

In situ FTIR spectroelectrochemical characterization of n- and p-dopable phenyl-substituted polythiophenes

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In situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroelectrochemistry during oxidation (p-doping) and reduction (n-doping) of three phenyl-substituted polythiophenes, namely POPT, PEOPT and POMeOPT is presented. All the three phenyl substituted polythiophenes show both n- and p-doping. The infrared active vibration (IRAV) patterns obtained during electrochemical oxidation (p-doping) and reduction (n-doping) are compared. HOMO and LUMO energy levels are estimated from cyclic voltammetric experiments and from IRAV patterns during oxidation and reduction. A comparison shows that the standard graphical procedure to determine the onset of oxidation and reduction peaks in the cyclic voltammogram can be improved using *in situ* spectroscopy.

I. Introduction

Since the discovery of electrical conductivity upon doping of polyacetylene in 1977,¹ the interest in organic semiconductors has continuously increased. Among the wide class of conjugated polymers, substituted polythiophenes are of particular interest due to their chemical stability and their good solubility in common organic solvents obtained by proper backbone functionalization with substituent side-groups: these properties are fundamental for the use of these compounds in low cost optoelectronics. As an example, the stability, the good solubility and the high hole-mobility properties of poly-(3-hexylthiophene) (P3HT) have been used in state-of-the-art organic solar cells in combination with a soluble fullerene derivative (PCBM).^{2,3}

Increasing the electrical conductivity of a conjugated polymer by doping can be done electrochemically, either by oxidation or reduction.⁴ The use of spectroscopic techniques coupled to the electrochemical systems allows the identification of structural changes in the polymer during these redox processes. The spectroscopic techniques used in association with electrochemical systems ("spectroelectrochemistry") include UV-Vis absorption spectroscopy, infrared absorption spectroscopy, Raman spectroscopy and electron spin resonance spectroscopy.^{5–15} The experiments can be carried out *in situ*: applying the electrode potential and simultaneously monitoring the spectroscopic changes. The vibrational features

observed for pristine and doped conjugated polymers are different and are used as signatures for the electronic and the molecular structural changes due to doping.^{16–18} Conjugated polymers in their conductive (doped) states are characterized by intense infrared active vibration (IRAV) bands. Indeed the doping of the polymers leads to the formation of charged quasi-particles like solitons or polarons, that break the chain symmetry and induce infrared vibrational activity of A_g modes.¹⁹ Usually, these IRAV bands are accompanied by electronic absorption bands, providing also information on electronic properties.

The experimental determination of the electronic energy levels is fundamental for the characterization of materials when searching for new systems to be used in optoelectronic devices. Usually, a graphical method based on cyclic voltammogram measurements is used to estimate the energy of HOMO and LUMO of the polymers: we show that the method can be extended and corrected with *in situ* spectroelectrochemistry.

Here we present the *in situ* Fourier transform infrared (FTIR) spectroelectrochemical characterization of oxidation (p-doping) and reduction (n-doping) processes of three phenyl-substituted polythiophenes, namely poly[3-(4-octylphenyl)thiophene] (POPT), poly[3-(4'-(1'',4'',7''-trioxaoctylphenyl)thiophene] (PEOPT) and poly[3-(2'-methoxy-5'-octylphenyl)thiophene] (POMeOPT). The chemical structures of the POPT, PEOPT and POMeOPT are depicted in Fig. 1. These polythiophenes were synthesized aimed at different purposes. Doped polythiophenes generally exhibit thermal undoping. A proper backbone functionalization can suppress the undoping process as in the case of POPT;²⁰ a different functionalization can also alter the photoluminescence properties increasing the photoluminescence quantum yield as in the case of POMeOPT;²¹ while, due to side chain functionalization, PEOPT exhibits interesting morphological properties, showing two different phases with ordered or disordered characteristics as a consequence of thermal treatment.²²

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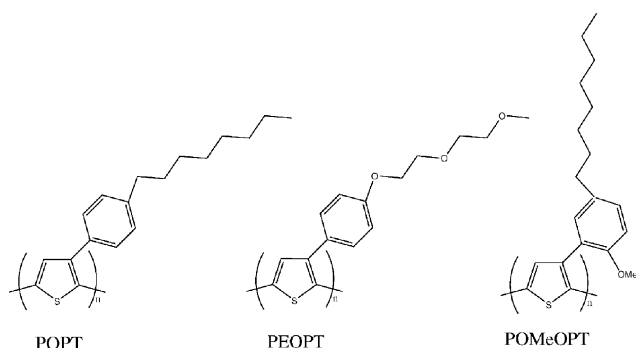


Fig. 1 Chemical structure of the studied compounds.

II. Experimental

All electrochemical experiments were carried out in a glove box in nitrogen atmosphere. The supporting electrolyte used was 0.1 M tetrabutylammonium hexafluorophosphate, Bu_4NPF_6 , dissolved in water-free acetonitrile (Aldrich). Cyclic voltammetric experiments were carried out with a platinum foil-working electrode covered with a dip coated polymer film from chloroform solution (6 mg ml^{-1}) at a sweep rate of 100 mV s^{-1} . As counter electrode a platinum foil and as quasi-reference electrode (QRE) a silver wire coated with AgCl were used. The potential of the QRE was determined as 50 mV vs. NHE by calibration with a ferrocene redox couple. The electrolyte solution was kept in a glove box filled with nitrogen to exclude moisture and oxygen during the electrochemical processes. The electrochemical equipment consisted of a computer controlled potentiostat Jaisle 1030 PC.T.

For the spectroelectrochemical studies, thin films of POPT, PEOPT and POMeOPT were drop cast from chloroform solution onto a germanium reflection element covered with a thin layer of evaporated platinum. The ATR-FTIR spectroelectrochemical measurements were carried out in a three-electrode spectroelectrochemical cell with the described reflection element as working electrode, a platinum foil counter electrode, and a silver wire/silver chloride quasi-reference electrode; details of the method are described in ref. 23. The spectroelectrochemical cell setup is shown schematically in Fig. 2. The spectroelectrochemical cell was sealed with paraffin to prevent leakage of the electrolyte solution. The cell was placed in the FTIR compartment and the instrument was purged with nitrogen continuously throughout the experiment. The electrolyte solution for the *in situ* spectroelectrochemical experiments was 0.1 M Bu_4NPF_6 in acetonitrile. A continuous flow system for the electrolyte was used where the electrolyte (placed in an external container in glove box) flows in and out of the electrochemical cell using teflon plastic tubes.

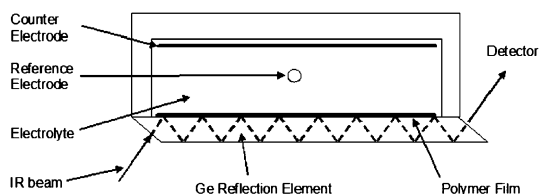


Fig. 2 The spectroelectrochemical cell set up scheme.

A Bruker IFS66S spectrometer with a mercury–cadmium–telluride (MCT) detector cooled with liquid nitrogen was used. The spectra were measured with a spectral resolution of 4 cm^{-1} . Spectral changes were recorded consecutively during potential sweeps of 5 mV s^{-1} . To obtain specific spectral changes during individual electrochemical reaction processes, a spectrum just before the considered reaction was chosen as the reference spectrum. The subsequent spectra were related to this reference spectrum, showing only the spectral changes Δ during the process. The spectra are plotted as $\Delta[-\log(T_{\text{ATR}})]$, where T_{ATR} is the transmission in ATR geometry. For each spectrum, 32 interferograms were coadded covering a range of about 60 mV in the cyclic voltammogram.

The UV-Vis absorption spectra of casted films from chloroform solution (6 mg ml^{-1}) on glass substrates were recorded using a Varian Cary 3G UV-Vis spectrophotometer.

III. Results and discussion

The cyclic voltammograms of POPT, PEOPT and POMeOPT are depicted in Fig. 3. It can be seen that all three polymers can be both oxidized (p-doped) and reduced (n-doped). The p-doping and n-doping of POPT, PEOPT and POMeOPT were also confirmed by *in situ* FTIR spectroscopy as presented below.

A common method to extract the energy level values of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is to correlate them with the onset of oxidation and reduction peaks in the cyclic voltammogram; usually the onsets are estimated from the intersection between the tangent at the rising of oxidation and reduction current peaks and the tangent to the background current. The potential values are corrected for the potential value of the QRE and the value of the potential of the NHE in the Fermi energy scale (a value of 4.75 eV is used for the latter²⁴). The values for HOMO and LUMO levels extracted in this way are reported in Table 1 together with the corresponding potential values (the latter are also indicated in Fig. 3 by solid arrows).

The values extracted from cyclic voltammograms are in the same range of previously reported values (HOMO of -5.66 eV and LUMO of -3 eV for POPT,²⁵ HOMO of -5.3 eV and LUMO of -3 eV for POMeOPT²⁶ and an energy gap of 2.6 eV for PEOPT²² as extracted from optical absorption maximum as no CV data were reported for this molecule). The values are not exactly the same because the graphic procedure of extracting HOMO and LUMO energy levels from cyclic voltammogram experiments is not devoid of ambiguity, as the drawing of the tangent to the curve at the rising of oxidation/reduction peak is not univocal. In order to eliminate this ambiguity we used FTIR spectroelectrochemistry to determine the potential values of the beginning of the electrochemical doping during the cyclovoltammetric experiments. If a spectrum just before the doping process starts is chosen as reference, the difference spectra relative to the reference start with a straight line. When doping occurs, the characteristic IRAV and electronic absorption features appear. The potential value of the first spectrum showing these spectral features is taken as the value for the determination of the HOMO and LUMO levels of the material

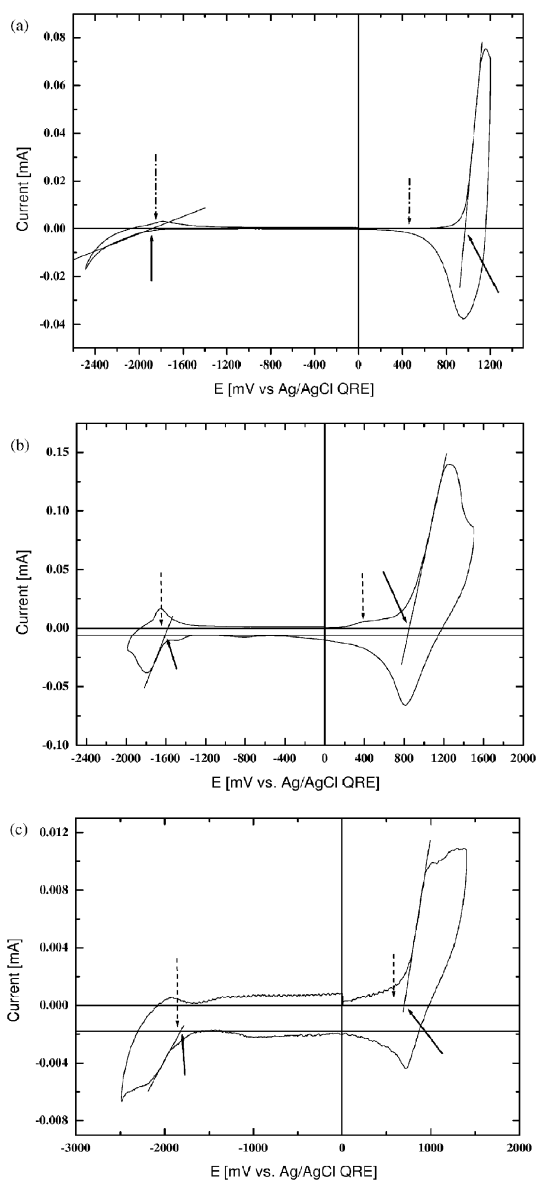


Fig. 3 Cyclic voltammogram of (a) POPT, (b) PEOPT, (c) POMeOPT. The straight lines are the tangents at the rising of the main oxidative/reductive current peaks; the solid arrows show the potential value for the onset of oxidative and reductive current as determined by the intersection between the tangents and the background current, while the dashed arrows show the potential values for which the development of the IRAV bands starts.

Table 1 Potential values for the onset of oxidative and reductive current peaks from cyclic voltammograms and for the onset of IRAV bands development and respectively extracted HOMO and LUMO values. See also arrows in Fig. 3

Polymer	Onset cyc./V	Onset IRAV dev./V	HOMO (cyc.)/eV	HOMO (IRAV dev.)/eV
Oxidation				
POPT	0.97	0.45	-5.77	-5.25
PEOPT	0.85	0.37	-5.65	-5.17
POMeOPT	0.70	0.58	-5.50	-5.38
			LUMO (cyc.)/eV	LUMO (IRAV dev.)/eV
Reduction				
POPT	-1.90	-1.83	-2.90	-2.97
PEOPT	-1.59	-1.65	-3.21	-3.15
POMeOPT	-1.83	-1.84	-2.97	-2.96

(with the uncertainty of the potential range covered by each spectrum).

Fig. 4 show the difference spectra during electrochemical oxidation of POPT, PEOPT and POMeOPT, respectively. The spectra are dominated by a broad absorption at high energy, correlated to the formation of new electronic states within the gap. In the vibrational part (from 1800 cm^{-1} to 600 cm^{-1}) a complicated band pattern is growing during oxidation. The band at about 842 cm^{-1} is due to the incorporation of hexafluorophosphate counterions, which balance the positive charge formed on the polymer during oxidation. The potential values for which the spectral evolution starts are reported in Table 1 and also indicated by the dashed arrows in the cyclic voltammograms in Fig. 3.

Among electro-active conjugated polymers POPT, PEOPT and POMeOPT are few examples that can be both oxidized and reduced reversibly. The difference ATR-FTIR spectra during electrochemical reduction of the POPT, PEOPT and POMeOPT are depicted in Fig. 5. For all three polymers the development of IRAV bands during electrochemical reduction starts at potentials that nearly coincide with the onset of reductive current peaks in the cyclic voltammograms (see Table 1 and arrows in Fig. 3). Therefore, the estimation of LUMO energy levels obtained with the spectroelectrochemical method (see Table 1) are in accordance with the values extracted graphically from cyclic voltammograms, as described above. However, for the HOMO energy levels, the situation is different for POPT and PEOPT on one side, and for POMeOPT on the other side. For the former polymers the development of IRAV bands starts at potentials different to the onset of oxidative current peaks, giving HOMO energy levels of -5.25 eV for POPT and -5.17 eV for PEOPT, with a difference of about 0.5 eV compared to the cyclic voltammogram experiments. These differences can be explained with differences in the distribution of the conjugation lengths of the polymer samples. If a broad distribution is present, the longer conjugated segments, which are oxidized at lower potential, may not give a significant contribution to the total charge for oxidizing the whole sample, and the main current may be correlated with shorter segments oxidized at higher potentials. This effect may lead to a certain arbitrariness in the determination of the exact point in the cyclic voltammogram in which the tangent line is drawn. In the *in situ* FTIR data, on the contrary, this arbitrariness is not present. Indeed the development of IRAV bands, starting with the longest chain

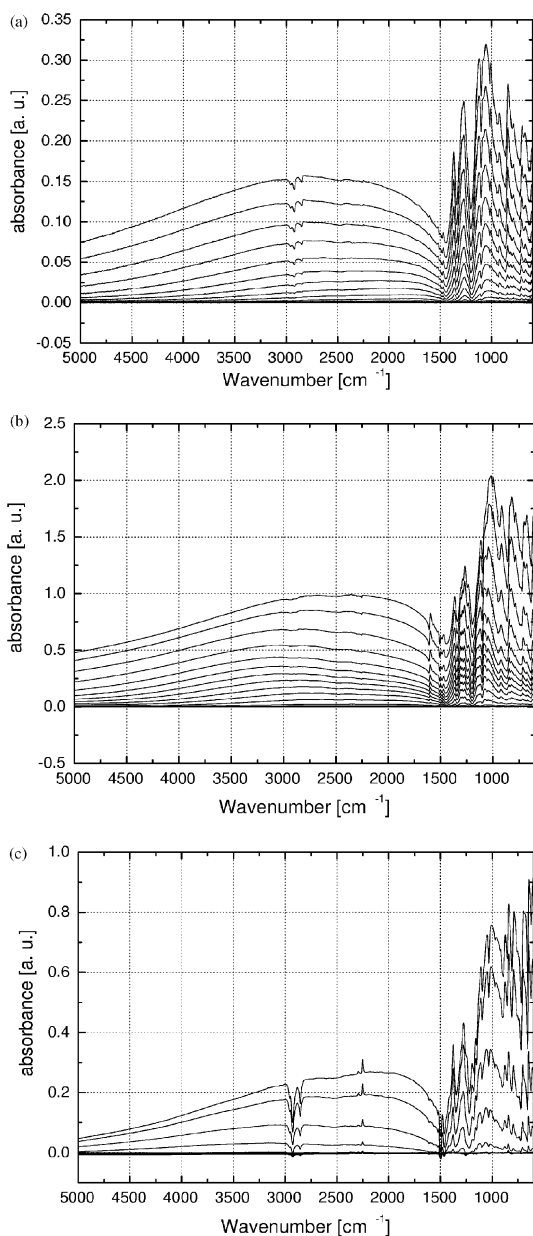


Fig. 4 Difference spectra during electrochemical oxidation of (a) POPT, (b) PEOPT, (c) POMeOPT. The spectra cover a range of: (POPT) 0.36 V to 1.20 V—reference spectrum at 0.30 V; (PEOPT) 0.24 V to 1.10 V—reference spectrum at 0.18 V; (POMeOPT) 0.36 V to 1.19 V—reference spectrum at 0.30 V.

segments, can be easily detected. Since the longest chain segments resemble more closely the infinite polymer chain, their oxidation potential are the values which correlate closely with the HOMO of the infinite polymer. This is the case for POPT and PEOPT. In principle this information may be already present in the cyclic voltammograms, but it may be hidden by the chosen data scaling and by the sensitivity. On the contrary the values from current and from IRAV measurements are quite similar for POMeOPT, indicating a narrow conjugation length distribution. Evidence for different conjugation length distributions can also be found from the UV-Vis absorption spectra of the compounds (Fig. 6). POPT

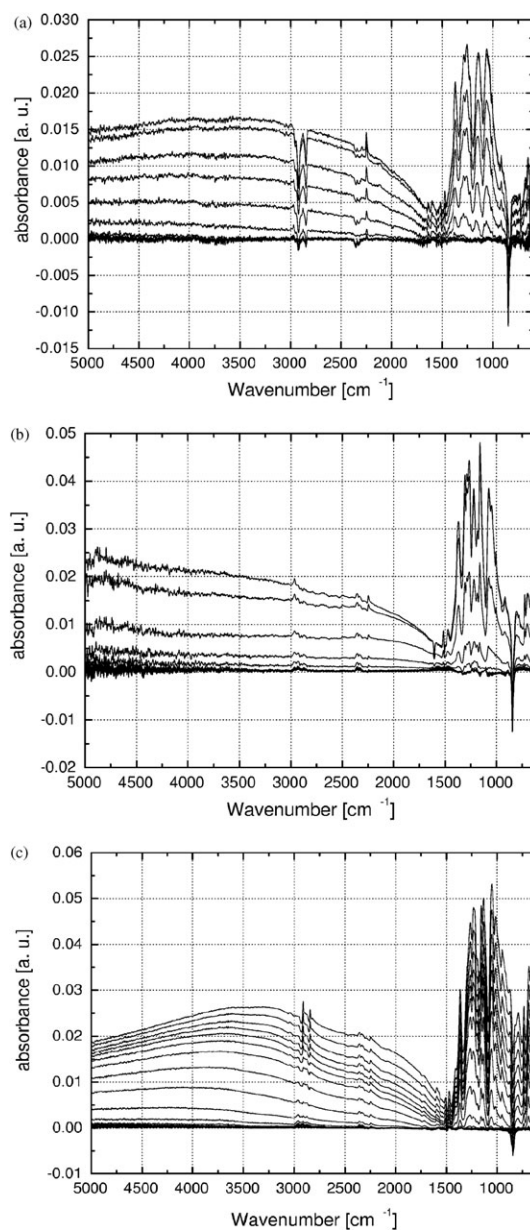


Fig. 5 Difference spectra during electrochemical reduction of (a) POPT, (b) PEOPT, (c) POMeOPT. The spectra cover a range of: (POPT) -1.50 V to -2.21 V—reference spectrum at -1.44 V; (PEOPT) -1.13 V to -1.94 V—reference spectrum at -1.08 V; (POMeOPT) -1.45 V to -2.48 V—reference spectrum at -1.39 V.

samples are in their amorphous phase (brown–red color) and PEOPT samples are in their orange phase as can be concluded from the lineshape of the absorption spectra.^{22,25} The sharp onset of absorption at low energies (long wavelengths) together with vibronic features for POMeOPT indicate a narrow conjugated length distribution, whereas broad ill defined absorption features are correlated with broad conjugation length distributions for the other polymers. Energy gaps from optical absorption are usually derived either by analyzing the absorption onset (band-like absorption) or by the absorption maximum (HOMO–LUMO absorption in molecules).

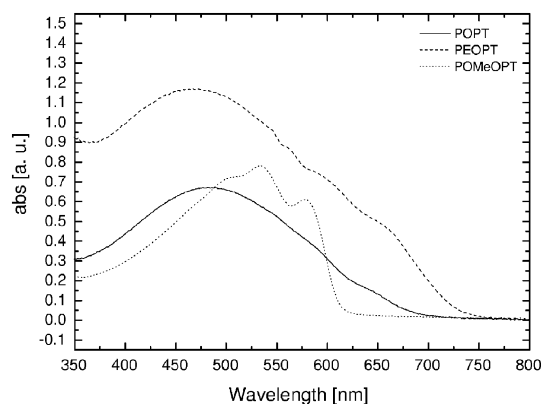


Fig. 6 Absorption spectra of samples cast from chloroform solution.

Table 2 Energy gap of the three materials (in eV)

Material	$E_{\text{gap}}^{\text{opt}}$	$E_{\text{gap}}^{\text{optmax}}$	$E_{\text{gap}}^{\text{CV}}$	$E_{\text{gap}}^{\text{IR}}$
POPT	1.72	2.56	2.87	2.28
PEOPT	1.61	2.65	2.44	2.02
POMeOPT	1.95	2.14	2.53	2.42

The energy gap $E_{\text{gap}}^{\text{CV}}$ estimated from cyclic voltammetric data, the energy gap $E_{\text{gap}}^{\text{IR}}$ estimated from *in situ* FTIR results, the energy gap $E_{\text{gap}}^{\text{opt}}$ from the onset of the optical absorption and the energy gap from the maximum absorption peak $E_{\text{gap}}^{\text{optmax}}$ are compared in Table 2. The values for $E_{\text{gap}}^{\text{opt}}$ are similar to values found in literature (1.7 eV for POPT from ref. 27, 1.75 eV for PEOPT from ref. 28 and 2.0 eV for POMeOPT from ref. 29).

Differences in the electronic gap obtained by optical absorption and by electrochemistry are not unusual for conjugated polymers. Photon absorption processes may be related to excitonic levels or, in the band picture, to electronic levels different to the band edge levels. On the other hand, electrochemical doping processes are related to these band edges. For different applications a different information may be useful. For instance, for optoelectronic devices like OLEDs it should be more important to consider the electrochemical energy gap. The working principle of such devices is based on charge injection, a process that involves energetic states corresponding to the band edges. Other applications may be more related to photon absorption processes. Unambiguous methods for the determination of the values, as the presented method for the determination of the electrochemical band gap, are therefore of crucial interest.

IV. Conclusions

In situ FTIR spectroelectrochemical studies of POPT, PEOPT and POMeOPT indicate that phenyl substituted polythiophenes can be electrochemically oxidized (p-doping) and reduced (n-doping). From the comparison of HOMO and LUMO energy levels extracted both from cyclic voltammetry experiments and *in situ* FTIR experiments it has been shown that the standard graphical procedure to determine the onsets of oxidation and reduction current peaks can be improved using the onset of the development of IRAV pattern

during oxidation and reduction. The results may have high importance for the characterization of materials used for organic electronic and optoelectronic devices, where the properties related to p- and n-doping are of crucial interest.

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