

# Spectral signatures of positive and negative charged states in doped and photoexcited low band-gap polydithienothiophenes

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## Abstract

Spectroelectrochemical studies of polydithienothiophenes (pDTTs), low band-gap conjugated polymers with polythiophene-like chain, using in situ FTIR-ATR and ESR spectroscopy, are shown. Spectral results obtained during p- and n-doping, as well as photoinduced spectral effects, are compared. The formation of paramagnetic positive and negative charge carriers with unusually high  $g$ -values is described.

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**Keywords:** Polythiophenes; p-Doping; n-Doping; IRAV; ESR; Spectroelectrochemistry

## 1. Introduction

The infrared spectra of conjugated polymers in their conductive states are characterized by intense infrared active vibration (IRAV) bands, typically ranging from 700 to 1600  $\text{cm}^{-1}$  [1]. These bands originate from a strong electron–phonon coupling and thus provide not only structural but also electronic information. Several theoretical models have been developed in order to explain the spectroscopic signatures of charge carriers, usually described as polarons, in conjugated polymers [2–5]. These theories, developed for relatively simple systems like polyacetylene and extended to few polyheteroaromatics, generally do not account for possible differences in the IRAV signatures of positive and negative charge carriers. However, some more complex conjugated polymers show a different behavior. These materials are often promising candidates for applications since they may combine low band-gap, outstanding optical properties and high stability in either or both the p- and n-doped states. Spectroscopic studies focussing on the differences between p- and n-doped states might be useful

to achieve better experimental and theoretical descriptions of the so far rarely observed negative charge carriers in conjugated polymers.

The low band-gap and both the p- and n-dopability of the polydithienothiophenes pDTT1 (band-gap 1.15 eV), pDTT2 (1.12 eV) and pDTT3 (1.05 eV; structures given in Fig. 1) [6] make them attractive for comparative spectroscopic studies of doping induced charge carriers.

In the present paper, spectral signatures of p- and n-doped pDTT1, pDTT2 and pDTT3 obtained with in situ ATR-FTIR spectroelectrochemistry and with in situ ESR spectroelectrochemistry are compared. As presented here and elsewhere in more detail [7], the IRAV pattern of pDTT1 and pDTT2 are different for p- and n-doping, whereas for pDTT3 similar spectra are obtained. For all polymers, the photoinduced absorption (PIA) pattern correspond to the p-doped material. ESR measurements reveal that the charge carriers exhibit unusually high  $g$ -values with systematically even higher  $g$ -values for negative charges.

## 2. Experimental

The monomers DTT1, DTT2 and DTT3 were synthesized following methods reported in the literature [8] and

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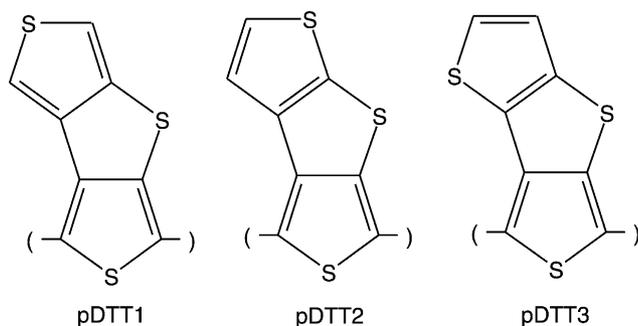


Fig. 1. Structures of pDTTs.

electropolymerized in anhydrous acetonitrile solution containing 0.1 M TBAPF<sub>6</sub> as supporting electrolyte either on Ge reflection elements for in situ ATR-FTIR spectroelectrochemistry and PIA measurements or on Pt foil electrodes for in situ ESR measurements. Doping induced spectral changes were measured during slow potential scans. Photoinduced absorption changes were obtained by relating the IR absorption of illuminated samples to the absorption in the dark. Details of the set-up and the measurement procedure are described in previous publications [9,10].

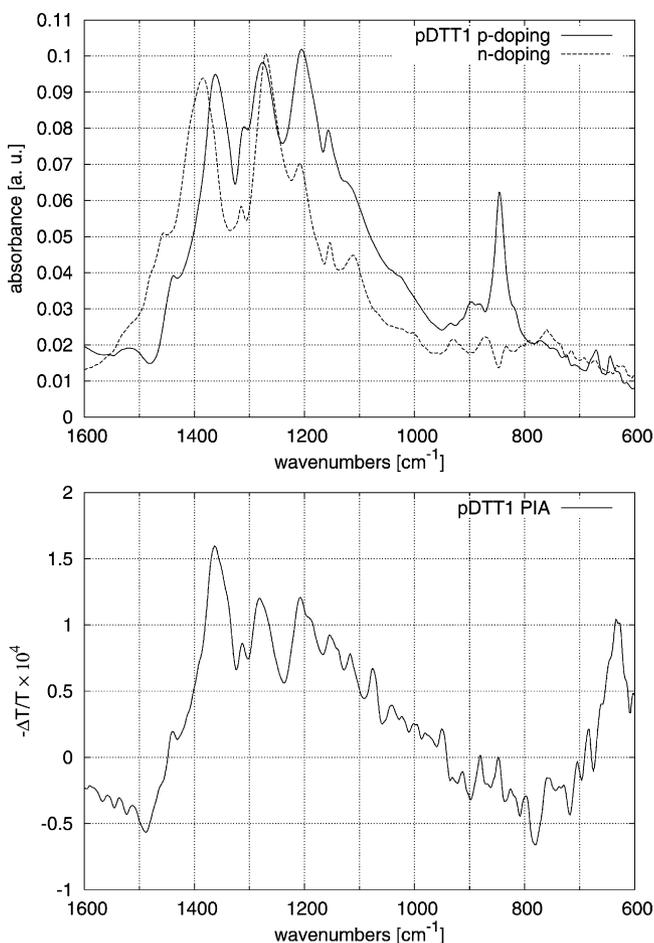


Fig. 2. Electrochemically p- and n-doping induced IRAV spectra compared with the photoinduced IRAV spectrum of pDTT1.

### 3. Results and discussion

Figs. 2–4 compare the p- and n-doping induced IRAV patterns of pDTT1, pDTT2 and pDTT3, respectively, with the corresponding PIA spectra. As can be seen, the difference between p- and n-doping is quite pronounced for pDTT1 and pDTT2. Such differences indicate a different delocalization for the positive and negative charge carriers, as already reported for other p- and n-dopable polymers like poly(ethylene-2,3-dioxythiophene) (pEDOT) [11] and poly(isothianaphthenemethine) [12].

For pDTT3 a similar pattern for p- and n-doping is obtained (the peak at 842 cm<sup>-1</sup>, growing only during p-doping of all polymers, is due to the incorporation of PF<sub>6</sub><sup>-</sup> ions during the oxidation process), thus indicating rather similar structures and delocalization extension for charge carriers of both signs.

In all cases, the photoinduced IRAV patterns correspond to the electrochemically p-doped material, inferring that mostly positive polarons are delocalized and behave as majority charge carriers in the photodoped material. Conversely, negative charges are probably trapped within certain sites of

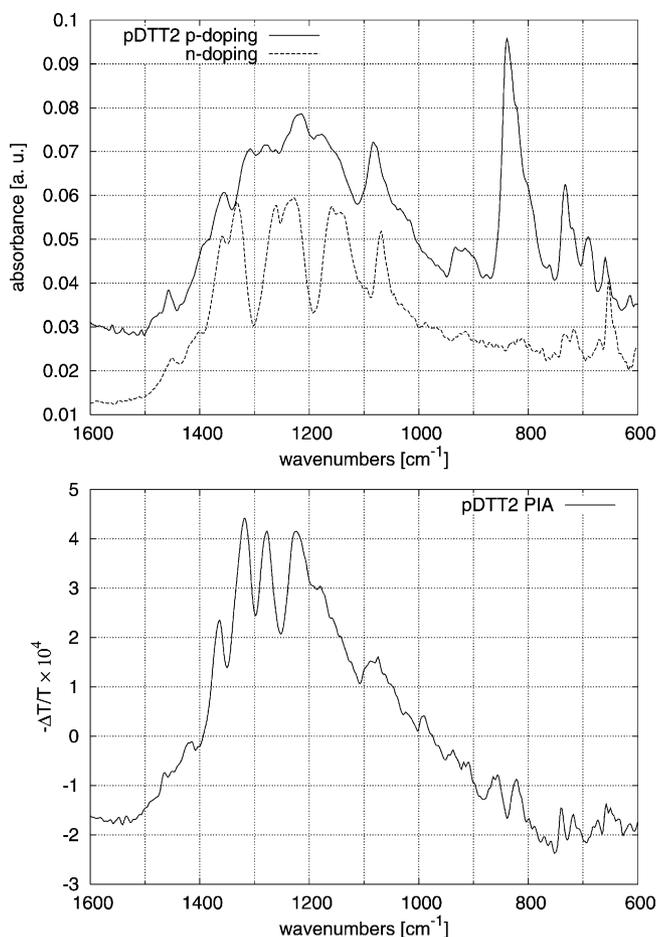


Fig. 3. Electrochemically p- and n-doping induced IRAV spectra compared with the photoinduced IRAV spectrum of pDTT2.

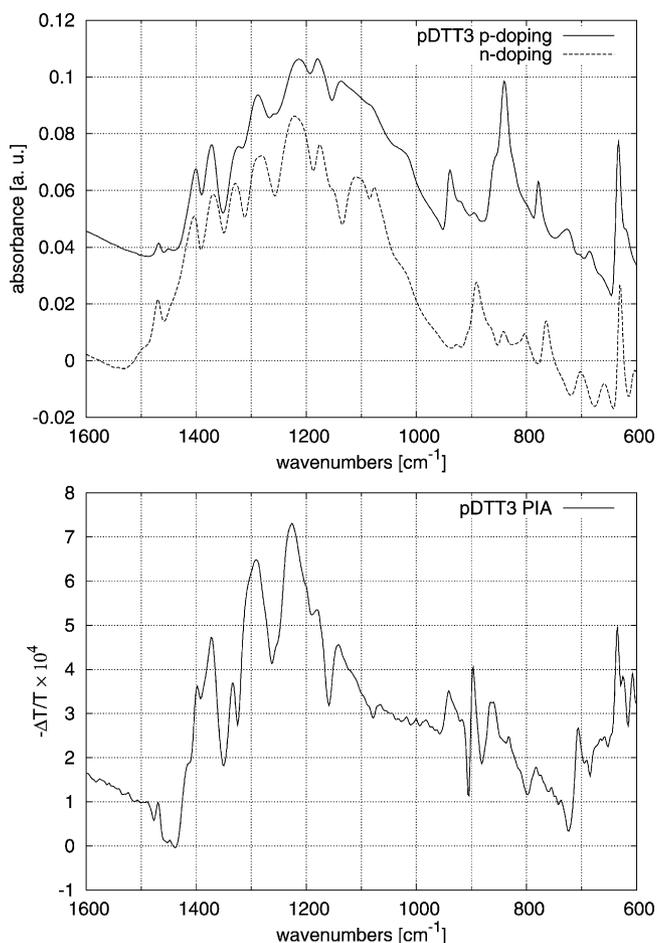


Fig. 4. Electrochemically p- and n-doping induced IRAV spectra compared with the photoinduced IRAV spectrum of pDTT3.

the polymer, e.g. chain defects, or localized in the repeating units themselves.

In addition to vibrational spectroscopy, ESR spectra of pDTTs were recorded in situ during electrochemical p- and n-doping in potential scan experiments. In all cases, the formation of paramagnetic charge carriers (polarons) is observed. The maximum signal obtained during p- and n-doping was used for the determination of the  $g$ -values. The rescaled spectra of the respective charge carriers in pDTT1, pDTT2 and pDTT3 are shown in Fig. 5.

$g$ -Values around and higher than 2.004 were found, which is higher than the values commonly observed for doped conjugated polymers [13] (due to improved rescaling, the recalculated  $g$ -values presented here are slightly lower than the values given in our previous publication [7]). Compared to p-doped pDTTs, the ESR signals of n-doped pDTTs appear at even higher  $g$ -values. Origin of the high  $g$ -values is assumed to be a stronger spin–orbit coupling within the pDTTs (which might be different for p- and n-doping), potentially related to the sulphur atoms in the fused moieties.

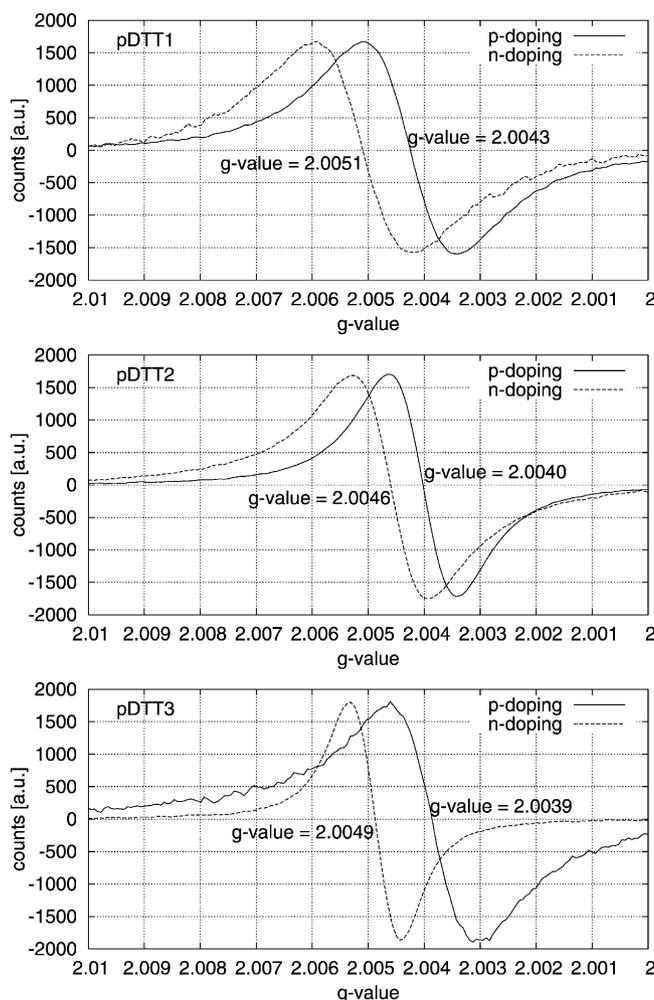


Fig. 5. Electrochemically p- and n-doping induced ESR signals of pDTT1, pDTT2 and pDTT3.

#### 4. Conclusion

Different IRAV patterns for p- and n-doping of pDTT1 and pDTT2 were found. In contrast, for pDTT3, which has the lowest band-gap, a similar pattern was obtained, suggesting potential bipolar transport properties, possibly favorable for certain optoelectronic devices and photovoltaic applications.

Differences in the spectral features for p- and n-doping of conjugated polymers may be used for the identification of charge carriers formed shortly after photoexcitation (e.g. via dissociation of excitons) using times resolved spectroscopy.

#### Acknowledgements

The work was supported by the European Commission, RTN Project No. HPRN-CT-2000-00127 “EUROMAP”.

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