

Multiple reduction states with different conductivities of polybenzimidazobenzophenanthroline (BBL) studied with infrared spectroelectrochemistry

Teketel Yohannes^a, H. Neugebauer^{a,*}, S.A. Jenekhe^b, N.S. Sariciftci^a

^aDepartment of Physical Chemistry, Johannes Kepler University Linz, Altenbergerstraße 69, A-4040 Linz, Austria

^bDepartment of Chemical Engineering, University of Rochester, Rochester, NY 14627-0166, USA

Abstract

Polybenzimidazobenzophenanthroline (BBL), a conjugated ladder polymer, has interesting features such as n-type conductivity, good photoconductivity, large nonlinear optical properties and the highest electron affinity among known n-type semiconducting polymers, which makes the material an interesting candidate for optoelectronic applications. BBL can be reduced (n-doped) electrochemically and shows various reduction states. We report results on FTIR spectroelectrochemical studies of the reduction reactions using ATR-FTIR spectroscopy. The spectra were recorded in a three electrode spectroelectrochemical cell in situ during continuous potential cycling of a BBL coated germanium reflection element in contact with the electrolyte solution under applied potential. In contrast to most of the other conjugated polymers, the polymer shows four reversible redox reactions during n-doping, corresponding to five different forms of BBL. From the spectral response, a reduction scheme insulator to conductor to insulator to conductor to insulator was found. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Conjugated polymers are intrinsically insulators in their undoped, pristine state due to large bandgap (E_g larger than 2 eV). Upon doping, however, mobile quasi-particles like solitons and/or polarons are created in the π -electron chain and thus, the conductivity jumps orders of magnitude to metallic values [1,2]. BBL (Fig. 1) is conjugated and supports mobile quasi-particles. Experimental and theoretical studies on structural changes and redox mechanisms of BBL during n-doping have been reported in the literature [3,4]. Wilbourn and Murray [3,5] observed that BBL shows two main redox waves in the cyclic voltammogram and two maxima in conductivity which differ by about ten times during n-doping (reduction). The two maxima observed in the in situ conductivity measurements cannot be explained by just two electrochemical reduction processes. In this work we present in situ spectroscopic evidence for the existence of four clearly distinct and spectroscopically well resolved processes with various forms and conductivities

during electrochemical reduction (n-doping) of BBL solid films.

2. Experimental

Tetrabutylammonium perchlorate Bu_4NClO_4 , (Fluka) was dried under vacuum at 130°C for 2 h before use. Water free acetonitrile (Merck) was stored over molecular sieve prior to measurement. Great precaution was taken in order to protect the electrolyte from atmospheric oxygen and water throughout the experiments. The chemical synthesis of BBL was reported elsewhere [6]. Thin films were prepared by spin coating from a solution of 0.8% BBL in gallium chloride/nitromethane on to glass substrates in laboratory atmosphere. The resulting polymer/Lewis acid complex film was washed with deionized water several times and subsequently placed in fresh deionized water overnight to remove the Lewis acid completely. Using a pair of tweezers the film was peeled off while still wet yielding a film floating on the water surface. The free standing film was then transferred on to a germanium reflection element covered with thin layer of evaporated platinum. The resulting solid film was dried in a vacuum oven for 6 h at 80°C.

* Corresponding author. Tel.: +43-732-2468-8766; fax: +43-732-2468-8770.

E-mail address: helmut.neugebauer@jk.uni-linz.ac.at (H. Neugebauer).

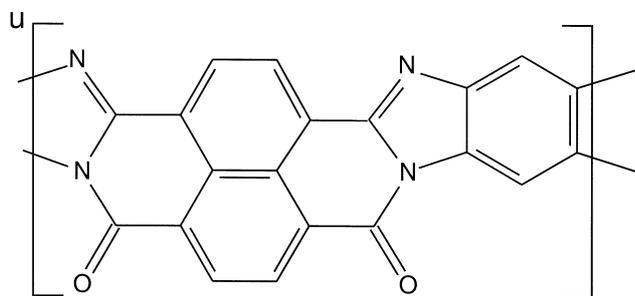


Fig. 1. The chemical structure.

The in situ ATR-FTIR spectroelectrochemical measurements (see [7,8] for more detail) were carried out in a three-electrode spectroelectrochemical cell with a germanium working electrode, a platinum foil counter electrode, and a silver wire coated with silver chloride reference electrode. The electrolyte for the in situ spectroelectrochemical experiments was 0.1 M Bu_4NClO_4 in acetonitrile. The spectroelectrochemical cell was sealed with paraffin to prevent leakage of the electrolyte solution. The cell was placed in the FTIR cell compartment and the instrument was purged with nitrogen continuously throughout the experiment. A continuous flow system for the electrolyte was used, where the electrolyte (placed in an external container where it was blanketed with argon after purging for few minutes) flows in and out of the electrochemical cell using teflon plastic tubes. To obtain n-doping, a potential scan between 0.6 and -2.0 V with a scan rate of 5 mV/s using a sweep generator Prodis 1/14 I and a potentiostat Jaissle Model 1002 T-NC was applied to the film. The cyclic voltammogram was recorded on an x - y recorder. During the scan, in situ FTIR spectra were recorded with a resolution of 4 cm^{-1} using a Bruker IFS 66S

spectrometer with an MCT detector. To obtain specific spectral changes during individual electrochemical reaction processes a spectrum just before the considered reaction was chosen as a reference spectrum. The subsequent spectra were related to the spectrum, showing only the spectral differences to this reference state. The spectra are plotted as $\Delta(-\log(T_{\text{ATR}}))$, where T_{ATR} is transmission in ATR geometry. For each spectrum 32 interferograms were coadded covering a range of about 90 mV in the cyclic voltammogram. The potential value given for each reference spectrum in this paper corresponds to the mean value of this range.

3. Results and discussion

The cyclic voltammetric response (CV) for the reduction (n-doping) and reoxidation (undoping) processes of BBL film on Pt and Ge electrodes in tetrabutylammonium perchlorate containing electrolyte are shown in Fig. 2. From the CVs four distinct and clearly observable reduction waves were obtained at $E_A \approx -0.6$ V (shoulder), $E_B \approx -0.9$ V (peak), $E_C \approx -1.1$ V (peak), and $E_D \approx -1.2$ V (shoulder) using Ge working electrode and at $E_A \approx -0.52$ V (shoulder), $E_B \approx -0.82$ V (peak), $E_C \approx -1.0$ V (peak), and $E_D \approx -1.1$ V (shoulder) using Pt working electrode. During reoxidation, the corresponding waves were found at $E_{D'} \approx -1.0$ V (shoulder), $E_{C'} \approx -0.89$ V (peak), $E_{B'} \approx -0.61$ V (peak), and $E_{A'} \approx -0.38$ V (shoulder) using Ge working electrode and at $E_{D'} \approx -1.05$ V (shoulder), $E_{C'} \approx -0.87$ V (peak), $E_{B'} \approx -0.66$ V (peak), and $E_{A'} \approx -0.45$ V (shoulder) using Pt working electrode. The differences in the position of the reduction and reoxidation waves at the two different electrodes is attributed to the differences in electrode material, reference electrode,

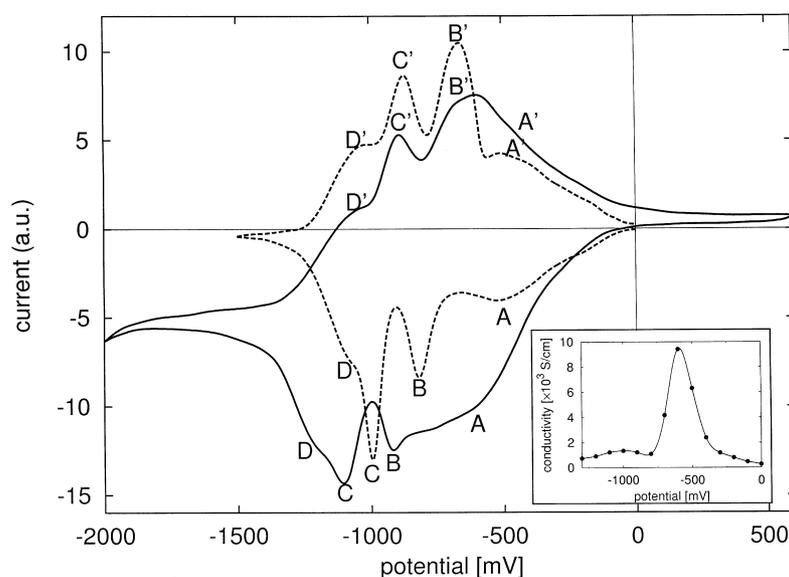


Fig. 2. CV for n-doping (reduction) of BBL. Solid line: on Ge working electrode; Ag/AgCl reference electrode; scan rate 5 mV/s. Broken line: on Pt foil working electrode; SCE reference electrode; scan rate 2 mV/s. Inset: conductivity measurements of a BBL film in 0.1 M Bu_4NClO_4 -acetonitrile electrolyte solution. Data taken from the literature [5].

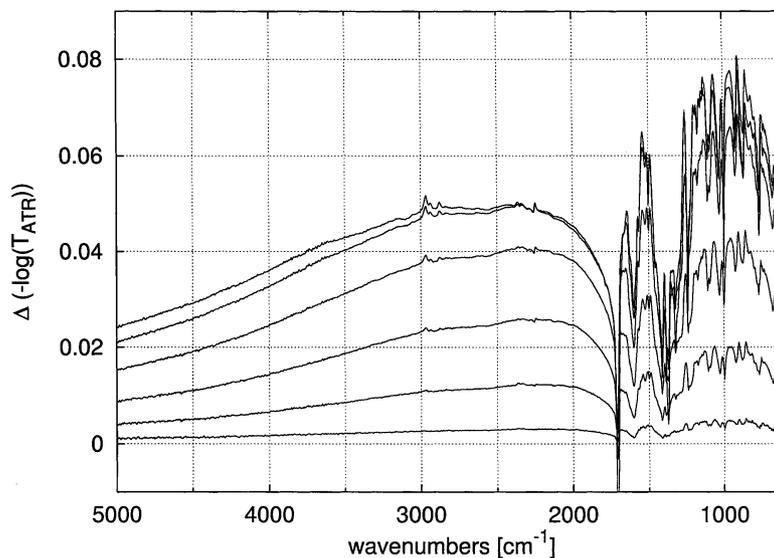


Fig. 3. Difference in situ ATR-FTIR absorption spectra during reduction process A for potentials from -95 to -618 mV. Reference spectrum taken around -48 mV.

and scan rate. Wilbourn and Murray reported that BBL shows only two main redox waves during n-doping (reduction) [3] in contrary to the four waves obtained in this study. In another paper, Wilbourn and Murray [5] studied how the conductivity varies with potential during electrochemical n-doping of the film and reported that the BBL conductivity depends on the electrochemical doping potential and displays two maxima that differ by about 10 times in conductivity (see inset in Fig. 2). The two consecutive insulator \rightarrow metal transitions cannot be explained by just two electrochemical doping reactions.

Evidence for the existence of clearly distinct and spectroscopically well resolved processes during electrochemical

reduction (n-doping) of BBL solid films with different states is obtained with the help of in situ ATR-FTIR spectroelectrochemical studies. Fig. 3 shows the difference in situ FTIR absorption spectra of BBL during the first reduction process (wave A). As can be seen from Fig. 3, a broad absorption band with absorption maximum above 2000 cm^{-1} appears. This broad absorption comes from an electronic transition of the polaronic states [9], and is correlated with the increase in the conductivity where the neutral insulating polymer (substance I) is transformed to an electrically conducting polymer (substance II). Usually, vibrational spectra of conjugated polymers show strong unusual effects during doping (redox) processes due to

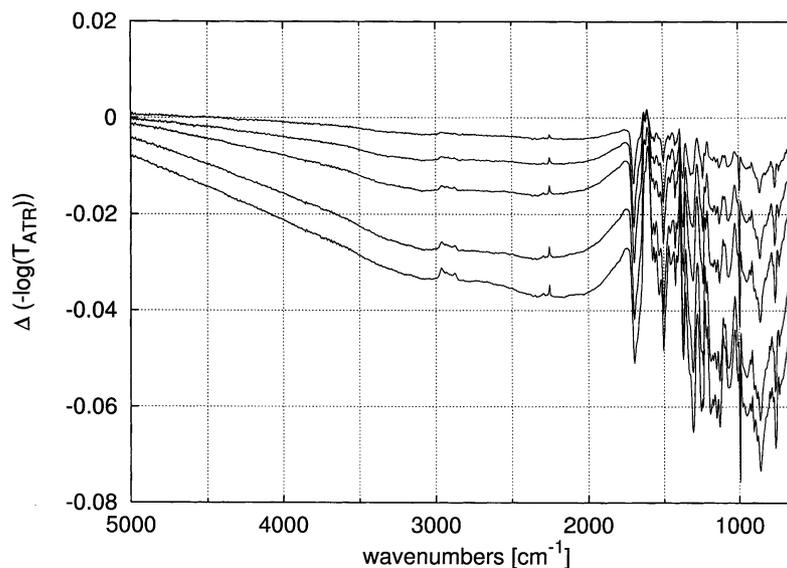


Fig. 4. Difference in situ ATR-FTIR absorption spectra during reduction process B for potentials from -618 to -1039 mV. Reference spectrum taken around -572 mV.

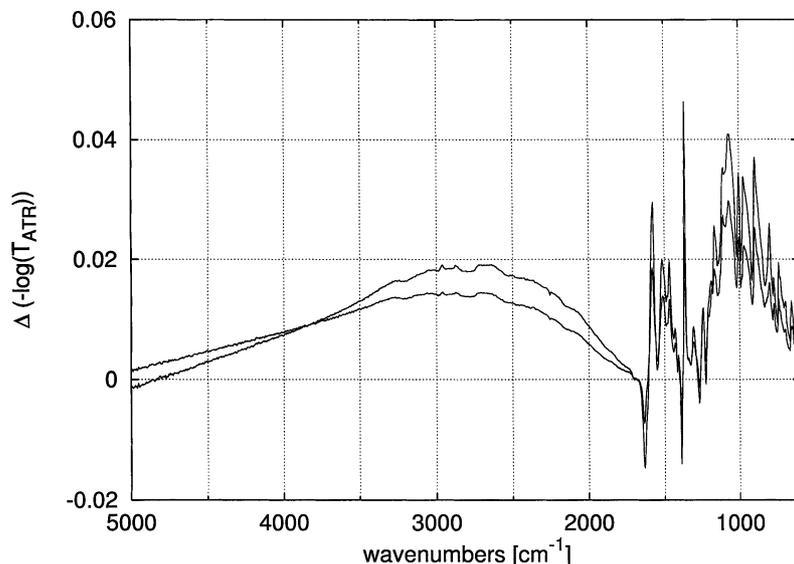


Fig. 5. Difference in situ ATR-FTIR absorption spectra during reduction process C for potential from -1039 to -1206 mV. Reference spectrum taken around -996 mV.

strong electron–phonon coupling [9]. Upon doping of BBL the infrared spectrum is dominated by new very strong doping induced infrared bands called infrared active vibration (IRAV) bands similar to other conjugated polymers. These growing IRAV bands also indicate the formation of a new substance II.

Fig. 4 shows the difference in situ spectra during the second reduction process (wave B). The broad negative band at high energy indicates the formation of a new substance III with decrease in conductivity. Further, decrease in the intensities of substance I and decrease in intensities of substance II together with an increase of sharper vibrational

bands are observed (formation of substance III). The sharpness of the vibrational bands is again in agreement to the conductivity measurements mentioned above.

Fig. 5 depicts the difference in situ FTIR spectra during the third reduction process (wave C). Increase in the broad band above 2000 cm^{-1} (but smaller than in the first reduction process A) was noticed with increase in applied reduction potential indicating again the increase in conductivity of the film. This smaller electronic band increase observed in this step is in agreement with the small increase in conductivity (inset in Fig. 2). The IRAV bands in the third reduction process C show lower intensities compared to

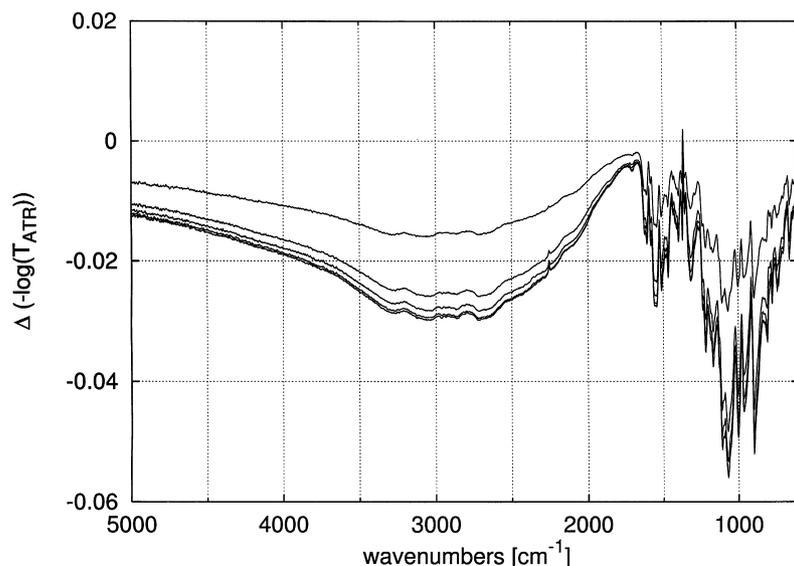
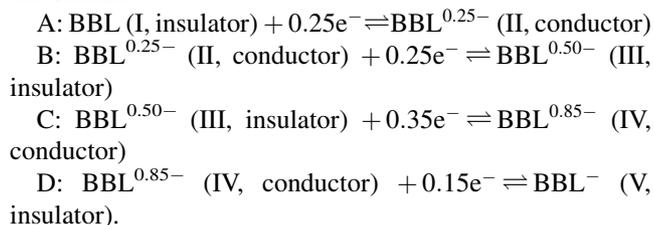


Fig. 6. Difference in situ ATR-FTIR absorption spectra during reduction process D for potential from -1206 to -1634 mV. Reference spectrum taken around -1164 mV.

IRAV bands in the first reduction process A. In addition, the bands are sharper than process A. The lower intensities and the sharper IRAV bands indicate that the delocalization of the positive charges on the chain is rather low in substance IV as compared to substance II.

In Fig. 6, the spectra for the fourth reduction process (wave D) are shown. A decrease in the electronic band at high energy is observed with increasing in doping level. This is again an indication of the decrease in the conductivity of the film with increase in the reduction potential. Decrease in the vibrational bands of substance IV and increase in few sharp bands are observed for substance V. Again this is in agreement with the conductivity measurement.

From the in situ FTIR measurements, one can clearly see that there is transition of different states from insulator \rightarrow conductor \rightarrow insulator \rightarrow conductor \rightarrow insulator when going in the direction from positive to negative potentials. Exactly reverse processes are found when going back from negative to positive potentials, where the difference spectra obtained during the reoxidation processes (waves D'–A') reverse the spectra of the corresponding reduction processes (waves A–D). These four processes are given in the following reaction scheme (in that scheme "BBL" refers to one repetitive unit in the polymer chain). The overall absolute charge during the reduction process was determined with coulometric assay to be equivalent to a consumption of one electron per BBL monomer unit [3]. The exact determination of the charges involved in the individual reduction steps is hindered by the overlapping peaks, but estimated from the CV on Pt electrode as shown in the scheme.



4. Conclusion

Four spectroscopically well resolved redox processes of BBL with different conductivities were found during electrochemical reduction reactions in correlation with the in situ electrical conductivity [5]. As such, this is the only conjugated polymer known with four consecutive redox reactions on the main chain. Conjugated polymers with four consecutive redox reactions on the main chain during n-doping are important candidates for molecular donor/acceptor systems.

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