Electrochemically- and Photo-Induced IR Absorption of Low Band-Gap Polydithienothiophenes: a Comparative Study

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ABSTRACT

Poly(dithieno[3,4-b:3',4'-d]thiophene) (pDTT1), *poly*(dithieno[3,4-b:3',2'-d]thiophene (pDTT2) and *poly*(dithieno[3,4-b:2',3'-d]thiophene) (pDTT3) are low band-gap polymers that undergo both *p*- (oxidation) and *n*- (reduction) type electrochemical reversible doping in organic electrolytes. In this work we report on the *in-situ* IR spectroscopic characterization of both doping types using attenuated total reflection (ATR) FTIR spectroelectrochemistry. Thin polymer films were prepared on Ge reflection elements by electrosynthesis. During electrochemical potential cycling experiments in a spectroelectrochemical cell, the evolution of infrared active vibrational (IRAV) modes, correlated with the generation of charge within the polymer chain, was studied. In addition to electrochemical doping, the polymers exhibit also charged excitations by photodoping. FTIR spectra recorded by illumination/dark cycles show photoinduced IRAV bands which are similar to those found for the electrochemically *p*-doped materials. The infrared spectroscopic results are compared with Raman spectra of the neutral polymers. The relationship between vibrational properties and structure of the polymers is discussed in terms of different contribution of the π-electrons within the repeating units to the electronic structure of the conjugated backbone.

INTRODUCTION

In the field of conjugated polymers (CPs), vibrational spectroscopy is twofold important. Due to the strong electron-phonon coupling that characterize these low dimensional systems, in both their neutral and doped conductive states, vibrational spectra give information not only on the molecular geometry, as usual, but also on the electronic properties of the polymers [1, 2]. The combination of electrochemical techniques and IR vibrational spectroscopy provides a powerful tool for the investigation of doping induced structural and electronic modifications in CPs [3].

By means of *in-situ* ATR-FTIR spectroelectrochemistry we have studied the doping induced evolution of IRAV bands during both electrochemical oxidation and reduction of low band-gap polydithienothiophenes (pDTTs), whose chemical structures and band-gap values are shown in figure 1(a) [4]. These polymers consist of repeating units composed of three fused thiophene rings, with different types of fusion. The pDTTs can be regarded as polythiophene derivatives: the electronic properties of the

"polythiophene-like" chain (sketched by bold bonds in figure 1(a)) are strongly affected by the presence of the other two fused rings (thienothiophene moiety) of the monomer. As shown in the inset of figure 1(a), the aromatic moiety fused to the ring that lies in the backbone forces "quinoidal" character along the polymer chain so that the increased inter-rings delocalization of the π-electrons reduces the polymer band-gap [5].
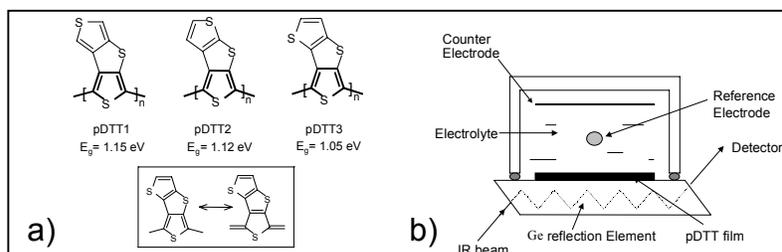

Figure 1: (a) Chemical structures and band gap values of pDTT1, pDTT2 and pDTT3; (b) Cell for the *in-situ* ATR-FTIR spectroelectrochemistry.

According to this picture, pDTTs have band-gaps that decrease with increasing of the aromaticity of the thienothiophene fused moiety [6]. Data from *in-situ* ATR-FTIR spectroelectrochemistry give further evidence for the strong influence of the different fused moieties to the "polythiophene-like" pDTTs chain properties. In addition, we confirm these results by the study of photodoping processes and by recording Raman spectra of the neutral polymers, using several excitation wavelengths (both off- and resonance with the π-π^* transition).

EXPERIMENTAL

The polymer films were electrosynthesized using the three electrodes spectroelectrochemical cell shown in figure 1(b). The working electrode consisted of a germanium reflection element coated with a thin evaporated layer of platinum. As counter and reference electrode, a platinum foil and a Ag/AgCl wire electrode were used, respectively. The electrochemical equipment consisted of a potentiostat (Jaissle 1002T-NC), a sweep generator (Prodis 1/14I) and an X-Y recorder (Rikadenki RY-PIA). For the polymerizations and for the in-situ spectroelectrochemical measurements, the electrolyte was 0.1 M tetrabutylammoniumhexafluorophosphate (TBAPF6) (dried at 180°C under vacuum prior the use) in dry acetonitrile. The electrolyte solutions were prepared and kept under argon flow to exclude moisture and oxygen during the electrochemical processes. The monomers, synthesized as reported in the literature [7], were dissolved into the electrolyte solution in a dry argon box using shielded glassware and then transferred to the spectroelectrochemical cell via syringe. After polymerization, the cell was carefully washed and filled with fresh electrolyte. All the experiments were done at room temperature. FTIR absorption spectra were recorded *in situ* during electrochemical

potential cycling measurements with a scan rate of 5 mV/s. To obtain specific spectral changes during the electrochemical doping a spectrum just before the considered process was chosen as reference. The subsequent spectra were related to this spectrum. The resulting spectra are plotted as $\Delta(-\log(T_{ATR}))$, where T_{ATR} is the transmission in ATR geometry. Each spectrum is calculated from a coaddition of 32 interferograms and covers a range of about 85 mV in the cyclic voltammogram. Details and the set-up for ATR-FTIR *in-situ* spectroelectrochemistry have been published elsewhere [3].

For photoinduced FTIR absorption measurements the films were mounted on the cold finger of an evacuated liquid nitrogen bath cryostat with ZnSe windows. The samples were excited in 45° geometry through a quartz window by the 488 nm line of an Ar^+ laser (30 mW/cm^2). The photoinduced absorption spectra were observed by collecting 300 repetitions of recording 10 coadded single beam spectra under illumination and 10 coadded single beam spectra in the dark. Combining the respective spectra the photoinduced absorption was calculated as $-\Delta T/T$. IR spectra were recorded with a resolution of 4 cm^{-1} using a Bruker IFS 66S spectrometer.

Raman measurements were performed at room temperature under vacuum using a Bruker IFS 66 + FRA 106 FT spectrometer, working with a Nd-YAG laser (1064 nm) in the NIR, and using a flat field triple monochromator (Jasco TRS 300) equipped with an EG&G intensified array (OMA 1420), working with Ar^+ and He/Ne laser lines in the visible.

RESULTS AND DISCUSSION

The difference spectra recorded during the *p*-doping process of pDTT3 are depicted in figure 2(a). The spectra are dominated by a broad absorption at high wavenumbers, which has maximum at about 2800 cm^{-1}, correlated to the formation of new intragap states. In the vibrational part of the spectrum (see figure 2 (b)) the activation of IRAV modes gives a complicated band pattern characterized by broad bands, especially above 1000 cm^{-1}, and sharp peak, at lower wavenumbers. As expected for systems whit
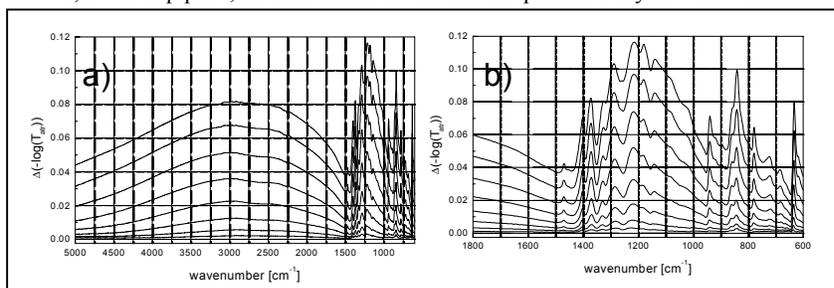

Figure 2: IR difference spectra during electrochemical *p*-doping of pDTT3.

a strong electron-phonon coupling the IRAV bands are quite intense. High intensities and broad shapes of the bands indicate a rather high delocalization along the chain for the positive charges injected to the polymer. Note that the very intense and sharp peak at 842 cm^{-1} is due to the incorporation of PF_6^- counterions that balance the positive charge

within the *p*-doped polymer. Low band-gap pDTTs are among the few CPs that are both *p*- and *n*-dopable. The difference IR spectra during the *n*-doping of pDTT3 are shown in figure 3. The spectrum arising during this process has a very high similarity to the spectrum of the *p*-doped material. Despite slight differences in the relative intensities of the IRAV bands, all the spectral features, with the exception of the missing counterion band, are observed in both types of doping. We want to point out that, in contrast to other thiophene based CPs [8], the spectra of *p*- and *n*-doped pDTT3 show IRAV bands with the same intensities. These relevant similarities indicate a similar delocalized nature for the charge carriers of both signs and a similar doping level.
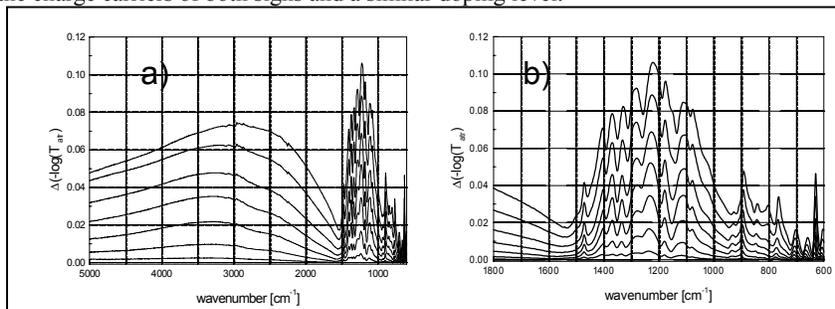

Figure 3: IR difference spectra during electrochemical *n*-doping of pDTT3.
(a) full range; (b) extended scale.

A different behavior, which resembles those of other CPs, has been found for pDTT1, which has the "largest" band-gap among the pDTTs studied in this work. Figure 4 shows the spectral changes in the IRAV region during electrochemical *p*-doping and *n*-doping (see figure 4(a) and 4(b), respectively). These two spectra show important differences in both intensity and pattern indicating a different nature for both types of charge carriers.
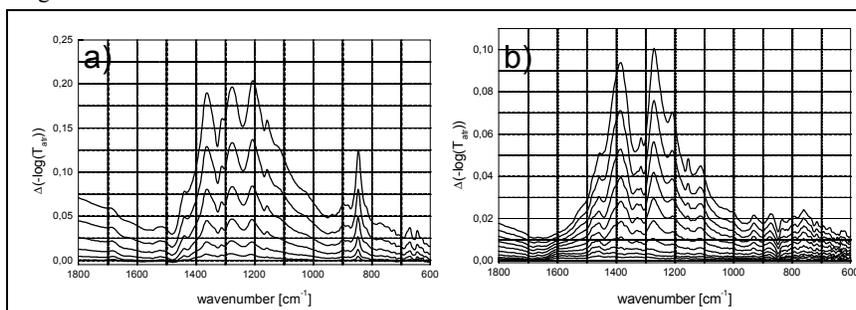

Figure 4: IR difference spectra during *p*-doping (a) and *n*-doping of pDTT1 (b).

Differences in the IRAV pattern, which are less pronounced than in the case of pDTT1, are also observed by comparing the spectra of *p*- and *n*-doped pDTT2. These results give the spectroscopic evidence of the important role, which strongly influences the properties of pDTT3, of different moieties fused to the same conjugated backbone.

The photoinduced absorption of pDTT1, pDTT2 and pDTT3 give spectra that are similar to those of the correspondent *p*-doped polymer, which indicates a positive charge for the photocarriers.
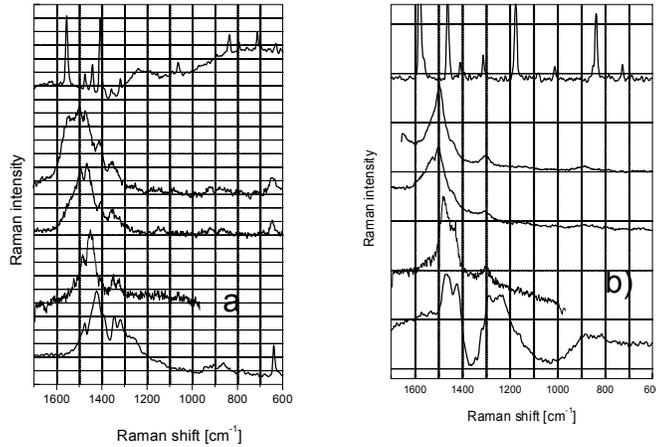

Figure 5: (a) Raman spectra of the monomer DTT3 (top, exc. at 1064 nm) and of pDTT3, excitation at 1064, 633, 514, 457 nm from bottom to top; (b) Raman spectra of monomer DTT1 (top, exc. at 1064 nm) and of pDTT1, excitation at 1064, 633, 488 and 547 nm from bottom to top.

The Raman spectra of neutral pDTT3 and pDTT1, taken with different excitation wavelengths, are shown in figure 5(a) and 5(b), respectively. In the region above 1000 cm^{-1}, mostly containing conjugated backbone vibrations, intense bands that show frequency dispersion and energy redistribution by changing the excitation wavelength, are observed for both the two polymers. The most striking difference is the presence of an intense and sharp peak at about 640 cm^{-1} in the pDTT3 Raman spectra. This peak can be easily correlate to the IRAV band observed at almost the same wavenumber in the IR spectra of the *p*- and *n*-doped polymer. The sharpness of this peak and the lack of dispersion indicate a localized nature for the corresponding vibration. In a carefully recorded photoinduced IR spectrum of polythiophene Schaffer and Heeger have detected, at similar wavenumbers, very weak features that were assigned to ring vibrations containing C-S stretching character [9]. Similarly, in pDTT3 the origin of this band can be tentatively assigned to a vibration within the repeating unit. In addition, in the off-resonant Raman spectrum (excitation at 457 nm) of pDTT3, presence of bands that coincide with Raman modes of the monomer give a further indication of the important influence of the fused rings within the repeating unit to the polymer vibrational and electronic properties. Sharp Raman modes at low frequency are detected also in the Raman spectra of pDTT2.

CONCLUSIONS

Polydithienothiophenes are both *p*- and *n*-dopable low band-gap polymers. IRAV bands arising upon doping of these polymers have high intensity and broad shape and indicate rather delocalized charge carriers. Especially for pDTT3, the polymer with the lowest band-gap, a high correspondence between IR spectra in its *p*- and *n*-doped states is observed. This unusual finding indicates a similar nature for the charge carriers of both signs and a similar doping level.

Despite the small difference in the chemical structure of pDTT1,pDTT2 and pDTT3, the properties of the polymers in respect tot heir electrnic structure are quite different. Our results with ATR-FTIR spectroelectrochemistry and Raman spectroscopy, which are highly correlated to the electronic structure, show the strong influences ofslightly different moieties, fused to the same conjugated backbone, to the electronic properties of the polymers.

ACKNOWLEDGMENT

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