

Electropolymerization and spectroscopic properties of a novel *double-cable* polythiophene with pendant fullerenes for photovoltaic applications

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Abstract

A novel *double-cable* polythiophene carrying fullerene side groups has been prepared electrochemically. Electrochemical and spectroscopic data show that this bipolar material, where phase separation cannot occur, retains the favorable optoelectronic properties of polythiophene/fullerene blends. Excited state spectroscopy reveals clear evidence of a photo-induced electron transfer from the donor cable (polythiophene) to the pendant acceptor cable (fullerene substituents).

Keywords: Polythiophene derivatives, Fullerene derivatives, Electrochemical polymerization, ESR spectroscopy

1. Introduction

The discovery of ultrafast photo-induced electron transfer from non-degenerate groundstate conjugated polymers to C₆₀ [1] has promoted the research on semiconducting polymers based solar cells. By using blends of conjugated polymers and fullerene derivatives, large-area and flexible *interpenetrating network* solar cells have been fabricated [2]. It has been shown that the overall efficiency of these devices is strongly affected by the morphology, e.g. phase separation, within the active film. The use of *double-cable* polymers, systems in which a number of fullerene electron acceptor moieties are covalently bound to the electron donor conjugated polymer backbone,

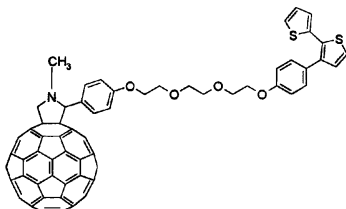


Fig. 1: Chemical structure of the fulleropyrrolidine-bithiophene monomer

appears to be a convenient route towards well defined morphology and donor-acceptor interactions in polymeric solar cells.

In this work we investigated the electrochemical and spectroscopic properties of a novel *double-cable* polymer that has been prepared *via* electropolymerization of the monomer shown in Figure 1, in which a fulleropyrrolidine is linked to a bithiophene unit through a flexible spacer [3]. In particular, the photo-induced electron transfer from the polythiophene backbone to the pendant fullerene moieties will be reported and discussed.

2. Discussion

The cyclic voltammogram (CV) of the monomer in organic electrolyte solutions (Fig. 2) shows an oxidation peak at *ca.* 1.3 V *vs.* Ag/AgCl wire, related to the formation of bithiophene radical-cations. Their coupling leads to the formation of a polymeric material, as can be seen by the growth of the redox wave centered at about 0.9 V with the scan number, which is related to the reversible oxidation/re-reduction of the polythiophene backbone

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(*p*-doping/dedoping). Similar results are obtained by using different solvents, electrodes and electrochemical conditions. In all cases, after dedoping by applying 0 V, smooth yellow-brownish films are obtained. Their UV-Vis absorption spectra show a rather broad band with maximum or shoulder at about 460 nm [4].

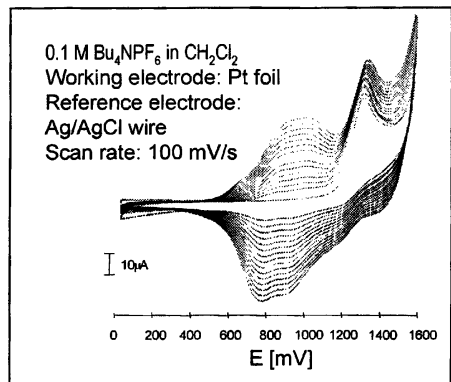


Fig. 2: Polymerization of the bithiophene derivative.

The CV of the polymer in monomer-free electrolyte solution exhibits a stable *p*-doping/dedoping redox system (Fig. 3 (a)), with anodic and cathodic peak maxima at about 0.96 and 0.61 V, respectively. In the cathodic region (Fig. 3 (b)), several redox waves, ascribed to the multiple reversible reduction steps of the fullerene moiety [5], are observed.

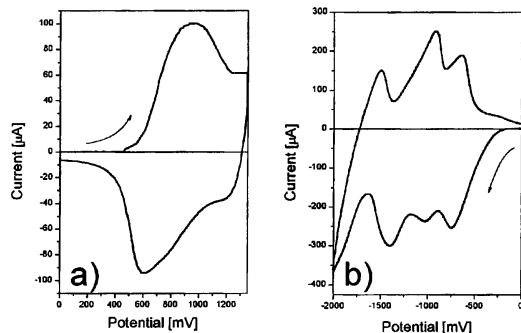


Fig. 3: CVs of the polymer in monomer-free electrolyte (0.1 M Bu₄NPF₆ in CH₃CN). Working electrode: Pt foil; reference electrode: Ag/AgCl wire. Scan rate: 100 mV/s. a) anodic regime; b) cathodic regime.

These results indicate that both polythiophene and fullerene moieties mostly retain their individual electrochemical properties (e.g. the donor and the acceptor do not undergo electronic groundstate interactions).

The polymer has been investigated by means of several spectroscopic techniques in the neutral and in the doped or photo-excited states. [4] Our results confirm that the polythiophene/fullerene *double-cable* retains the favorable optoelectronic properties of physically mixed polythiophenes and fullerenes. The photogeneration of charged states, which is crucial for photovoltaic

applications, has been revealed by the observation of both sub-gap electronic absorption and infrared active vibrational bands (IRAVs) in the photo-induced UV-Vis and IR absorption spectra. [4]

We have further investigated the photoexcited polymer by light induced electron spin resonance (LESR) measurements. The LESR spectrum, obtained by subtracting the dark ESR signal from the light on signal, is depicted in Figure 4. The spectrum shows the generation of two photo-excitations with spin 1/2. The positive polarons on the conjugated backbone have a *g*-factor of 2.0022, while the signal at *g*-factor 2.0004 is typical of the low *g*-value fullerene radical-anions. The results prove the occurrence of a photo-induced electron transfer from the conjugated backbone to the fullerene moieties.

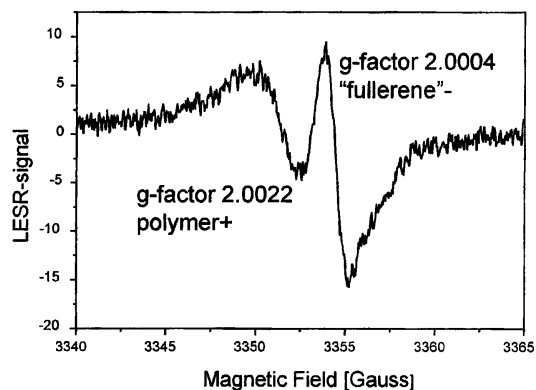


Fig. 4: LESR (light on - light off) spectrum of the polymer on ITO coated plastic foil. Excitation at $\lambda = 488$ nm (20 mW/cm²); T = 77 K.

In conclusion, we have shown that the electrochemical polymerization of a novel fullerene-based bithiophene derivative leads to a *double-cable* polymer that retains the properties of polythiophene/fullerene blends, including the occurrence of photo-induced electron transfer. Since phase separation cannot take place in this non-composite material, *double-cable* polymers are confirmed to be attractive for photovoltaic applications.

This work was supported by the European Commission JOULE III Programme (Contract No.: JOR3CT980206).

C. J. Brabec is gratefully acknowledged for the helpful discussions

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