

In situ UV-VIS-NIR and Raman spectroelectrochemical studies of the conjugated ladder polymer polybenzimidazobenzophenanthroline (BBL)

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Abstract

In situ UV-VIS-NIR and Raman spectroelectrochemical studies of polybenzimidazobenzophenanthroline (BBL), a conjugated ladder polymer, are reported. BBL films were reduced potentiostatically in spectroelectrochemical cells suitable for *in situ* UV-VIS-NIR and *in situ* Raman spectroscopy. The polymer shows four reversible reduction processes during *n*-doping in contrast to most of the other conjugated polymers. The spectral changes, obtained *in situ* during the individual processes, are correlated with *in situ* ATR-FTIR spectroelectrochemical measurements.

Keywords: Polybenzimidazobenzophenanthroline (BBL), Ladder polymer, Conducting polymer, *n*-doping, Spectroelectrochemistry

1. Introduction

Spectroelectrochemical techniques have been used to study doping induced reactions in conjugated polymers [1–6]. These techniques are fast and sensitive and are used to probe structural changes and electronic band modifications during doping reactions. The experiments can be carried out *in situ* during applied electrode potential and simultaneously monitoring the spectroscopic changes.

The conjugated polymer polybenzimidazobenzophenanthroline (BBL) is a member of the structurally diverse class of materials called ladder polymers, which are double-stranded, highly conjugated macromolecules with rigid chain structure. Here, we report *in situ* UV-VIS-NIR and Raman spectroelectrochemical results of reduction reactions (*n*-doping) of BBL solid film.

2. Experimental

The chemical synthesis of BBL was reported elsewhere [7]. Thin films were prepared by spin coating from a solution of 0.8 % BBL in gallium chloride/nitromethane onto 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 onto indium doped tin-oxide (ITO) coated glass. The resulting solid film was dried in a vacuum oven for 6 hours at 80°C.

The *in situ* UV-VIS-NIR and Raman spectroelectrochemical measurements were carried out with a three-electrode conventional spectroelectrochemical cell containing ITO-coated glass working electrode, a platinum foil counter electrode, and a SCE reference electrode. The films were *n*-doped potentiostatically during which the *in situ* UV-VIS-NIR and Raman spectra were recorded at room temperature keeping the sample under vacuum. The Raman spectra were obtained with a resolution of 4 cm⁻¹ using a Bruker IFS66+FRA106 FT spectrometer with laser excitation wavelength of 514 nm. The *in situ* UV-VIS-NIR absorption spectra were recorded using a Cary 2400 spectrophotometer.

3. Results and Discussion

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In situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopic evidence for the existence of four distinct and spectroscopically well resolved redox processes during electrochemical reduction of BBL solid films (*n*-doping) have been reported [8]. This result was in correlation with the *in situ* electrical conductivity data [9].

In addition to *in situ* ATR-FTIR spectra, Raman spectra are important for the understanding of vibrational properties and behaviours of infrared active vibration (IRAV) bands in conjugated systems. *In situ* Raman spectra of BBL were measured during the reduction reactions with excitation at 514 nm. The spectra of the various reduction states are shown in Fig. 1. The Raman spectrum of the neutral BBL film (spectrum 1) in contact with the electrolyte solution consists of five main bands at 1597, 1539, 1389, 1282 and 926 cm^{-1} (the band at 926 cm^{-1} comes from the electrolyte). The four reduction processes observed in the *in situ* ATR-FTIR spectroelectrochemical studies [8] were also distinguished from the *in situ* Raman spectra of the BBL films. A decrease of the Raman bands (spectra 2 and 3) corresponds with the first process A. As the applied potential decreases, additional bands at 1627 cm^{-1} (as a shoulder) and at 1125 cm^{-1} start to appear and the band at 1389 cm^{-1} shifts to 1360 cm^{-1} (spectrum 6, process B). By further decrease of the potential, sharp bands at 1627, 1346 and 1258 cm^{-1} appear (spectra 7–9, process C). These main features start decreasing at an applied potential more negative than -1340 mV (not shown in Fig. 1, process D).

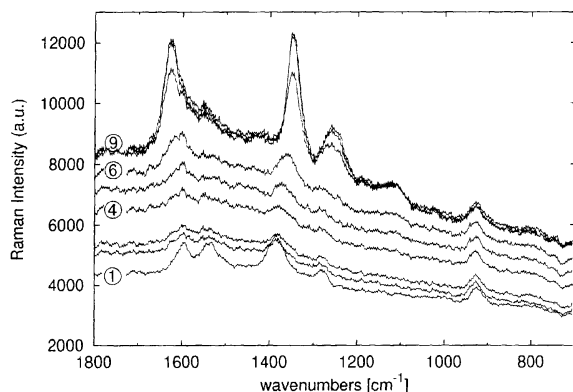


Fig. 1. *In situ* Raman spectra of BBL during reduction (*n*-doping) at various reduction potentials. 1: 0 mV, 2: -300 mV, 3: -430 mV, 4: -560 mV, 5: -690 mV, 6: -820 mV, 7: -950 mV, 8: -1080 mV, 9: -1210 mV. Excitation wavelength at 514 nm.

The *in situ* Raman spectroelectrochemical results can be correlated with *in situ* UV-VIS-NIR optical absorption spectroelectrochemical measurements. Fig. 2 shows *in situ* UV-VIS-NIR absorption spectra at different doping potentials. The wavelength used for the Raman excitation (514 nm) is indicated with asterisk in the figure. The optical absorption band at 571 nm, assigned to the $\pi \rightarrow \pi^*$

transition, starts decreasing continuously as the doping proceeds while new bands appear. The decrease in the Raman bands of the neutral BBL film in process A corresponds to a decrease in the optical absorption band at 571 nm since the Raman excitation energy is partly in resonance with this absorption. Due to resonance, the strong Raman band increase in process C can be correlated to an increase in the optical absorption at 510 nm (shoulder on band at 480 nm). The three processes A, B and C can also be seen by isosbestic points in the spectra. No isosbestic point for D was found, probably due to very small spectral changes in the potential range studied.

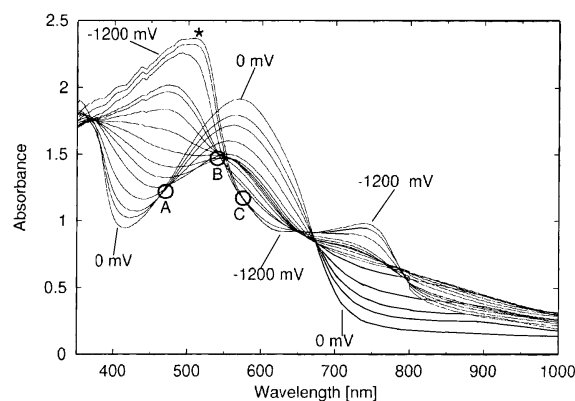


Fig. 2. *In situ* UV-VIS-NIR absorption spectra of BBL during *n*-doping at various reduction potentials. Isosbestic points are marked with A, B and C.

4. Conclusion

In situ UV-VIS-NIR and Raman spectroelectrochemical studies of BBL confirmed the existence of four distinct redox processes with different conductivities obtained by *in situ* ATR-FTIR spectroelectrochemical studies. To our knowledge, there are no reports on conjugated polymers with four consecutive redox reactions on the main chain during *n*-doping.

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