

Tuning of the photoinduced charge transfer process in donor–acceptor double-cable copolymers

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Abstract

We present a study on the photoinduced charge transfer properties of a series of alkylthiophene copolymers carrying anthraquinone type acceptor molecules covalently linked to the conjugated backbone. FTIR photoinduced absorption and light-induced electron spin resonance (LESR) experiments demonstrate the photoinduced electron transfer from the polythiophene backbone to the anthraquinone moieties. By changing the content of acceptor molecules, it is possible to tune the number of photogenerated charges as well as their lifetimes. Changes induced by the acceptors to the polythiophene properties are also observed and discussed.

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1. Introduction

The use of conjugated polymers as photoactive materials in photodetectors and in photovoltaic devices is based on the photoinduced charge transfer between organic materials with different electron affinities. Since the discovery of an efficient photoinduced charge separation between conducting polymers, acting as donors, and fullerene and its derivatives, as acceptors [1,2], the possibility to use conjugated polymers to fabricate inexpensive and flexible large area solar cells and photodetectors is intensively investigated [3,4].

The most promising active layer is the so called bulk-heterojunction where the electron donor polymer and the acceptor molecules are blended together. To obtain a good charge photogeneration and transport, it is necessary to attain an intimate mixing of the donor–acceptor components and to control the morphology of the photoactive layer. A proposed approach to get these properties is the covalent linking of electron accepting and conducting moieties to a hole transporting conjugated polymer backbone.

These macromolecules have in principle two different pathways (cables) for different signs of charges, being thus ideally viewed as “double cables” with a balanced transport of electrons and holes. With this approach, different types of conjugated polymers, bearing acceptor substituents, have been synthesized and the possibility to use them for photovoltaic applications has been investigated [5].

One of the major issues in the chemical design of “double cables” polymers is to improve the processability of these polymers, in order to obtain soluble polymers with a high content of acceptor moieties. For example, to obtain soluble materials, the conjugated polymers containing fullerene acceptor molecules [5] exhibit a content of acceptors not exceeding 20%.

To obtain donor–acceptor “double cables” polymers with good processability, we have prepared a series of polythiophene copolymers containing in the backbone alkylthiophene units and thiophene rings with anthraquinone acceptor moieties in the substituent chain (see the inset of Fig. 1). The peculiar feature of these materials is that the content of acceptor can be easily tuned and even a 100% anthraquinone substitution is leading to a soluble polymer.

In this work, we report preliminary photophysical study of the photoinduced charge transfer properties of these copolymers films.

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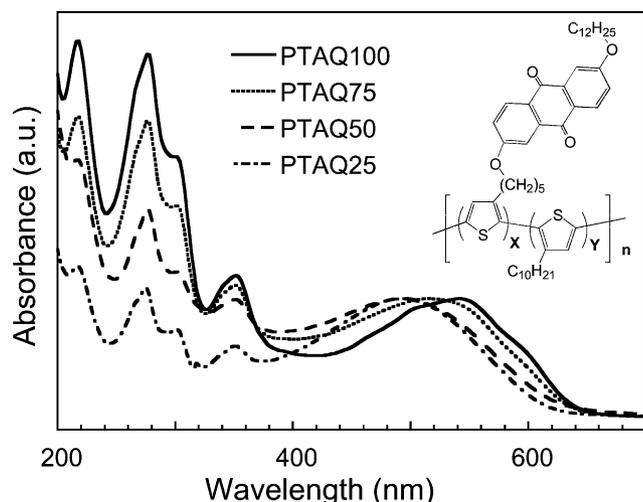


Fig. 1. UV-Vis absorption spectra of the PTAQs copolymers. The formula of the copolymers are reported in the inset.

2. Experimental

The copolymers, containing decylthiophenes and anthraquinone-substituted thiophenes monomers, have been prepared by chemical oxidative coupling with FeCl_3 . We synthesized a polymer with all the thiophene rings substituted with anthraquinone and three copolymers containing 25, 50 and 75% of unit containing the acceptor molecules (herein PTAQ100, PTAQ25, PTAQ50 and PTAQ75). The macromolecular characterization indicates [6] that the resulting random copolymers have the same composition of the monomers feed. Their photophysical behavior has been compared to a polydecylthiophene (PDT) obtained with the same synthetic route and thus with the same degree of regioregularity.

The PA spectra have been measured with a FTIR spectrometer covering a spectral range from 0.05 to 1 eV. The fractional changes in transmission have been measured in response to a 514 nm laser line incident on the sample, by the subsequent accumulation of scans with laser on and laser off. The on/off modulation has been driven by a mechanical shutter with frequencies varying from 0.5 to 0.0141 Hz. For the PA measurements, solution drop cast films have been prepared on KBr windows and the film thickness of the different copolymers has been adjusted in order to obtain similar absorbance at the laser excitation wavelength (OD of 1.7 at 514 nm). The temperature has been kept at 80 K.

Light-induced electron spin resonance (LESR) has been measured with a Bruker EMX spectrometer (X band), with a 459 nm laser line excitation at a temperature of 20 K. A microwave power of $20 \mu\text{W}$ was used for all measurements. The g -values were determined using a Bruker weak pitch samples to calibrate the spectrometer. The detailed measurement procedure is described elsewhere [7].

3. Results and discussion

The UV-Vis absorption spectra of the copolymers films are reported in Fig. 1. The spectra display an absorption band in the visible region which is due to the π - π^* transition of the polythiophene backbone, and a series of bands in the UV region, originating from the anthraquinone moieties [8]. The absorption band of the thiophene backbone is affected by the copolymer composition. A red shift is observed upon increasing the anthraquinone content, suggesting that these substituents are inducing a better conjugation and/or a better three-dimensional organization of the copolymer chains. The homopolymer PTAQ100 displays the spectrum mostly red shifted, with a λ_{max} at 540 nm. This feature can be reasonably ascribed to a better order due to the homogeneity of the side chains. However, considering that the λ_{max} of PDT films is at 510 nm and this homopolymer has the same degree of regioregularity of PTAQ100, we infer that the anthraquinone molecules play a specific role in driving the chain ordering.

The photoluminescence of PTAQs films is quenched by 2–3 orders of magnitude with respect to PDT and the quenching increases with the anthraquinone content. This is suggesting that electron transfer from the photoexcited polythiophene backbone to anthraquinone is occurring and that the charge transfer is fast enough to compete with the radiative recombination of the excitons.

The PA spectra of PTAQs are reported in Fig. 2. The electronic broad band as well as part of the infrared active vibrations (IRAV) has the same spectral pattern of polyalkylthiophenes (see the inset), probing thus the formation of polaron charged excitations into the polythiophene backbone. The bleaching of two anthraquinone IR bands at 1589 and 1668 cm^{-1} are indicative for the formation of anthraquinone radical anions [8]. Therefore, the PA spectra provide a spectroscopical indication that the electron transfer from the photoexcited polythiophene to the anthraquinone

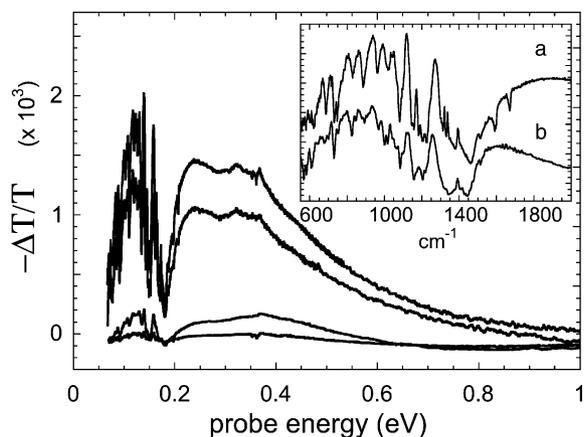


Fig. 2. FTIR PA spectra of PTAQs. From the bottom to the top: PTAQ25, PTAQ50, PTAQ75 and PTAQ100. The inset: IRAVs bands of PTAQ100 (a) and of PDT (b). Temperature: 80 K; excitation wavelength: 514 nm, 1.75 mW cm^{-2} ; shutter modulation frequency: 0.21 Hz.

is occurring, forming long living metastable polaron cations into the polythiophene backbone and radical anions into the anthraquinone moieties. It is interesting to notice that a high energy and a low energy contribution to the polaron electronic band coexists in the PA spectra. These features can be ascribed to different organizations of the polyalkylthiophenes. Previous assignments [9,10] suggest that the high energy contribution is due to disordered chains while the low energy contribution probes a more ordered phase, with the chains in a lamellar structure. Therefore like the UV-Vis spectra, the PA spectra suggest that a high content of anthraquinone molecules is beneficial to the copolymer chain organization.

The PA signal is increasing with the anthraquinone content because of the increased number of metastable charged states arising from the photoinduced charge transfer process. Longer lifetimes may also account for this feature. By varying the laser on/off exposure time, we have found that the copolymer composition is indeed affecting the lifetimes of the photogenerated charged states. We have observed that the steady state condition is fulfilled for PTAQ25 and PTAQ50: the variation of the shutter modulation frequency is not changing the PA signal. Considering our experimental conditions, this indicates that the recombination of the photogenerated charged states occurs within 1 s. For PTAQ75 and PTAQ100, the PA signal is reduced by increasing the shutter frequency. Thus the lifetimes of the metastable charged states can be longer than 10 s when more than 50% of the thiophenes are carrying an acceptor molecule. In analogy to polymer/fullerene bulk heterojunctions [7,11], the very long-lived charges are suggesting the presence of persistent charges whose origin is intrinsic to the photoexcitation mechanisms of the donor–acceptor composite systems.

The LESR measurements of the copolymers are reported in Fig. 3. The spectra display two overlapping lines at magnetic field of ~ 3361 and ~ 3365 G corresponding, respec-

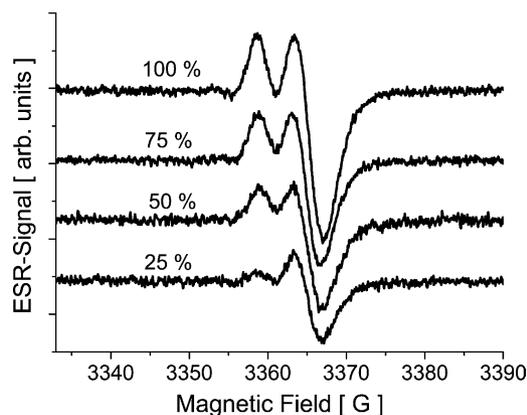


Fig. 3. LESR spectra of PTAQs. Measurements were performed at 20 K, microwave power $20 \mu\text{W}$. The shown spectra are corrected for the weak dark signal and shifted on the y-axis.

tively to $g = 2.0042$ and 2.0024 . The high g -value signal is assigned to radical anions on the anthraquinone molecule [12] and the low g -value signal to positive polarons on the polythiophene chain [13]. Microwave saturation studies show different relaxation times for these spins, giving a clear evidence of independent photoinduced spins. The number of photogenerated spins is increasing with the content of anthraquinone acceptors in the copolymers.

In conclusion, the photo-physical study here reported shows that in these new series of polythiophene copolymers bearing an anthraquinone substituent, the photoinduced electron transfer from the polythiophene backbone to the anthraquinone acceptor moieties is occurring and that this process is easily tuned by tailoring the content of acceptor substituents in the polymer. We have observed that the number of photogenerated charges and their lifetimes are increasing with the number of acceptor molecules. These preliminary data are suggesting an interesting interplay between the copolymer composition, the chain organization and the charge photogeneration. These features make these copolymer series a good model system towards the donor–acceptor “double-cable” polymer approach.

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