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Combined theoretical and spectroscopic Raman study of 3,4-ethylenedioxy and *S,S*-dioxide substituted terthiophenes and their parent polymers

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Abstract

This paper reports on the analysis of the Raman spectra, supported by DFT quantum chemical calculations, of a series of terthiophenes which present the novelty of being selectively functionalized with sulfone groups to increase their photoluminescence properties. The spectra have been carefully assigned on the basis of the theoretical vibrational eigenvectors. They suggest the occurrence of a segmentation of the electronic structure which can become a crucial feature for optimizing linear and non linear optical properties. Sulfonation fixes the two lone electron pairs of the sulfur atom, in particular that involved in the aromatization of the thiophene ring, thus coexisting two different kind of five member (aromatic and non aromatic) units in the same chain. This duality of the structure gives rise to the splitting of the characteristic Raman lines associated to the C=C/C–C stretching modes into components mainly located either on the external rings or on the internal one. The study also focuses on the electrosynthesized polymers obtained upon electropolymerization of the corresponding terthiophenes.

Keywords: Oligothiophenes; Light emitting materials; π-Conjugation; Electronic structure; Raman spectroscopy; DFT calculations

1. Introduction

Oligothiophenes are presently one of the most intensive field of research in the class of conjugated molecules. They have been used as active organic layers to construct electronic devices such as field-effect transistors and light-emitting diodes [1,2]. Most of conventional aromatic thiophene oligomers generally display very low photoluminescence quantum yields in the solid state. Recently, however, it has been reported that the insertion of one thienyl-*S,S*-dioxide moiety into the aromatic backbone gives rise to an amazing increase of their photoluminescence making these thiophene oligomers useful for LED applications [3–6]. In addition, the introduction of an 'oxidized thiophene' among the heteroaromatic rings increases the electron affinity of the whole molecule which favors electron injection. The suitable combination of this good photoluminescence with the improved electron acceptor features makes these new thiophene derivatives very attractive for electroluminescence devices.

In this paper the compounds depicted in Fig. 1 are studied. The relatively small molecular size of these terthiophenes offers the possibility of using accurate quantum chemical calculations to model their structures with a relatively low computational cost. Generally speaking the validity of theoretical calculations is enhanced when are closely compared with experiments. In this sense vibrational spectroscopy is quite well suited for these theory-experiment purposes since the recording of infrared and Raman spectra allows the measure of many bands to compare with a relatively high precision for their wavenumbers and relative

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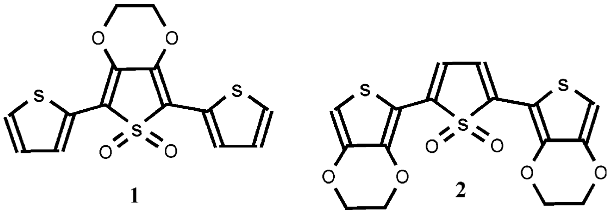

Fig. 1. Chemical structures of **1** and **2**.

intensities. In particular the use of Raman spectra of polyconjugated molecules for assessing information regarding their structural and electronic parameters is nowadays well established in the field of material science [7,8].

This work focuses on the analysis of the vibrational properties in relationship with the structural and electronic features, as deduced by theoretical calculations, of these thienyl-*S,S*-dioxide oligothiophenes. As an additional figure of merit of the work, the samples are also substituted by ethylendioxy side chains what lowers the oxidation potentials and, regarding their parent polymer systems, strongly reduces the amount of oxidative defects. These structures alternating electron rich moieties (ethylendioxy) and poor moieties (*S,S*-dioxide) in a same polythiophene chain has already been shown to render polymers with a finite window of conductivity although their electroluminescence and photoluminescence quantum efficiencies are still somewhat low [6]. We propose, by first time, a full assignment of the Raman spectra of the two aforementioned functionalized trimers and then we compare the Raman scattering pattern of one of them with those recorded for the electrochemically synthesized polymers.

2. Experimental and theoretical details

The synthesis of the terthiophenes (whose chemical structures are displayed in Fig. 1) has been reported elsewhere [6]. A FT–Raman spectra were measured using an FT–Raman accesory kit (FRA/106-S) of a Bruker Equinox 55 FT–IR interferometer. A continuous-wave Nd–YAG laser working at 1064 nm was employed for Raman excitation. A germanium detector operating at liquid nitrogen temperature was used. Raman scattering radiation was collected in a back-scattering configuration with a standard spectral resolution of 4 cm^{-1}. In order to avoid possible damage and the fluorescent background, laser beam was loosely focused on the sample and its power was kept at a level lower than 100 mW and 500 scans were averaged for each spectrum.

Electropolymerizations were carried out in saturated solutions of the terthiophenes in acetonitrile using tetrabutyl ammonium perchlorate as solid electrolyte in a 0.1 M concentration. Either a Pt disk of 1×1 cm^2 area or an ITO electrode were used as working electrodes on which the polymers were grown. A Pt disk and an Ag/AgCl electrode were used respectively, as auxiliary and as pseudo-reference. The polymerization was carried out in cyclic voltammetry conditions between 0 and 1 V at 25 °C. For full electrochemical characterization of the polymers, saturated solutions of the monomer were replaced by freshly prepared solutions of the electrolyte.

Full geometry optimizations were performed in the framework of the Density Functional Theory using the B3LYP functional, with the A.7 revision of the GAUSSIAN 98 program package running on a SGI Origin 2000 computer [9,10]. The 3-21G* basis set was chosen to reduce the high dimension of the problem [11]. In the first step of the procedure, all geometrical parameters (bond distances, bond angles and dihedral angles) were left free to optimize. On the resulting equilibrium geometries vibrational spectra were computed, and no negative eigenvalues were predicted thus assuring that the previously optimized geometries actually represent a stable minimum on the potential energy surface and therefore a reliable conformation for the molecules.

All calculations were carried out in the vacuum considering the molecules as isolated entities. It has already been shown that the B3LYP functional yields similar geometries for medium-sized molecules as MP2 calculations do with the same basis sets. Moreover, and in detriment to many other theoretical approaches, DFT calculations predict wavenumbers and intensities for the vibrational spectra in better agreement with experiments [12]. The calculated harmonic vibrational frequencies were scaled down uniformly by a factor of 0.98 as recommended by Scott and Radom [13].

3. Theoretical geometries

B3LYP/3-21G* optimized geometries and Mülliken atomic charge distribution are shown in Fig. 2. Calculations provide two main messages: (a) the rings are disposed in an all-anti configuration, and (b) the two oxygens of the sulfone group lie almost perpendicular to the plane of the thiophene with its sulfur at the center of a tetrahedron. For compound **1**, one end-thiophene is slightly bent relative to the others, which are nearly coplanar. This feature is not observed for compound **2** in which the three thiophenes are almost coplanar. The driving force for this slight deformation could be the interaction between one oxygen of the sulfone and the closest hydrogen at the β position of adjacent thiophene ring, resulting in a interatomic distance of 2.62 Å. This interaction precludes for a close approximation of the other oxygen and H atoms (atomic distance of 3.28 Å) since it should likely translate into a large deformation of the tetrahedron. Further insights into this intramolecular feature come from the S–O bond distances for both compounds in Fig. 2: for 1 the hydrogen bond makes the two S–O bonds to be non equivalent (lengthening that involved in the interaction) which is not the case for compound **2**.

For both the trimers, the single and double CC bonds of the central ring are larger and shorter, respectively than their