

PHOTOINDUCED ELECTRON TRANSFER IN DONOR/ACCEPTOR *DOUBLE-CABLE* POLYMERS

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Abstract

Fullerenes are promising as electron accepting/transporting materials in organic devices. In particular, mixtures of fullerenes and conjugated polymers are attractive for the fabrication of low-cost, large-area flexible solar cells and photodetectors. The preparation of a well structured, ordered fullerene phase in these composite films seems to be crucial for donor-acceptor interactions and to get continuous conducting pathways for the photogenerated electrons. With the so-called "double-cable" polymers, where fullerene units are covalently linked to a polyconjugated chain, the formation of interconnected, continuous donor and acceptor networks should be driven by the primary structure of the polymer. Unwanted phase separation should be avoided with this strategy.

Starting from a novel bithiophene-fulleropyrrolidine dyad we have prepared electrochemically a polythiophene carrying fullerene moieties. Thin solid films of this double-cable polymer have been studied by means of cyclic voltammetry and photoexcited spectroscopy (photoinduced absorption, light induced ESR). The results show that the donor and the acceptor moieties, which are mutually independent in the ground-state, undergo electron transfer upon illumination. Thus, the necessary condition for photoactivity in solar cells is fulfilled.

INTRODUCTION

In the last decade, the properties and potential application of fullerenes and conjugated polymers have been increasingly drawing the attention of academic and industrial research (1, 2). In particular, since the discovery of a photoinduced electron transfer from non-degenerate ground state conjugated polymers to fullerenes, these materials became appealing for the fabrication of inexpensive and flexible photovoltaic devices and photodetectors (3). For efficient devices, the electron and hole transport should be balanced. The most efficient polymeric solar cells today are fabricated using *bulk heterojunctions*, which consist of a p-type conjugated polymer network with a soluble fullerene derivative mixed into it as n-type material (3(c), 4). Photoinduced charge generation, charge recombination and charge transport in these

blends have been extensively investigated (3(c)). It has been shown that the morphology within the active layer strongly affects the photoinduced charge generation and transport in this class of devices. In particular, the rather poor miscibility of the two components causes the separation of fullerene domains, which affects the photoinduced charge generation as well as the electron mobility and, therefore, the overall device's efficiency (4).

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 design *double-cable* polymers and supramolecular structures for photovoltaic devices (5). In this work we report the electrochemical and spectroscopic properties of a novel *double-cable* polymer that has been prepared *via* electropolymerization of the monomer **1**, in which a fulleropyrrolidine is linked to a bithiophene unit through a flexible spacer (Fig. 1). Electrochemically prepared poly-**1** exhibits crucial properties as listed below:

independent electrochemical
as well as optical properties in the ground-state (“*the cables do not short*”);

backbone onto the fulleropyrrolidine unit and photogeneration of free charge carriers.

EXPERIMENTAL

1 will be reported elsewhere (6). Thin films of poly-**1** were electrodeposited potentiodynamically by sweeping the potential between 0 and 1.6 V, at a rate of 100 mV/s, at room temperature and under argon atmosphere. A conventional three-electrode cell was used where 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 the potential values refer to this *quasi*-reference electrode. The electrolyte used for electropolymerization was 0.1 M tetrabutylammo-

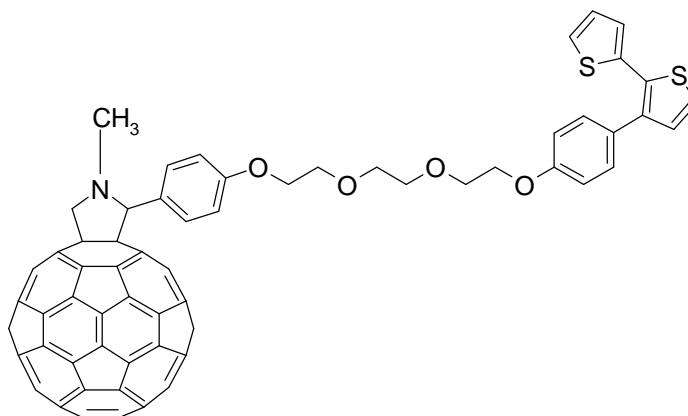
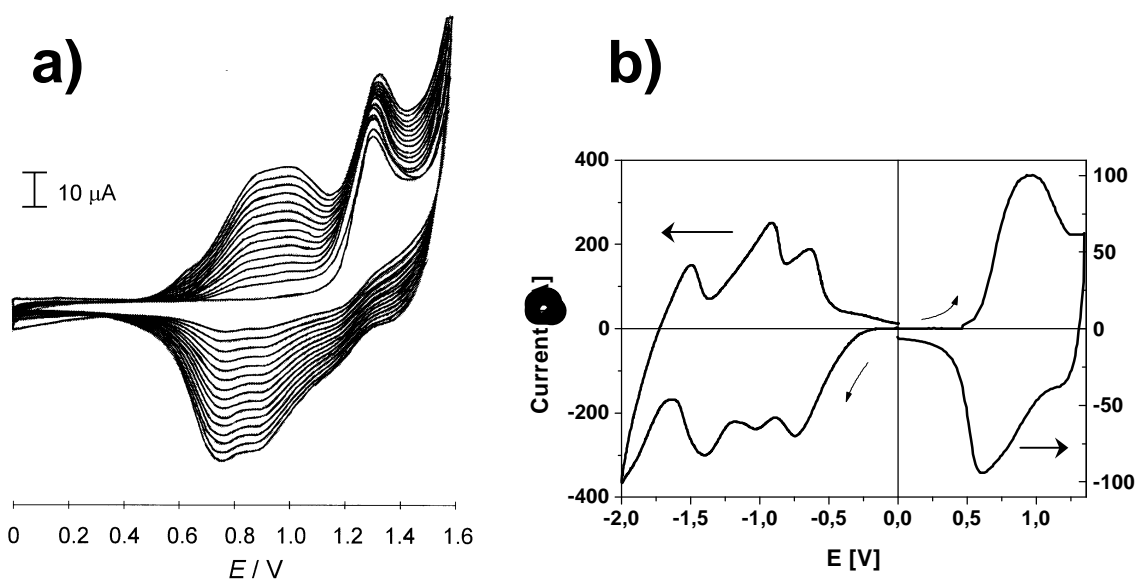


Fig. 1: Chemical structure of the bithiophene-fulleropyrrolidine monomer **1**.

Bu_4NPF_6 , dried under vacuum prior of the experiments) in anhydrous CH_2Cl_2 . After polymerization, the samples were neutralized by applying 0 V until no current flow was observed and rinsed with fresh CH_2Cl_2 . Residual charges in the polymeric films were minimized by repeating this procedure in monomer-free electrolyte medium (0.1 M Bu_4NPF_6 in CH_3CN). Finally, the films were rinsed with CH_3CN and dried by an argon flow. For the cyclic voltammetry (CV) of poly-**1** films in monomer free conditions, the solvent was anhydrous CH_3CN . UV-Vis absorption measurements have been carried out at room temperature by means of a Cary-3 double beam spectrophotometer.

For photoinduced absorption spectra, the line at 476 nm of an Ar^+ laser served as excitation source (40 mW on a 4 mm diameter spot). The pump beam was modulated mechanically at 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). PIA measurements were performed at 100 K.

-**1** films on ITO coated plastic were cut in stripes (10 mm \times 2 mm) and placed into quartz ESR tubes, which were sealed under Ar atmosphere. The 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^+ laser was used for illumination of the polymer films. "Dark" spectra and "light-off" spectra were taken prior and after illumination, in order to account for residual charges due to the polymerization process and persistent light induced charges, respectively. The LESR spectrum was then calculated as "light-on" signal minus "dark" signal.



: (a) Polymerization of **1**; (b) Cyclic voltammograms of poly-**1** in monomer-free conditions. Positive and negative potential regions are scaled individually.

RESULTS AND DISCUSSION

1 (Fig. 2(a)), the oxidation peak at about 1.3 V corresponds to the formation of bithiophene radical-cations, which afford the polythiophene chain via subsequent coupling and re-aromatization steps (7). The potential sweeping leads to the growth of a polymer film attached to the electrode, as can be seen by the new redox wave centered at about 0.9 V and related to the formed poly-**1**. Very similar results were obtained working in different conditions, e.g. by using different solvents and electrodes, as well as by potentiostatic deposition. After dedoping, insoluble, non luminescent yellow-brownish films were obtained. Their UV-Vis absorption spectra show a band extending from about 600 nm to the UV (not shown here).

-1 films in monomer-free electrolyte solution (Fig. 2(b)) shows, scanning to positive potentials, a stable redox system with anodic and cathodic peaks at 0.96 and 0.61 V, which correspond to the oxidation/rereduction (the so-called p-doping/dedoping) of the polythiophene chain. Scanning to negative potentials several waves mainly related to the multiple reduction processes of the fullerene moieties are found (8). Note that there is an irreversible peak at -0.74 V, with unclear origin (6), which has been observed only during the first scan. The electrochemical behavior suggests that both the polythiophene chain and the pendant fullerene moieties of the *double-cable* basically retain their individual electrochemical properties.

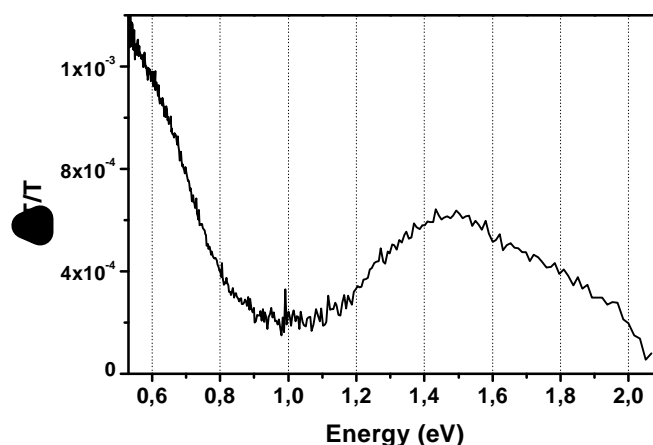


Fig. 3: Photoinduced Vis-NIR absorption of poly-**1**. Excitation at $\lambda = 476$ nm, $T = 100$ K.

-NIR-MIR Absorption

-1 was observed by means of photoinduced absorption (PIA) in the Vis-NIR-MIR. The PIA-MIR spectrum (not shown here) exhibits sub-gap electronic absorption bands with maxima at about 4000

cm^{-1} (0.49 eV) and above 7000 cm^{-1} . We assign these spectral features to photoinduced charged states (widely accepted to be polarons) on the polythiophene

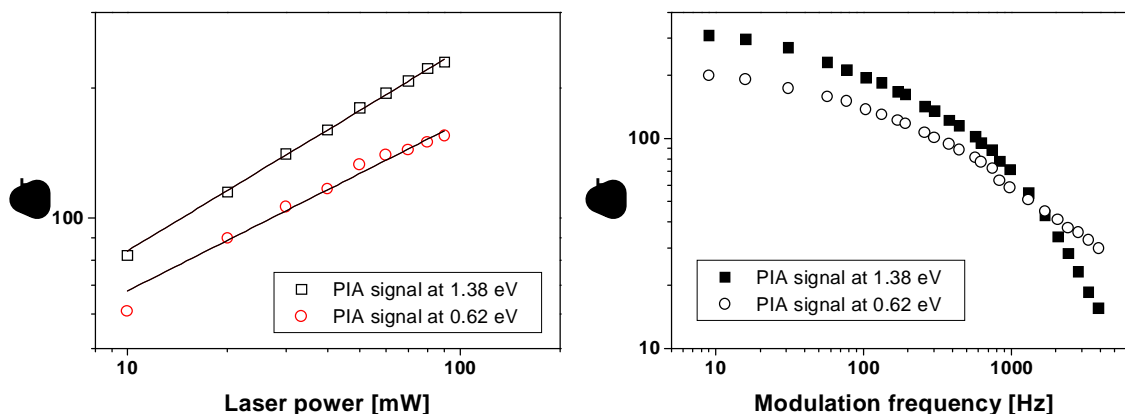


Fig. 4: PIA Vis-NIR. (a) Pump beam intensity dependence; (b) modulation frequency dependence.

of infrared active vibration (IRAV) bands at 1315 , 1128 and 1039 cm^{-1} , which show high correspondence to the typical IRAV bands of positively charged polythiophenes (9). Correspondingly, the sub-gap electronic absorption bands are seen also in the PIA Vis-NIR spectrum (Fig. 3), with maxima at about 1.5 eV and below 0.6 eV . In order to investigate the relaxation kinetics of the charged excitation in a *double-cable* polymer, we have performed intensity and frequency modulation dependence measurements (Fig. 4) (10). Both PIA features, evaluated by the signal measured at 1.38 and 0.62 eV , show a square root excitation intensity dependence, thus indicating bimolecular recombination kinetics as commonly observed in conjugated polymers/fullerene blends. From the modulation frequency dependence, a broad distribution of charged state lifetimes ranging from 0.8 up to 10 ms , is observed. Even though these results prove the photoinduced generation of metastable charged states on the polythiophene backbone, a definitive evidence of a photoinduced electron transfer from the latter to the pendant fullerene moieties is obtained only by ESR, as discussed below.

-1 shows only one line at a g-factor of 2.0022 , which we assign to residual radical-cations formed during the polymerization process (residual p-doping). The light induced ESR spectrum, obtained by subtracting the "dark" ESR signal from the "light-on" signal, is depicted in Figure 5. The spectrum shows the photogeneration of two species with spin $1/2$. The positive polarons on the conjugated backbone maintain a g-factor of 2.0022 , which corroborates the above assignment, while the signal at low g-factor, 2.0004 , is typical of fullerene anions (11). These results prove the occurrence of a photoinduced electron transfer from the conjugate backbone to the fullerene moieties in *double-cable* poly-1.

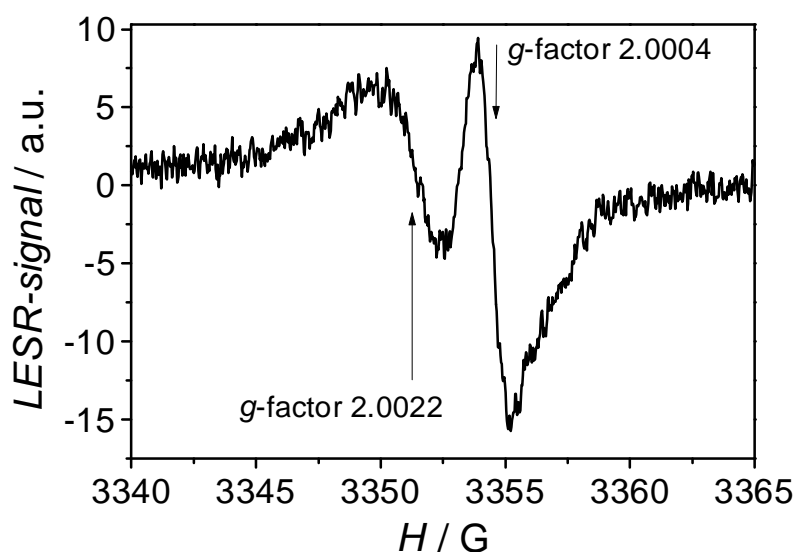


Fig. 5: Light induced ESR spectrum of poly-1. Excitation at $\lambda = 476$ nm; T = 100 K.

CONCLUSION

In conclusion, we have shown that the electrochemical polymerization of a novel fullerene-based bithiophene derivative leads to an intrinsic donor/acceptor *double-cable* polymer that retains the favorable photoactive properties of polythiophene/fullerene blends, i.e. the occurrence of a photoinduced electron transfer. Since in this class of non-composite materials phase separation cannot take place, double-cable polymers are an attractive route for controlling the morphology in thin-film photovoltaic and electronic devices.

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REFERENCES

- Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego (1996).
2. (a) *Handbook of Conducting Polymers*, Skotheim, T. A., Editor, Marcel Dekker, New York (1986); (b) *Handbook of Conducting Polymers*, 2nd edition, Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Editors, Marcel Dekker, New York (1998); (c) *Semiconducting Polymers, Chemistry Physics and Engineering*, G. Hadziioannu and P. F. van Hutten, Editors, Wiley, Weinheim (2000).

3. (a) N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, *Science*, **258**, 1474 (1992); (b) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science*, **270**, 1789 (1995); (c) C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, *Adv. Funct. Mater.*, **11**, 15 (2001); (d) G. Yu, J. Wang, J. McElvain, A. J. Heeger, *Adv. Mater.*, **10**, 1431 (1998).
4. S. E. Shaheen, C. J. Brabec, F. Padinger, T. Fromherz, J. C. Hummelen, N. S. Sariciftci, *Appl. Phys. Lett.*, **78**, 841 (2001).
5. (a) European Community funded R&D project 1998-2000, JOULE III Programme; (b) A. Cravino, G. Zerza, M. Maggini, S. Bucella, M. Svensson, Mats R. Andersson, H. Neugebauer, N. S. Sariciftci, *J. Chem. Soc., Chem. Commun.*, **24**, 2487 (2000); (c) G. Zerza, A. Cravino, H. Neugebauer, N. S. Sariciftci, R. Gómez, J. L. Segura, N. Martín, M. Svensson, M. R. Andersson, *J. Phys. Chem. A*, (2001) in print.
6. A. Cravino et al., manuscript in preparation.
7. (a) G. Zotti in *Handbook of Organic Conductive Molecules and Polymers*, H. S. Nalwa, Editor, Vol. 2, Chapter 4, Wiley, Chichester, (1997); (b) J. Simonet and J. Rault-Berthelot, *Prog. Solid St. Chem.* **21**, 1 (1991).
8. L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, **31**, 593 (1998).
9. See for example: M. Del Zoppo, C. Castiglioni, P. Zuliani, G. Zerbi, in *Handbook of Conducting Polymers*, 2nd edition, T. A. Skotheim, J. R. Reynolds, Editor, Chapter 28, Marcel Dekker, New York, (1986).
10. G. Dellepiane, C. Cuniberti, D. Comoretto, G. F. Musso, G. Figari, A. Piaggi, A. Borghesi, *Phys. Rev. B*, **48**, 7850 (1993).
11. V. Dyakonov, G. Zorinaints, M. C. Scharber, C. J. Brabec, R. A. J. Janssen, J. C. Hummelen, N. S. Sariciftci, *Phys. Rev. B*, **59**, 8019 (1999).