 and 1.24eV for all three acceptors. All PIA features have a power law excitation intensity dependence with an exponent close to 0.5 as expected for bimolecular kinetics. The modulation frequency dependent excited state absorption decreases with a power law. LESR studies of all donor-acceptor combinations show one radical line at a $g = 2.0028$ with $\Delta H = 3.5$ Gauss, originating from TCAQ anion and the polymer cation.

INTRODUCTION

Light induced charge transfer from conjugated polymers and their oligomers to different tetracyano-p-quinodimethane (TCNQ) derivatives and fullerenes has been studied extensively with different methods [1-4]. It is well known that the charge transfer process from a conjugated polymer to C₆₀ takes place on an ultra-fast timescale [2]. The back transfer is remarkably slow; lifetimes of the order of milliseconds can be observed for the charge separated states.

Various PIA studies on thin films of pristine conjugated polymers have shown the formation of the triplet state after photo-excitation. In mixed films of polymers with electron acceptors the triplet state absorption is quenched due to 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 -1.6 eV is due to excited triplet states (spin 1) whereas mixed films of MEH-PPV and C₆₀ show additional photoinduced absorption features but being due to charged separated states of spin 1/2 [5]. LESR studies on mixed films of MDMO-PPV and a C₆₀ derivative 1-(3-methoxy-carbonyl)-propyl-1-phenyl-(6,6)C₆₁ (PCBM) showed two light induced ESR lines, one with a g-factor of 2.0025 being due to the polymer and the other one with a g-factor 1.9995 stemming from the fullerene anion [6]. In an other more comparative study

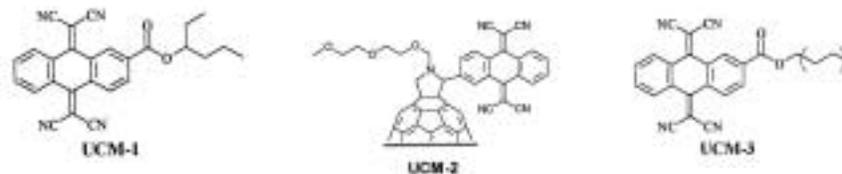


Figure 1: Chemical structure of the three TCAQ derivative electron acceptors used in the experiments.

different TCNQ derivative acceptors were tested with respect to their charge transfer efficiency to conjugated polymer [4]. Both the amount of luminescence quenching and the PIA signal of the charged states were investigated for MEH-PPV and various TCNQ derivatives as electron acceptors with different electron affinity. TCAQ was found to be a more efficient electron acceptor than TCNQ despite its lower electron affinity, but still worse than C_{60} . Although in that work it could not be excluded that phase segregation and the relatively low solubility of these electron acceptors can cause a problem in interpreting the observed results.

To overcome this problem with solubility in this work better soluble TCAQ derivatives with alkyl side chains were prepared, one of them attached to a C_{60} molecule forming an acceptor dyade as shown in Fig. 1. The photoinduced charge transfer from MDMO-PPV to these acceptors was studied using PIA in the VIS/NIR as well as LESR. In addition the charge transfer from the polymer to an electron acceptor dyade consisting of an C_{60} unit and an TCAQ unit was investigated.

EXPERIMENT

The MDMO-PPV polymer was delivered by Aventis Inc. and used as received. For LESR studies samples were prepared as films on a KBr. A mass ratio of 1:1 between polymer and the acceptor material was dissolved in toluene in a concentration of 1 mg/ml. The solution was dropped on KBr powder and dried under vacuum before being filled in the ESR-tubes. These samples were placed in the high-Q-cavity of a X-band ESR spectrometer and illuminated with 488nm light of an Ar-ion laser. The samples were irradiated and light off spectra were taking directly afterwards to be subtracted from the former one to compensate for the persistant charges produced in the samples. For PIA studies in the VIS/NIR spectral region the samples were prepared as solution cast films onto glass substrates using a mass ratio of 4:1 between the polymer and the electron acceptors and a concentration of 1mg/ml sample in toluene. PIA spectra were taken using an Ar-ion laser at 488nm as a pump (typically 40mW on a 4mm diameter spot). Using mechanical modulation of the pump beam at 132 Hz, the changes in the white light (120W tungsten-halogene lamp) probe beam transmission ($-\Delta T$) were detected after dispersion with a 0.3m monochromator in the range from 0.55 to 2.1 eV with a Si-InGaAsSb detector and recorded phase sensitively with a dual-phase lock-in amplifier. The probe light transmission (T) was recorded separately using the same chopper frequency. The PIA spectra ($-\Delta T/T \approx \Delta\alpha d$) are obtained after correction for the

sample luminescence. All measurements for LESR and PIA-VIS/NIR spectra are done at a temperature of approximately 100 K and under high vacuum ($< 10^{-5}$ mbar) conditions.

LIGHT INDUCED ESR STUDIES

No ESR signals have been found in the pristine MDMO-PPV films neither before nor during illumination with 488nm light. Samples of the pure acceptors UCM-2 and UCM-3 showed very weak, barely detectable light-induced signals consisting of one line

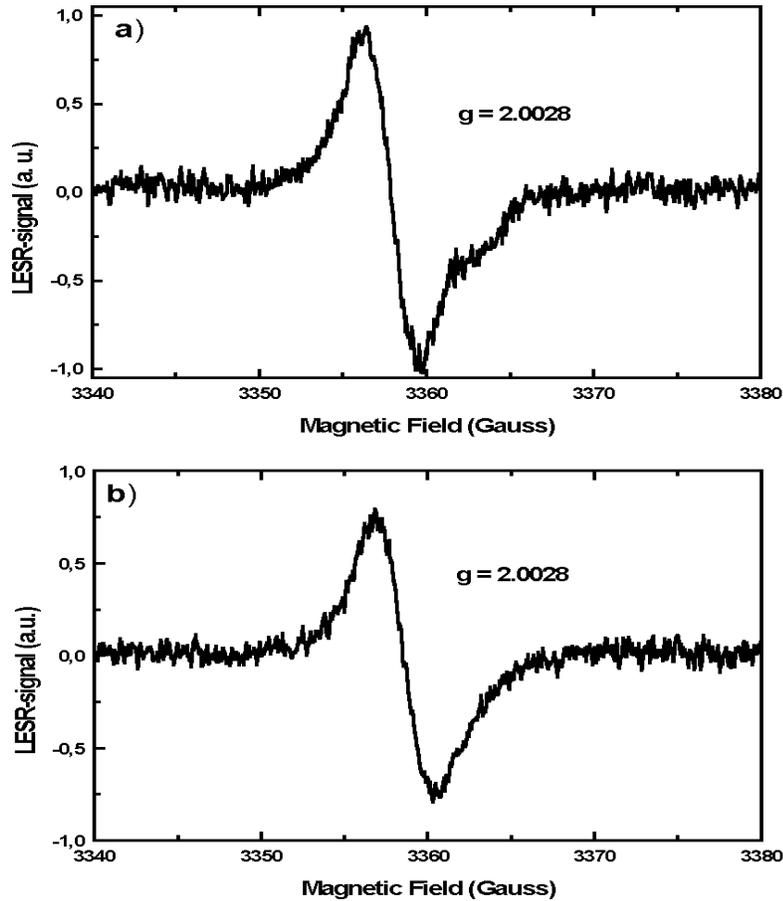


Figure 2: LESR signal of a) MDMO-PPV:UCM-2 and b) MDMO-PPV-UCM-3 films. Excitation wavelength 488nm, $T=100K$.

with a g-value close to this observed for the mixed films of polymer and acceptor. The light induced ESR signal for the mixed samples of the polymer and the electron acceptor consists of mainly one single line with a g-factor of 2.0028(3) as shown in Fig.2. From ESR studies it is known that the g-factor of both the TCAQ anion (2.0027(1)) as well as this of the MDMO-PPV polymer cation (positive polaron) (2.0025) are in the observed range [6,7]. So both, TCAQ and the polymer, could contribute to the observed LESR signal at $g=2.0028$. For MDMO-PPV samples containing the molecule UCM-2 (Fig. 1), which combines the two strong electron acceptors TCAQ and C_{60} , a weak additional feature close to $g=2.000$ is observed (Fig.2). This could correspond to the ESR signal of a fullerene anion, as for instance PCBM, which is known to have a g-factor of close to 2.000 [3, 6]. C_{60} has already been observed to be the more effective electron acceptor than TCAQ or TCNQ [4], despite the higher electron affinity of TCAQ. The final state of the charge transfer from the polymer to the acceptor dyade UCM-2 (Fig.1) can be both TCQA and the fullerene unit, if so signals at g-factors of 2.000 and 2.0028 should be observable. There also could be a stepwise charge transfer involving C_{60} as a first, fast step and to the TCAQ unit, due to its higher electron affinity, as final step. In this case a signal at a g-factor of 2.000 should not be detected in a steady state experiment as it is presented here.

PHOTOINDUCED ABSORPTION STUDIES

The photoinduced absorption studies have been carried out for a pristine MDMO-PPV film as well as for composite films of MDMO-PPV with the three TCAQ derivatives shown in Fig. 1 acting as electron acceptors. In Fig. 3 these results are shown for the energy range of 0.55 to 2.1eV for an excitation wavelength of 488nm. In the case of the pristine MDMO-PPV film a single excited state absorption line at 1.36 eV is observed. This photoinduced absorption feature, only slightly blue shifted compared the PIA spectra of pristine MEH-PPV [4], is generally associated with the triplet state of the polymer. Compared to this triplet state photoexcitation several new features are observed in the PIA of the composite films presented in Fig. 3. A plateau between 1.6 and 1.9eV is followed by two closely spaced peaks at 1.24 and 1.33eV and a rising signal below 0.9eV. For all three electron acceptors used, the shape of the PIA spectra is quite similar (Fig. 3) and the peak positions are identical. All these additional photoinduced absorption features can be attributed to charged species generated by the electron transfer from the polymer to the TCAQ type electron acceptors. Janssen *et al.* report on similar PIA features for films of MEH-PPV mixed with different TCNQ derivatives on nearly the same energetic position [4]. The absorption of the radical anion of C_{60} is known to lie around 1.18eV [8]. As in this energetic region the bands are rather broad and overlapping an unambiguous assignment of the shoulder at 1.2 eV in our PIA spectra (Fig. 3) to a fullerene anion absorption is impossible. Moreover the same shoulder can be observed for all samples, independent if they contain a fullerene unit (like UCM-2) or not (like UCM-1, UCM-3). Further it should be noted that the intensity of the PIA signals is at least 3 times higher for the fullerene containing dyade UCM-2 as compared to the other pure TCAQ type electron acceptors (Fig. 3).

Also from the results of the PIA studies, as we already mentioned before for the LESR studies, we would tentatively state, that the last stage in the electron transfer from the polymer to the acceptor can be both the fullerene unit and the TCAQ unit.

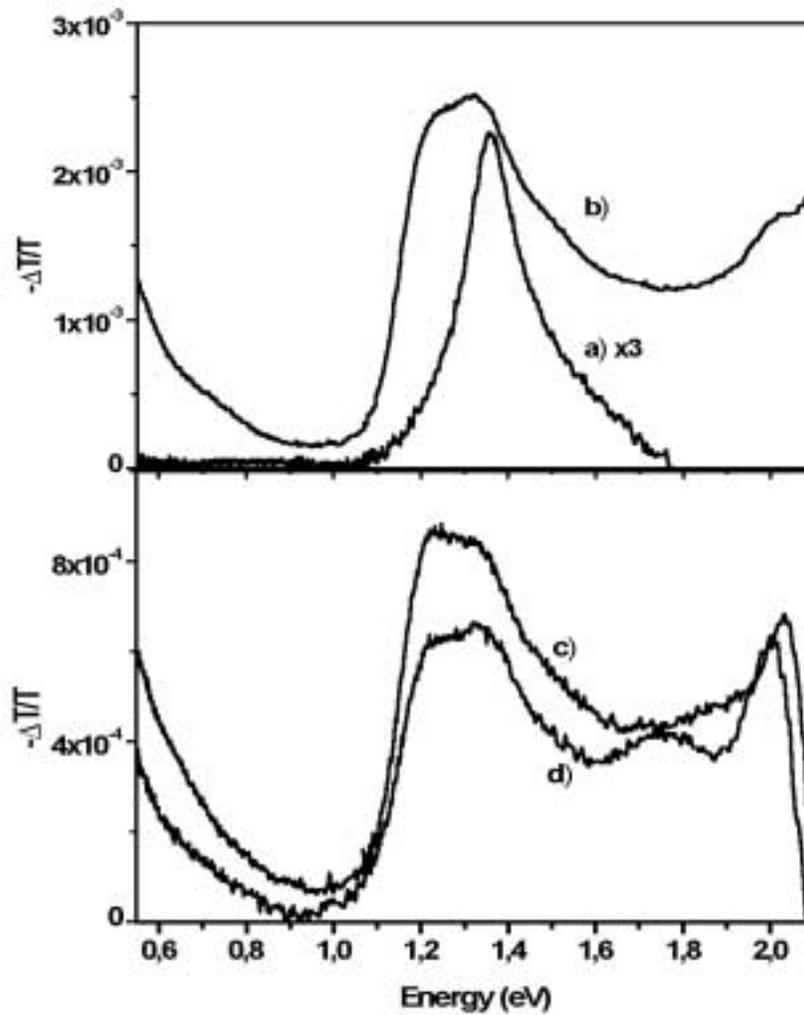


Figure 3: Photoinduced absorption spectra of a) pristine MDMO-PPV film and composite films with b) MDMO-PPV:UCM-2 = 4 : 1, c) MDMO-PPV:UCM-1 = 4 : 1, d) MDMO-PPV:UCM-3 = 4 : 1. Excitation wavelength 488nm, 40mW, $T=100K$.

To sum up the results from intensity and frequency dependent PIA spectra:
 -For the pristine MDMO-PPV films a mono-molecular kinetics with lifetimes components of the order of 100 μs is observed. The light-induced signal at 1.36eV is assigned to a triplet-triplet absorption.

-For all the composite MDMO-PPV films with the three different TCAQ derivative electron acceptors following photo-excitation a predominantly bimolecular recombination kinetics ($\text{PIA} \sim t^{0.5}$) is involved in the PIA signals (<0.9, 1.24 and 1.34eV). But it is not possible to isolate one single lifetime for these charged excitations; this is most probably due to trapped states with a distribution of different trap depth.

CONCLUSIONS

Both light induced ESR studies as well as photoinduced absorption experiments indicate effective electron transfer from the MDMO-PPV polymer to the TCAQ type acceptors resulting in long lived charge separated states. Comparative PIA experiments show that the fullerene containing electron acceptor (UCM-2) leads to a more efficient charge separation as compared to the pure TCAQ electron acceptors (UCM-1, UCM-3). Moreover for the fullerene-TCAQ electron acceptor dyade it was found that both the TCAQ unit as well as the fullerene unit can be the end stage of the electron transfer and that a stepwise unidirectional charge transfer can most probably be excluded.

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