

Photoinduced Charge Carriers in a Donor-Acceptor *Double-Cable* Polythiophene with Covalently Bound Tetracyanoanthraquinodimethane Moieties

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ABSTRACT

The preparation of *double-cable* polymers, which consist of a hole conducting conjugated chain carrying pendant electron accepting/conducting moieties, is a promising strategy to prevent donor/acceptor phase segregation and to achieve defined microscopic structure in organic *bulk heterojunction* solar cells. In this paper we report the electrochemical synthesis and the investigation of a *double-cable* consisting of a polythiophene backbone bearing, via covalent bonds, electron accepting tetracyanoanthraquinodimethane (TCAQ) type moieties. Electrochemical studies and UV-VIS absorption spectroscopy reveal, that in dark, the polythiophene chain and the TCAQ moieties retain their individual ground-state properties. Upon illumination photoinduced electron transfer occurs, which is studied by photoinduced VIS-NIR absorption spectroscopy.

INTRODUCTION

In the last two decades, the physical properties and potential application of conjugated polymers have been increasingly drawing the attention of academic and industrial research[1]. Indeed, a conspicuous amount of work has been done and devices based on conjugated polymers are today entering the large scale commercialization like, for instance, light emitting diodes (LEDs). Furthermore, their potential for low cost photovoltaic solar cells opened a new field of possible applications[2]. Efficient photovoltaic devices require balanced electron and hole transport. Most of the conventional conjugated polymers are hole conductors (p-type) while efficient electron conducting (n-type) polymers are rare. The most efficient polymeric solar cells fabricated today are so-called *bulk heterojunction* solar cells, which consist of a p-type conjugated polymer network with a fullerene derivative mixed into it as n-type material[2a,b, 3]. Photoinduced charge generation, charge transport and charge recombination in these blends have been investigated. To obtain efficient photoinduced charge generation and transport in this class of devices, morphology, influencing the interaction between electron donating and electron accepting units, is of crucial importance. It has been shown that the different solubility of the donor and acceptor components and their limited miscibility cause the separation of fullerene domains, affecting the photoinduced charge generation as well as the electron mobility and, therefore, the overall efficiency of devices[3].

One possibility of circumventing the problem of phase separation is given by the concept of donor-acceptor *double-cables*. We call *double-cables* materials that consist of a hole conducting conjugated polymer chain carrying pendant electron acceptor moieties. We expect that the primary structure of such *double-cables* forces controlled interactions between

the donor and the acceptor moieties and prevents phase separation. In addition, this challenging approach could represent the first step towards further control of the final morphology by means of self-assembling secondary and tertiary structures. On these bases, we engaged to specifically design *double-cable* polymers and supramolecular structures for photovoltaic devices[4].

In this paper we present the preparation as well as the electrochemical and spectroscopic properties of such a *double-cable* built from monomer **1**, which consists of a bithiophene with a pendant tetracyanoanthraquinodimethane (TCAQ) electron acceptor moiety (Fig. 1). Electrochemically prepared poly-**1** exhibits the necessary properties of a successful *double-cable*:

- a) mutually independent electrochemical properties as well as optical properties of the donor and acceptor units in the ground-state (“*the cables do not short*”);
- b) a photoinduced electron transfer from the electron donating polythiophene backbone onto the electron accepting TCAQ unit as a prerequisite for photogeneration of free charge carriers.

EXPERIMENTAL

The synthesis of compounds **1** and **2** (Fig. 1) will be reported elsewhere[5]. We used the bithiophene **1** for the preparation of the polythiophene-TCAQ *double-cable*, while **2** served as monomer for the preparation of a reference polymer. Thin polymer films have been electrodeposited, by sweeping the potential between 0 and +1.3 V with a sweep rate of 100 mV/s, at 0 °C under argon atmosphere. A conventional three-electrode cell was used where, for the preparation of spectroscopic samples, the working electrode was an indium tin oxide (ITO) coated glass or plastic foil (10 mm × 20 mm). A Ag/AgCl wire (-0.44 V vs. ferrocene) and a Pt foil served as quasi-reference and counter electrodes, respectively. In this paper all potential values refer to this quasi-reference electrode. The electrolyte solution used for electropolymerization was 0.1 M tetrabutylammonium-hexafluorophosphate (Bu₄NPF₆, dried under vacuum prior of the experiments) in anhydrous CH₂Cl₂. For cyclic voltammetry (CV) of the poly-**1** film in monomer free electrolyte solution, anhydrous CH₃CN was the solvent. After polymerization, the samples were neutralized by applying 0 V until no current flow was observed. Residual charges in the polymeric films were minimized by repeating this procedure in monomer-free electrolyte medium (0.1 M Bu₄NPF₆ in CH₃CN). Finally, the films were rinsed with CH₃CN and dried by an argon flow. A similar procedure was used for the preparation of electrochemically oxidized and reduced *double-cable* samples applying 1.0 V and -0.37 V, respectively.

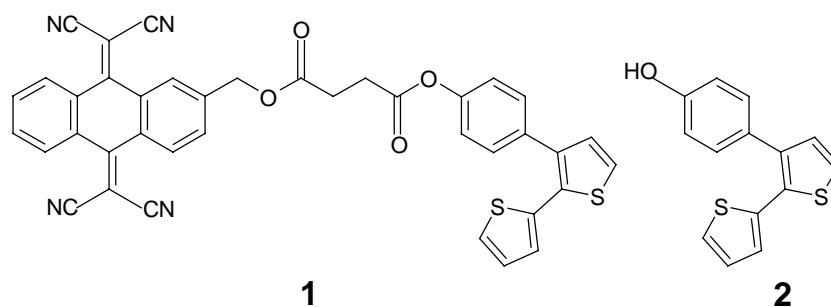


Figure 1. Chemical structure of the monomers. While **1** gives the double-cable, compound **2** has been polymerized to serve as reference polythiophene.

UV-Vis absorption measurements have been carried out at room temperature by means of a Cary-3 double beam spectrophotometer.

For photoinduced absorption spectra an Ar⁺ laser beam served as excitation source; poly-**1** and monomer **1** were excited at 476 and 351 nm, respectively (40 mW on a 4 mm diameter spot). The pump beam was modulated mechanically with a frequency of 210 Hz; 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 2.15 eV with a Si-InGaAsSb sandwiched detector. The detector signals were recorded phase sensitively with a dual-phase lock-in amplifier. The PIA spectra ($-\Delta T/T$) were corrected for the sample luminescence and normalized on the probe light transmission (T). Measurements have been done at 100 K.

RESULTS AND DISCUSSION

Electrochemical polymerization and cyclic voltammetry

The donor-acceptor *double-cable* has been prepared electrochemically starting from monomer **1**, in which a TCAQ moiety is linked to a bithiophene unit through a flexible spacer (Fig. 1). To serve as reference for the spectroscopic investigations described in the following, poly-**2** has been also prepared in a similar way. Both polythiophenes give, on the ITO coated electrodes, red colored films with excellent optical quality.

Figure 2(a) shows the cyclic voltammogram (CV) recorded in CH₂Cl₂ during the polymerization of **1** by sweeping the potential between 0 and +1.3 V, the latter being just above the threshold for the oxidation of **1**. The formation of poly-**1** can be seen by the growing redox wave centered at about 0.8 V, which corresponds to the oxidation/re-reduction of the polythiophene backbone. Figure 2(b) shows the CV (monomer free, CH₃CN

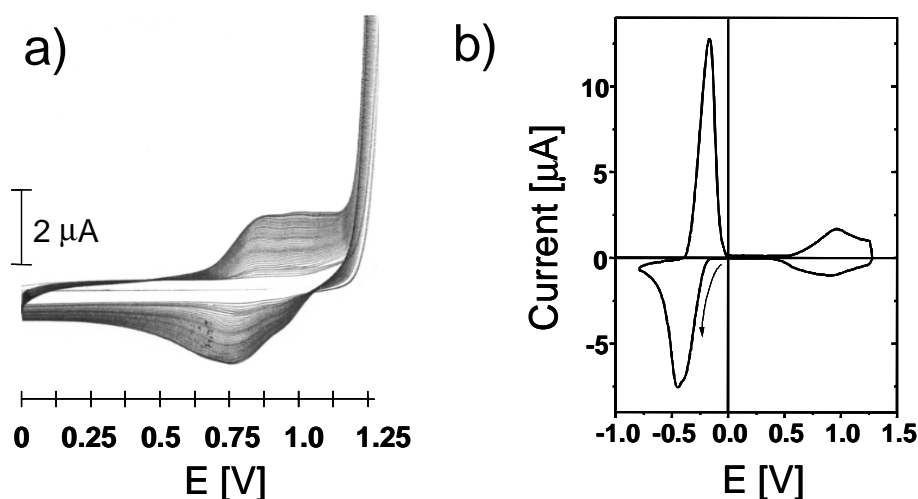


Figure 2. Cyclic voltammograms recorded during a): the electropolymerization of **1**; b): the electrochemical oxidation and reduction of a film of poly-**1** in monomer free electrolyte medium. Working electrode: ITO coated glass. Scan rate 100 mV/s.

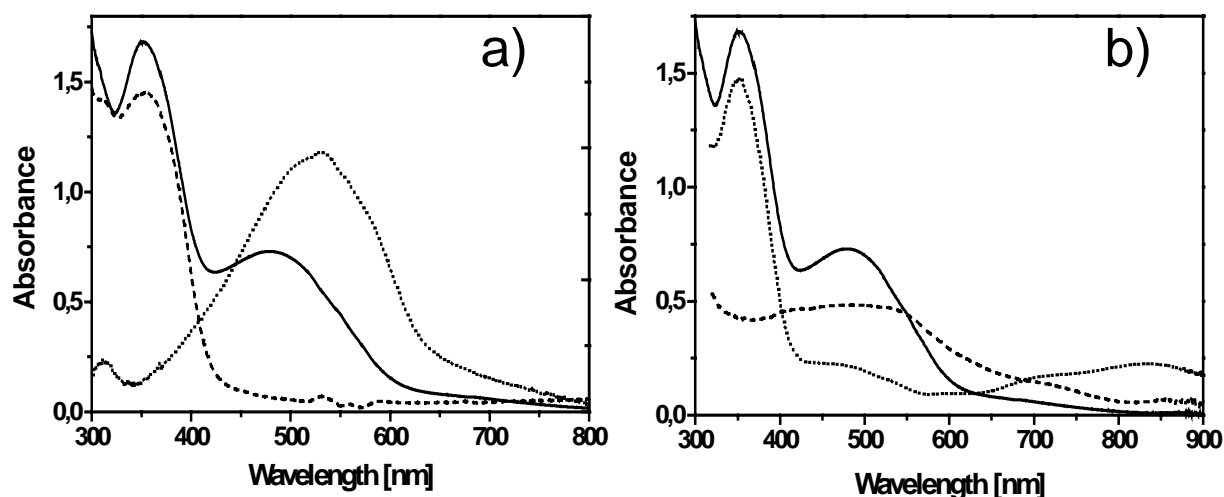


Figure 3. a): UV-Vis absorption spectra of films of monomer 1 (dashed line), neutral poly-1 (solid line) and poly-2 (dotted line); b): UV-Vis absorption of films of neutral (solid line), oxidized (dotted line) and reduced (dashed line) poly-1.

as solvent) of a poly-1 film in the potential range from -0.8 to $+1.3$ V. The cathodic region of the CV shows only one wave at -0.30 V, which is assigned to the reversible reduction of the TCAQ moiety[6]. In the anodic region the CV shows one reversible wave centered at $+0.62$ V, which corresponds to the oxidation/re-reduction of the polythiophene backbone. These results indicate that the polythiophene backbone and the pendant TCAQ moieties mostly retain their individual electrochemical properties.

UV-Vis absorption

Figure 3(a) shows the electronic absorption spectrum of a drop cast film of monomer 1 along with that of dedoped, neutral poly-1. For comparison figure 3(a) also shows the absorption spectrum of poly-2, prepared as a reference sample. The monomer 1 absorption spectrum has an onset around 430 nm and a maximum at 350 nm, the latter corresponding to the lowest electronic transition of the TCAQ unit [6]. The electropolymerized poly-1 shows the same UV absorption band at 350nm. In addition, a rather broad band with a maximum around 490 nm is seen in the polymer spectrum, representing the π - π^* -transition of the extended π -electron system. Further confirmation for the assignment given above comes from the absorption spectra of the reference poly-2. This spectrum consists essentially of only one rather broad band with a maximum around 530 nm due to the conjugated backbone. As expected, the 350 nm peak attributed before to the TCAQ absorption is missing. The 40 nm blueshift of the π - π^* -absorption peak of poly-1 as compared to poly-2 is understood as due to a shortening of the effective conjugation length in the former. Such a shortening of the effective conjugation length in poly-1 may be explained by steric hindrance caused by the TCAQ side groups or by the poor solubility of monomer 1 as compared to monomer 2, leading to a low molecular weight polymer. Similar effects have also been already observed for other *double-cable* polymers[4, 7]. The difference in the absorption spectra of poly-1 and poly-2 can also be due to the *para*-hydroxyphenyl substituent in the latter, which may donate more electrons into the conjugated backbone [4].

Figure 3(b) shows the UV-Vis absorption spectra of films of poly-1 in its electrochemically oxidized and reduced state. Electrochemical oxidation at a potential of

1.0 V affects only the polythiophene backbone of this *double-cable*. A new absorption band between 700 and 900 nm grows at the expense of the 490 nm π - π^* absorption, which is reduced relative to the TCAQ absorption at 350 nm. Oscillator strength is transferred from the neutral polymer π - π^* transition to the in-the-gap NIR transitions, probably of polaronic origin. On the other hand, the electrochemical reduction, done by keeping the samples at -0.37 V, affects only the TCAQ moiety of the *double-cable*, as can be seen by the drop of the intensity of the 350 nm absorption band due to the neutral TCAQ moiety and the enhancement of that in the 550-600 nm range, which is due to TCAQ type radical-anions and dianions[6]. This behavior further confirms that the donor and acceptor moieties do not undergo strong ground-state interaction.

Photoinduced electron transfer

The photoinduced absorption (PIA) spectra of films of monomer **1** and of poly-**1** are compared in figure 4(a). The PIA spectrum of the monomer excited in the UV at 351 nm shows mainly one peak at 1.15 eV and a shoulder rising around 2.0 eV. Both photoinduced features are assigned to radical anions on the TCAQ units[6]. The PIA spectrum of poly-**1** consists of two new bands in addition to the TCAQ radical anion features observed already for the monomer: one at around 1.5 eV as a plateau and another one peaking below 0.6 eV. Both of these absorption features are assigned to charged excitations on the polythiophene backbone. Also shown in Figure 4(a) is the absorption spectrum of the electrochemically oxidized poly-**1** in the Vis-NIR spectral range, which further supports the assignment we made for the PIA spectrum of the neutral poly-**1**. Electrochemical oxidation (p-doping) results mainly in two broad absorption bands at 1.5 eV and below 0.6 eV and gives further evidence that the peaks in the photoinduced absorption spectra (Fig. 4(a)) have charged excitations as origin. For a further support of the assignment given above a fit of a sum of four gaussian curves to the PIA spectrum of poly-**1** is shown in Fig. 4(b). The two Gaussian curves with maxima at 1.15 eV and above 2 eV represent the TCAQ anion radical absorption and the other two curves peaking at 1.5 eV and below 0.6 eV correspond to the polaronic absorption of the polymer. The sum of these four Gaussians yields excellent agreement with

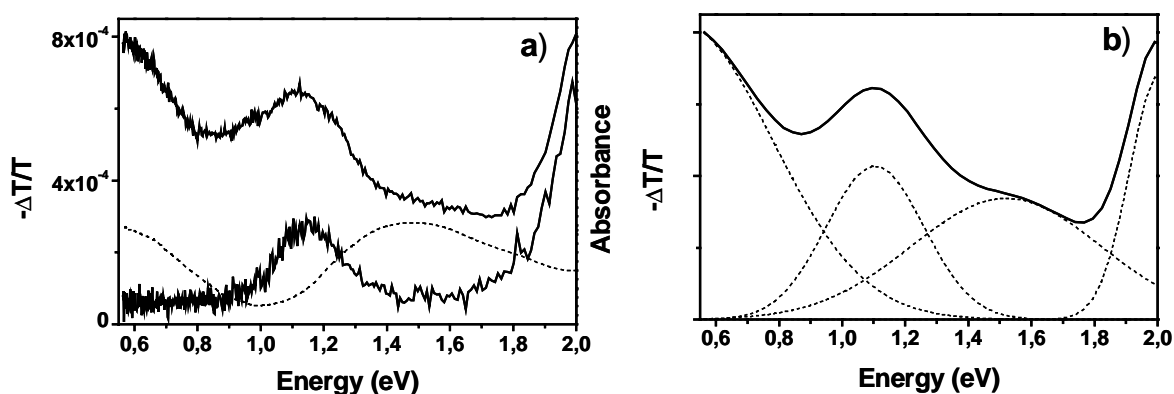


Figure 4. a) PIA spectra of monomer **1** (lower trace, left axis) excited at 351 nm and poly-**1** (upper trace, left axis) excited at 476 nm compared to Vis-NIR absorption spectrum of electrochemically oxidized poly-**1** (dotted trace, right axis); b) Fit to the PIA spectrum of poly-**1** (solid trace) by a sum of four Gaussians (dotted trace).

the PIA spectrum of poly-1 depicted in figure 4(a). All PIA features exhibit a square root excitation intensity dependence suggesting bimolecular recombination kinetics. As already shown for the modulation frequency dependence of polaronic absorption peaks of different types of conjugated polymers, a broad distribution of charged state lifetimes is observed [8]. A series of three time constants between some 100 microseconds up to tens of milliseconds has been assumed for best fitting the measured relaxation kinetics.

CONCLUSIONS

We have prepared, by electrochemical polymerisation, films of a polymer whose repeating units consist of a bithiophene derivative with a covalently linked TCAQ moiety. This electron donor-acceptor *double-cable* has been investigated for its electrochemical and photophysical properties. The polythiophene backbone and the pendant TCAQ moieties have been found, as necessary for application in photovoltaic systems, to be mutually independent in the ground state of the polymer. Photoinduced charge transfer occurs clearly in this *double-cable* polymer as revealed by the observation of polarons and TCAQ radical-anions absorption in the PIA spectrum. *Double-cable* polymers, which are a proposed strategy for circumventing the phase separation problem in *bulk-heterojunction* solar cells, are now under investigation for the production of photovoltaic devices.

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