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## Vibrational Spectroscopy study of doping induced charged defects in a series of $\alpha,\alpha'$ -Dimethyl end-capped Oligothiophenes

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### Abstract

We present some preliminary results of a vibrational spectroscopic investigation carried out on a series of  $\alpha,\alpha'$ -dimethyl end-capped oligothiophenes doped with iodine. The evolution of the doping-induced infrared bands has been followed by means of *in situ* FT-IR spectroscopy, by allowing thin films of neutral oligothiophenes to react with dry iodine vapours at different concentrations. FT-Raman spectra recorded on powdered samples of I<sub>2</sub>-doped  $\alpha,\alpha'$ -dimethylquinquethiophene indicate the existence of a polaron-type defect.

**Keywords:** (Infrared and Raman spectroscopy, polythiophene and derivatives)

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### 1. Introduction

Oligomers are currently being studied as model compounds of polyconjugated polymers. Oligothiophenes suffer, though, from the inherent reactivity upon doping of the  $\alpha$ -carbon atoms at both side chain ends. This instability may be overcome by blocking these  $\alpha$ -positions with alkyl substituents [1].

The defects induced by the ionization of the materials originate new features in the IR spectrum, which are associated with electronic transitions involving midgap electronic levels [2-3].

Raman spectroscopy can also provide valuable structural information on these charged domains in doped conducting polymers and oligomers [4]. However, only very few data of acceptable quality are so far available for ionized molecules.

In this communication, we report on a self-localized excitation which occurs for iodine doped solid samples of  $\alpha,\alpha'$ -dimethyl-quinquethiophene. These data enable us to inspect the vibrational structure of the radical cation of Me-(Th)<sub>5</sub>-Me.

### 2. Experimental Section

The synthesis and purification of the compounds have been published elsewhere [5]. All IR measurements were carried out by using a demountable cell for gases. Thin films of the neutral compounds were deposited onto NaCl windows and

doped by slow *in situ* sublimation of solid iodine at room temperature. IR spectra were collected with a Perkin Elmer 1760 X FT-IR spectrometer under dry Ar gas. Raman spectra were recorded on a Bruker RFS 100 FT-Raman spectrometer, with a 1064 nm exciting line.

### 3. Results and Discussion

#### 3.1. Infrared spectra

Figure 1 shows some infrared absorption spectra collected during the chemical ionization of a thin film of Me-(Th)<sub>5</sub>-Me, at different times of exposure to iodine vapours. Electronic absorption measurements [1] performed on these end-capped oligothiophenes showed that, in each case, the iodine doping could yield only the first oxidized species (attributed to a radical cation), that are characterized by two subgap peaks (i.e., at 1.57 and 0.86 eV for a thin film of I<sub>2</sub>-doped Me-(Th)<sub>5</sub>-Me).

By considering the evolution of the infrared spectrum from the neutral state to the first oxidized state, we firstly notice that both band frequencies and intensities are significantly affected. A close look at the details shows that the ionization induces the quick appearance of at least six new IR absorptions at 1414, 1327, 1162, 1099, 993 and 946 cm<sup>-1</sup>, whose intensity increases with increasing doping level.

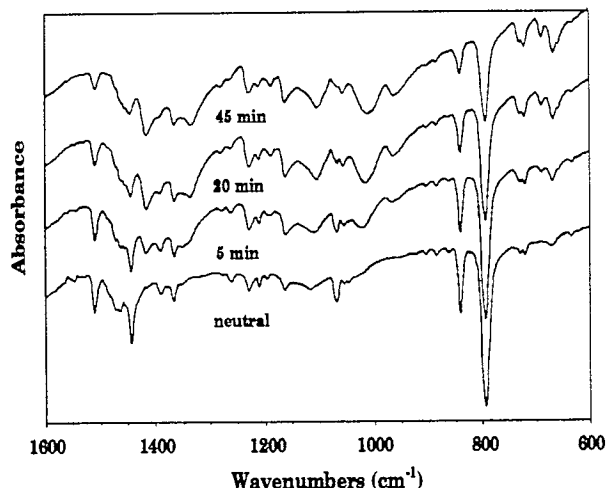


Fig. 1. FT-Infrared spectra recorded in situ during the oxidation process of  $\alpha,\alpha'$ -dimethyl end-capped quinquethiophene.

### 3.2. Raman spectra

The FT-Raman spectrum of the radical cation of Me-(Th)<sub>5</sub>-Me is shown in Fig. 2. In the C=C stretching region, between 1600–1400  $\text{cm}^{-1}$ , we clearly observe four strong doping induced lines, centered at 1483, 1462, 1440 and 1422  $\text{cm}^{-1}$ , which are accompanied by another weak line at 1520  $\text{cm}^{-1}$ . These Raman bands are correlated with the bands of neutral Me-(Th)<sub>5</sub>-Me centered at 1562, 1525, 1481, 1474 and 1450  $\text{cm}^{-1}$  (see Fig. 3) [6,7]. Similar data have been reported by Furukawa et al. [4] for the radical cation of unsubstituted Th<sub>5</sub>.

For bands below 1400  $\text{cm}^{-1}$ , the measured frequencies upon doping do not drastically differ from the corresponding values in the neutral molecule. Thus, Raman lines at 1224, 1164, 1071, 1050, 732 and 697  $\text{cm}^{-1}$  of the radical cation are correlated to bands at 1219, 1160, 1049, 734 and 695  $\text{cm}^{-1}$  of the neutral molecule. In this energy region, one of the main spectral differences between both molecular systems concerns bands at 1224, 1164 and 732  $\text{cm}^{-1}$ , which clearly become more intense upon ionization. Another difference is that the sharp band around 1049  $\text{cm}^{-1}$  of the neutral Me-(Th)<sub>5</sub>-Me, which is due to an in-phase C-H wagging slightly coupled with CC stretches, appears split into a doublet at 1071 and 1050  $\text{cm}^{-1}$  in the spectrum of the radical cation.

### 4. Acknowledgements

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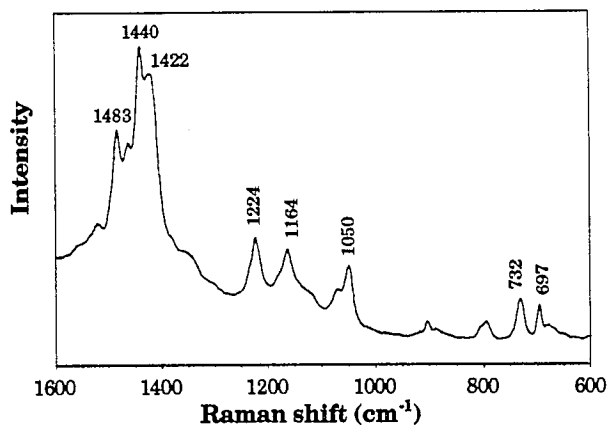


Fig. 2. FT-Raman spectrum of the radical cation of  $\alpha,\alpha'$ -dimethyl end-capped quinquethiophene.

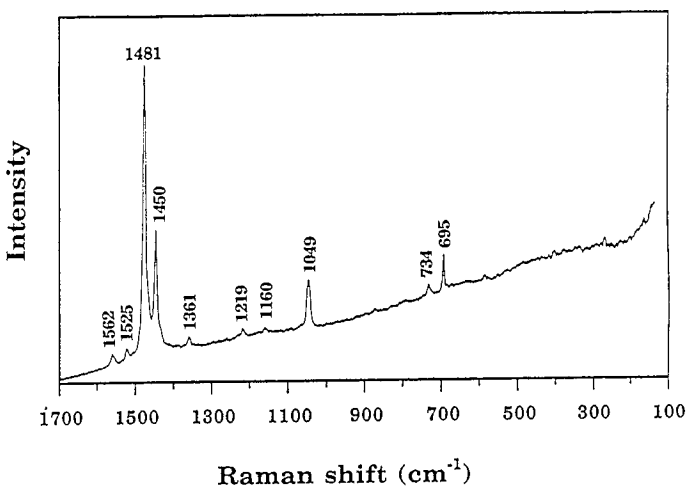


Fig. 3. FT-Raman spectrum of neutral  $\alpha,\alpha'$ -dimethyl end-capped quinquethiophene.

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