

Fullerenes as Functional Moieties in Conjugated Polymers: Towards Donor – Acceptor Double Cable Polymeric Materials

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Abstract. The properties of a novel poly(bithiophene-fulleropyrrolidine), which belongs to the class of so called “double cable” polymers, are studied. The polymer consists of covalently linked electron acceptor moieties to an electron donor polymeric backbone. Photoinduced charge transfer is studied by photoinduced absorption spectroscopy and by light induced ESR spectroscopy.

INTRODUCTION

The properties of plastic solar cells using the “interpenetrating network” concept are heavily influenced by the morphology of the mixture of the photoactive compounds [1]. Due to limited miscibility, phase separation can occur. A convenient and elegant way to overcome these problems seems to be the preparation of covalently linked electron acceptor moieties to electron donor polymeric chains (“double cables”). The double cable polymers have to fulfill several requirements to be used in photovoltaic devices: 1) No ground state interaction. In dark, the electron donor and acceptor part should retain their individual properties. 2) Photoinduced charge transfer. 3) Good device characteristics. In the present paper, the properties of a novel poly(bithiophene-fulleropyrrolidine) (structure shown in Fig. 1), which belongs to the class of double cable polymers, are shown. The polymer is electropolymerized from monomer solution and forms an insoluble film on the electrode, thus preventing the construction of a photovoltaic device. Nevertheless, from the optoelectronic properties, the polymer can be considered as a prototype for the synthesis of similar double cable polymers with better processability.

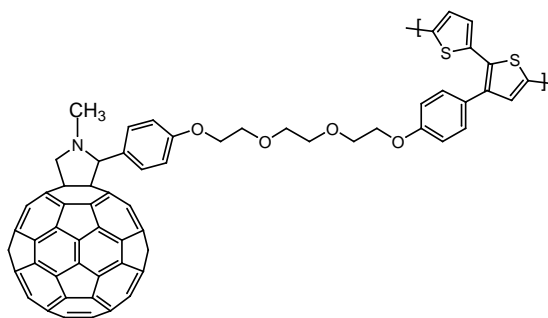


FIGURE 1. Structure of poly(bithiophene-fulleropyrrolidine)

EXPERIMENTAL

The preparation of the monomer, bithiophene-fulleropyrrolidine, has been described in a previous paper [2]. The electropolymerization was performed in a conventional three-electrode cell with a suitable working electrode, Pt foil as counter electrode and Ag/AgCl wire as quasi reference electrode (-0.44 V vs. ferrocene) by repetitive sweeping the electrode potential between 0 and $+1.6$ V in an electrolyte solution containing the monomer and 0.1 M Bu_4NPF_6 in CH_2Cl_2 . Cyclic voltammograms (CVs) of the polymer were measured in a monomer free solution of the same electrolyte in CH_3CN . Photoinduced absorption (PIA) in the Vis-NIR was measured with the polymer prepared on the surface of an ITO/glass substrate with chopper modulated excitation at 467 nm (Ar^+ -laser) and recording the absorption changes using a lock-in-amplifier. In the IR, PIA changes were recorded from the absorption differences light-on – light-off in consecutive scans using a Bruker IFS 66/S FTIR spectrometer. In both spectral ranges, PIA was measured at LN_2 temperature. For light induced ESR (LESr) spectroscopy, the polymer was prepared on ITO coated plastic stripes, mounted in the high-Q-cavity of an X-band ESR spectrometer Bruker EMX, cooled to LN_2 temperature, and illuminated at 476 nm. LESr spectra were calculated by subtracting the dark signal from the light-on signal.

RESULTS AND DISCUSSION

Cyclic voltammetry

The CV of the polymer is shown in Fig. 2. In the positive region one redox wave, corresponding to the p-doping/dedoping of the polythiophene backbone [3], is seen at about $+0.75$ V. In the negative region several waves, mainly related to the multiple reduction of the fullerene moieties [4], are found. From the cyclovoltammetric response, both electron donor (polythiophene backbone) and acceptor (fullerene moiety) substantially retain their individual electrochemical properties.

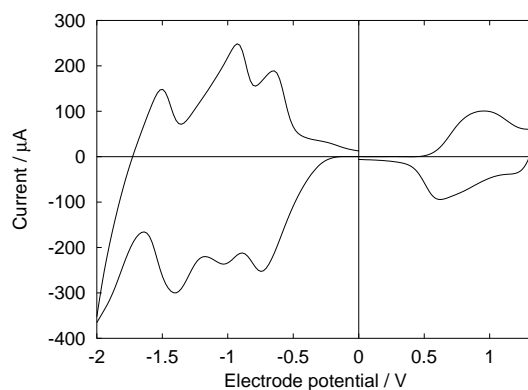


FIGURE 2. Cyclic voltammogram

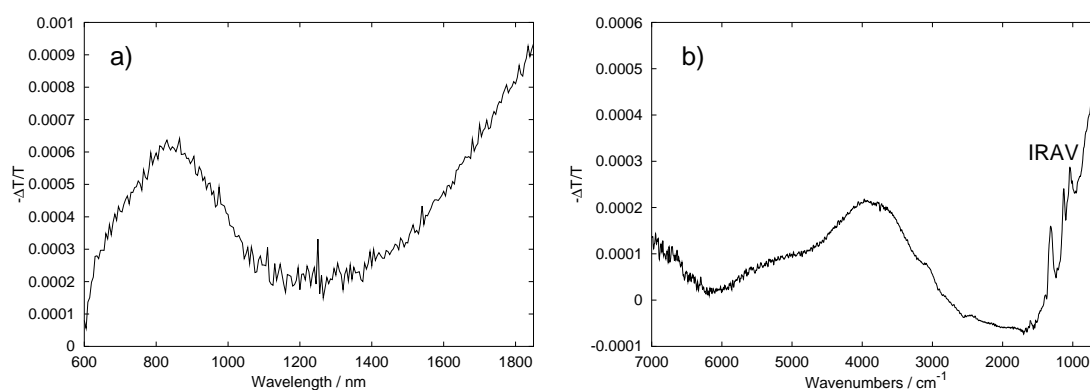


FIGURE 3. Photoinduced absorption in the Vis-NIR region (a) and IR region (b)

Photoinduced absorption spectroscopy

Photoinduced absorption spectra in the Vis-NIR and the IR spectral range are shown in Fig. 3a and b, respectively. In the Vis-NIR range, two broad photoinduced absorption bands with maxima at 850 nm and above 1800 nm are found. In the IR, the maximum of this lower energy band can be seen at 4000 cm^{-1} . In addition, infrared active vibration (IRAV) bands occur at 1315, 1128 and 1039 cm^{-1} . The spectral features correspond to positive charge carriers (p-polarons) on the polythiophene backbone [5].

Light induced ESR spectroscopy

In Fig. 4, the difference light-on – dark ESR signal of the polymer is shown. Two spin signals at different fields, separated by about 3 Gauss, are found. The two signals correspond to the photoinduced occurrence of p-polarons on the polythiophene

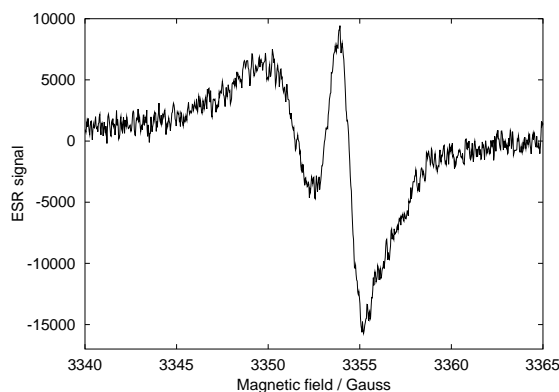


FIGURE 4. Light induced ESR spectrum (light-on – dark)

backbone and to negative charges on the fullerene moiety [6].

CONCLUSION

The cyclovoltammetric and spectroscopic results prove that the electron donor and acceptor parts of poly(bithiophene-fulleropyrrolidine) retain their individual electrochemical behavior. Under illumination a photoinduced electron transfer occurs. With these properties, the polymer can be considered as a prototype for similar substances with possible application in plastic solar cells and other optoelectronic devices like photodetectors.

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