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ARTICLES

Photoinduced Electron Transfer in Donor−Acceptor Double-Cable Polymers: Polythiophene Bearing Tetracyanoanthraquinodimethane Moieties

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To circumvent the problems of morphology and donor−acceptor phase segregation in organic bulk heterojunction solar cells, double-cable materials, consisting of a hole conducting conjugated polymer chain carrying pendant electron accepting moieties, are proposed. We report the electrochemical synthesis of a double-cable material consisting of a polythiophene backbone with covalently bound tetracyanoanthraquinodimethane (TCAQ) moieties. Cyclic voltammetry and UV−vis absorption measurements reveal that in this functional material both the polythiophene chain and the TCAQ moieties maintain their individual electrochemical and electronic ground state properties. Photoinduced absorption (PIA) and light-induced electron spin resonance (LESR) studies clearly indicate photoinduced electron transfer from the polythiophene backbone to the TCAQ moieties upon photoexcitation. The results of the PIA are comparatively studied with UV/vis and near-infrared absorption spectra upon electrochemical doping.

Introduction

In the past two decades, research on conjugated, semiconducting polymers has experienced increasing attention in the scientific community[1] because of their application in light emitting diodes (LEDs), which are today entering large-scale commercialization.[2−7] In addition, due to their potential for low-cost photovoltaic solar cells, these materials are increasingly being the focus of academic and industrial optoelectronic research and development.[8−12] To obtain efficient photoinduced charge generation for photovoltaic applications in this class of materials, photoinduced electron-transfer type interactions between electron donating and electron accepting units are of crucial importance.[8] In this context, special attention has been drawn to photoinduced charge generation,[13−25] charge transport, and charge recombination in donor−acceptor mixed phases as well as at donor−acceptor interfaces.[26−28] Investigations concerning the nature of the primary photoexcitations in conjugated polymers are also important in understanding the photophysics involved.[29]

For realization of efficient LEDs and photovoltaic devices, both electron and hole transport have to be balanced. While most of the conventional conjugated polymers are hole conductors (“p-type”), efficient electron-conducting (“n-type”) polymers are rare.

The most efficient polymer solar cells fabricated today are based on the concept of bulk heterojunctions.[9−12] They consist of a p-type conjugated polymer network with a fullerene derivative mixed into it as an n-type material. The different solubilities of the two components in the organic solvents used for the film preparation and their limited miscibility cause morphologic problems, such as phase separation, which in turn influence the photoinduced charge generation as well as the charge carrier mobility in the blend and thus the efficiency of the whole device.

One way to circumvent the problem of phase separation is given by the concept of donor−acceptor “double cables”. We call double cable such materials that consist of a hole-conducting conjugated polymer chain carrying pendant electron-conducting moieties. In this way, electron-acceptor and -donor units are forced from the primary structure to form a p- and n-conducting network with well-defined links. Different groups have already reported similar structures consisting of a conducting polymer and pendant fullerenes as electron accepting unit prepared either by electrochemical polymerization or by copolymerizaion without a specific commitment to photovoltaic applications.[30,31]

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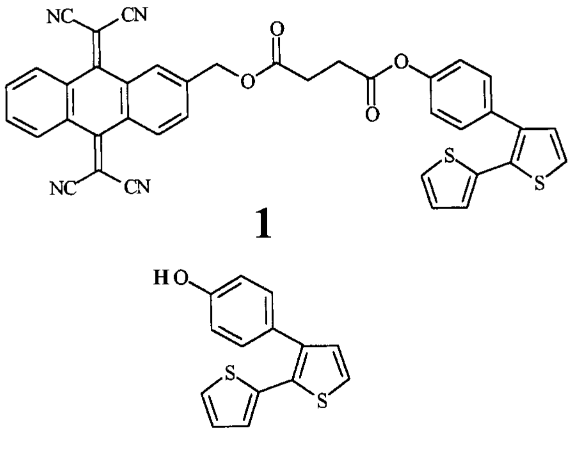

1

2

Figure 1. Chemical structure of the monomers **1** and **2**.

On the basis of this double-cable idea, we recently began to specifically design and realize materials for polymeric solar cells.[32]

In this work, we present the preparation as well as the electrochemical and photophysical properties of a double cable built from a monomer that consists of bithiophene with a pendant tetracyanoanthraquinodimethane (TCAQ) electron-acceptor moiety (**1** in Figure 1). Electrochemically prepared poly-**1** clearly exhibits the necessary physical properties of a successful double cable: (a) mutually independent electrochemical as well as optical properties of the donor and acceptor units in the ground state ("cables do not short") and (b) a photoinduced electron transfer from the electron-donating polythiophene backbone onto the electro-accepting TCAQ unit as a prerequisite for photogeneration of free charge carriers.

Experimental Section

Details of the synthesis of **1** and **2** will be reported elsewhere.[33] We used the bithiophene **1** (Figure 1) for the preparation of the polythiophene−TCAQ double cable. Compound **2** served as monomer for the preparation of a reference polymer. Thin polymer films were electrodeposited anodically, 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 an ITO-coated plastic foil (10 × 20 mm^2). A Ag/AgCl wire (−0.44 V vs ferrocene) and a Pt foil served as quasi-reference and counter electrodes, respectively. All potential values refer to this quasi-reference electrode. The electrolyte solution used for electropolymerization was 0.1 M tetrabutylammonium−hexafluorophosphate (Bu_4NPF_6, dried under vacuum prior to the experiments) in anhydrous CH_2Cl_2. For cyclic voltammetry (CV) of the poly-**1** film in monomer-free electrolyte solution, anhydrous CH_3CN served as solvent. After polymerization, the samples were dedoped by applying 0 V until no current flow was observed. Concentration of residual charges in the obtained polymeric films was minimized by repeating this procedure in monomer-free 0.1 M Bu_4NPF_6 in CH_3CN. Finally, the films were washed with CH_3CN and dried under argon. A similar procedure was used for the preparation of oxidized and reduced double-cable samples, applying +1.0 and −0.37 V, respectively.

UV−vis absorption spectra of the polymer films were taken at room temperature on a Cary-3 double-beam spectrophotometer.

For photoinduced absorption (PIA) spectra of the polymer films, an Ar^+-ion laser beam at 476 nm served as a excitation source, whereas the PIA spectra of the monomer compound were obtained using the 351 nm line of the Ar^+-ion laser (typically 40 mW on a 4 mm diameter spot). The pump beam was mechanically modulated at a frequency of 210 Hz, and 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 sandwich detector. The detector signals were 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 ($-\Delta T/T$) were obtained after correction for the sample luminescence and normalization on the probe light transmission. For the PIA experiments, the samples were cooled to 100 K in a liquid-nitrogen cryostat.

For light-induced electron spin resonance (LESR) studies, 2 × 10 mm^2 stripes of poly-**1** on ITO-coated plastic were placed into quartz ESR tubes, which were sealed under Ar atmosphere. These samples were placed in the rectangular high-Q-cavity of an X-band ESR spectrometer and cooled to 100 K by a liquid-nitrogen cryostat. For the "light on" ESR spectra, the 476 nm line of an Ar^+-ion laser was used for illumination of the polymer films. "Dark spectra" and "light off" spectra were taken directly before and after illumination, respectively, in order to take into account the presence of residual charges from the polymerization process and persistent light-induced charges. According to our definition, the LESR spectrum is the difference between spectrum "light on" minus that of "light off".

Results and Discussion

Electrochemical Polymerization and Cyclic Voltammetry. The electron donor−acceptor double cable was prepared electrochemically starting from **1**, in which a TCAQ moiety is linked to a bithiophene unit through a flexible spacer (Figure 1). To serve as reference for the spectroscopic investigations monomer **2** was also polymerized in the same way as monomer **1** (Figure 1). Both polymeric compounds form, on the ITO-coated substrates, red films of excellent optical quality.

Figure 2a shows the CV taken during the polymerization process of monomer **1** by sweeping the potential between 0 and +1.3 V, the latter being just above the threshold for the irreversible oxidation of **1**. The formation of the polymer can be seen by the growing redox wave centered at about 0.8 V, which corresponds to the oxidation/rereduction of the polythiophene backbone. Figure 2b shows the CV of a poly-**1** film in monomer-free electrolyte solution in the potential range from −0.8 to +1.3 V. The cathodic region of the CV shows only one wave, which is due to the reversible reduction of the TCAQ moiety at −0.30 V.[34] In the anodic region, the CV shows one reversible wave centered at +0.62 V, which corresponds to the well-known oxidation/rereduction of the polythiophene backbone. The CV shown in Figure 2b is not completely reversible: after a number of 100 potential sweeps, the peak current values of all features in the CV were reduced by 50%.

UV−vis Absorption. Figure 3 shows the optical absorption spectra of a drop-cast film of **1** along with that of an electropolymerized film of neutral poly-**1**. For comparison, Figure 3 also shows the absorption spectrum of poly-**2**, prepared as a reference sample (Figure 1). The monomer **1** absorption spectrum has an onset around 430 nm and peaks at 350 nm, which corresponds to the lowest electronic transition of the TCAQ unit.[34] The electropolymerized sample poly-**1** also shows

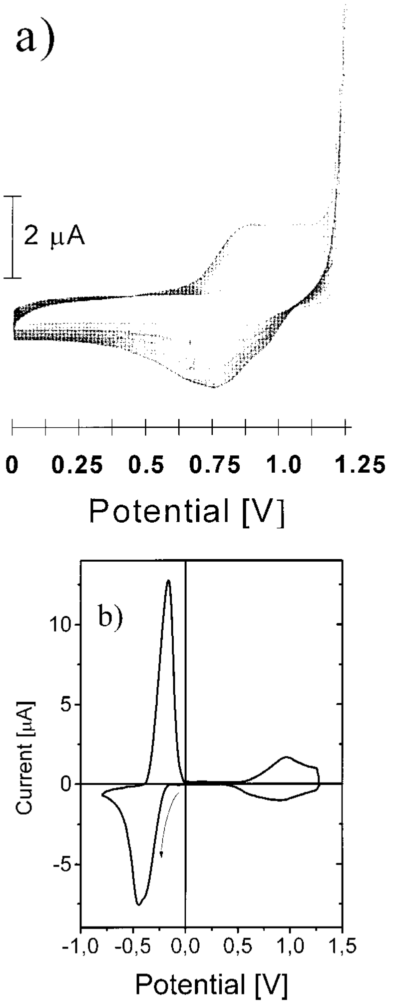

Figure 2. Cyclic voltammograms taken during (a) the electropolymerization process of **1** on an ITO-coated glass electrode and (b) the electrochemical oxidation and reduction of a film of poly-**1** on an ITO-coated glass electrode in a monomer-free electrolyte solution.

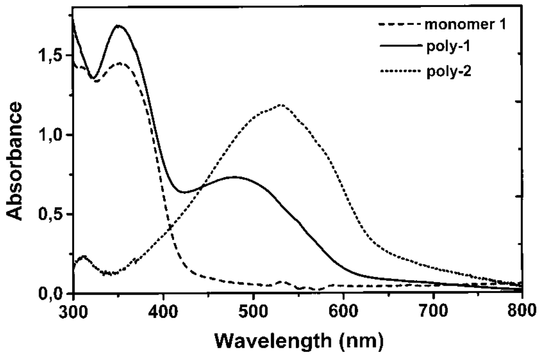

Figure 3. UV−vis absorption spectra of films of monomer **1** (dashed line), poly-**1** (solid line), and poly-**2** (dotted line).

the same UV absorption band at 350 nm. In addition to this, a rather broad band with a maximum around 490 nm and a long tail extending up to 650 nm emerges in the polymer spectrum, representing the $\pi-\pi^*$-transition of the extended π-electron system. Further confirmation for the assignment given above comes from the absorption spectra of the reference poly-**2** (Figure 3). 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 $\pi-\pi^*$-absorption peak of poly-**1** as compared to that of poly-**2** is understood as being due to a shortening of the effective conjugation length in the former. This 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 **1** as compared to that of **2** leading to a low-molecular-weight polymer. A blueshift in the π-system absorption spectrum has also been observed for some other double-cable-like materials.[30−32] The difference in the absorption spectra of poly-**1** and poly-**2** can also be due to the *p*-hydroxyphenyl groups in the latter, which may donate more electrons into the conjugated backbone.

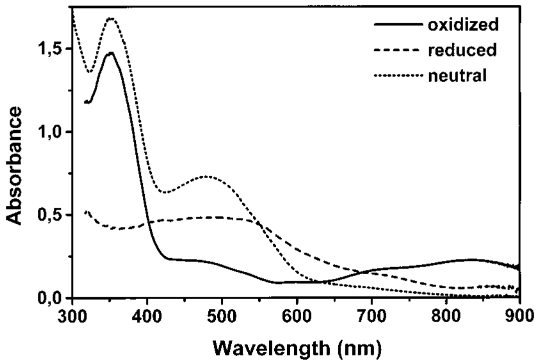

Figure 4. UV−vis absorption spectra of thin films of poly-**1** in different oxidation states: neutral polymer (dotted line), oxidized polymer (solid line), and reduced polymer (dashed line).

Figure 4 shows the UV−vis absorption spectra of films of poly-**1** in the 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 $\pi-\pi^*$ absorption, which is reduced relative to the TCAQ absorption at 350 nm. Oscillator strength is transferred from the neutral polymer to the polymer in-the-gap absorption, probably of polaronic origin, in the near-IR spectral range. On the other hand, the electrochemical reduction affects only the TCAQ moiety of the double cable. This can be seen by the decrease of the intensity of the 350 nm absorption band of neutral TCAQ and the enhancement of the absorption in the 550−600 nm range due to the formation of TCAQ anion and dianion radicals.[34]

Photoinduced Charge Transfer. Figure 5a shows a comparison of the PIA spectra of films of monomer **1** and of poly-**1**. The PIA spectrum of the monomer excited in the UV at 351 nm shows mainly one peak at 1.15 eV and a rising shoulder at 2.0 eV. Both photoinduced features may be assigned to radical anions of the TCAQ unit.[34] The PIA spectrum of poly-**1** consists of some 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 a thiophene-based conjugated backbone as observed previously in polythiophene.[35] The high- and low-energy absorption bands of polarons of long oligothiophenes ($n \geq 9$) are around 1.5 eV and below 0.5 eV, respectively.[36] Also shown in Figure 5a 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 peaks at 1.5 eV and below 0.6 eV and gives further evidence that the peaks in the photoinduced absorption spectra (Figure 5) have charged excitations as origins.

For additional clarification of the assignment given above a fit of a sum of four Gaussian curves to the PIA spectrum of

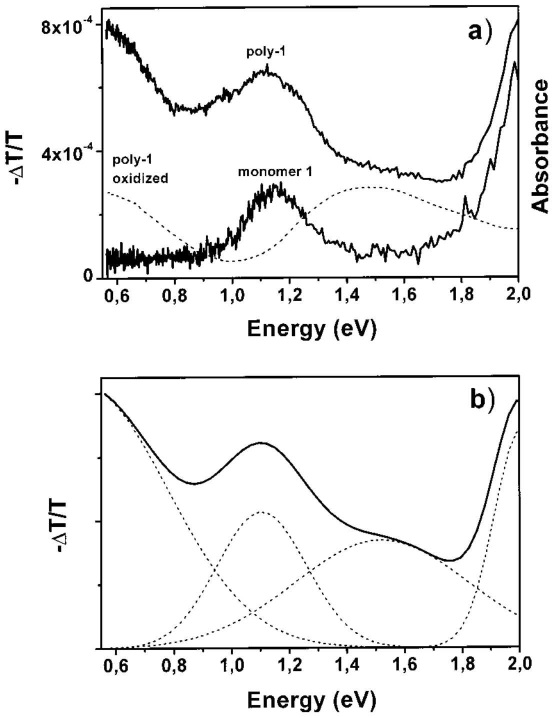

Figure 5. (a) PIA spectra of **1** excited at 351 nm (lower trace, left-hand axis) and poly-**1** excited at 476 nm (upper trace, left-hand axis) compared to absorption spectrum of a electrochemically oxidized poly-**1** (dashed line, right-hand axis). (b) Fit to the PIA spectrum of poly-**1** by sum of four Gaussians: sum of Gaussian peaks (solid line), single Gaussian peaks (dashed lines).

poly-**1** is shown in Figure 5b. 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 agreement with the PIA spectrum of poly-**1** in Figure 5a.

Excitation intensity and modulation frequency dependencies of the PIA signals of poly-**1** are shown in Figure 6. All PIA features exhibit a square-root excitation intensity dependence, suggesting a bimolecular recombination kinetics. As already shown for the modulation frequency dependence of polaronic absorption peaks of different kinds of conjugated polymers, a broad distribution of lifetimes of the charged states is observed. A series of three time constants between ca. 0.1 and 10 ms has to be assumed for best fitting the measured relaxation kinetics.[37]

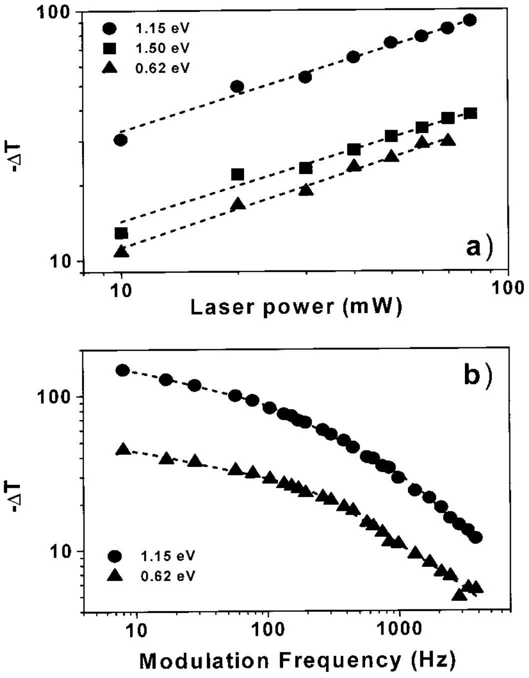

Figure 6. PIA spectrum of poly-**1**: (a) excitation intensity dependence, (b) modulation frequency dependence of PIA signal at 0.62 (triangles), 1.15 (circles), and 1.5 eV (squares).

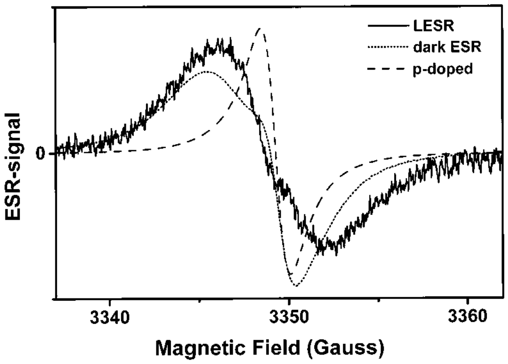

Figure 7. ESR spectra of poly-**1** at 100 K. Dark ESR spectrum (dotted line), LESR spectrum (solid line), and ESR of electrochemically p-doped polymer (dashed line).

ESR spectra of poly-**1** are shown in Figure 7. The polymer films already show a very strong dark ESR signal, consisting of broad lines with *g*-values of 2.0026 and 2.0043. Those could originate from a residual doping on the polymer backbone due to the electropolymerization process. Light-induced ESR gives rise to a single broad line centered at a *g*-value of 2.0029 (Figure 7), but with only 15% of the intensity of the dark signal. The LESR signal may be assigned to an overlap of the two neighboring lines from the TCAQ anion and polymer cation radicals produced by the photoinduced charge transfer. Both TCAQ anions and oligothiophene cations are known to have *g*-factors in the range between 2.0023 and 2.0028.[34,36] A single-line ESR spectrum is observed for an electrochemically oxidized poly-**1** sample (Figure 7). The *g*-factor is 2.0026, close to that observed for radical cations of conjugated polymers, and the line width is narrower by a factor of 2 as compared to that of the light-induced signal.[25,37] The narrowing of ESR line for heavily oxidized conducting polymers has been studied and interpreted as due to motional as well as exchange narrowing of a large number of mobile polarons.[38]

Conclusions

We have prepared electrochemically films of a polymer whose repeating units consist of a bithiophene derivative with a covalently linked TCAQ moiety. This electron donor—acceptor double-cable was investigated for its electrochemical and photophysical properties. Photoinduced charge transfer occurs clearly in this double-cable polymer, as revealed by the features of polarons and TCAQ anion radicals in the PIA and LESR studies. Double-cable polymers, which are a proposed strategy for circumventing the phase separation problem in bulk-heterojunction solar cells, are under investigation for the production of highly efficient photovoltaic devices.

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