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Vibrational dynamics study of the effect of the substituents on the π-conjugation of different bithiophene molecules

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Abstract

We report on the FT-Raman spectroscopic study, aided by DFT model chemistry calculations, of three different classes of π-conjugated oligomers: (i) a dicyanomethylene end-capped bithiophene with a quinoidal chemical structure, (ii) a symmetrically dimethyl-substituted system bearing a non-polar aromatic structure in its ground electronic state and (iii) a highly polarized push–pull system with an electron-donor dimethylamino and a electron-acceptor cyano groups attached to its end α,ω-positions. We have optimized the molecular geometries of these three bithienyls at the DFT//B3LYP/6-31G** level, and compared the main skeletal bond lengths of the π-conjugated backbone in terms of the so-called bond-length-alternation (BLA) parameter. The overall summations of the B3LYP/6-31G** atomic charges for the thienyl rings and the various types of end α,ω-substituents have also been compared along the bunch of compounds. Finally we make use of the well-known effective conjugation coordinate (ECC) theory to assess useful information about the π-conjugation, computing the B3LYP/6-31G** value of the force constant associated to the collective ECC vibrational normal mode.

Keywords: Oligothiophenes; π-Conjugated materials; FT-Raman spectroscopy; DFT calculations

1. Introduction

Organic semiconductors are currently receiving significant attention as new functional materials to be used in organic field-effect transitions (OFETs) [1], organic light emitting diodes (OLEDs) [2], photodiodes [3], and capacitors [4]. At present, OLED displays are being brought to the marketplace, and OFETs are strong candidates for switching devices for OLED, electronic paper and flat-panel liquid-crystal displays [5]. Additionally, low-cost 'smart cards', radio-frequency ID tags and printable transistors are under active investigation [6].

p-Type organic semiconductors such as oligothiophenes, acenes, phathalocyanines and poly-3-alkylthiophenes, in which holes are the main carriers, have been extensively studied over the last years. However, there are not many n-type organic semiconductors compared to p-types ones. High performance n-type molecular materials will enable the fabrication of p–n junction devices and complementary logic circuits. Recently, n-type thiophene-based compounds such as fluorocarbon and fluorophenyl-substituted oligothiophenes [7] and some dicyanomethylene-substituted quinoidal oligothiophenes [8] have been reported as high performance electron-transporting materials. These n-type materials were obtained by modifying known p-type 'cores' with strong electron-withdrawing substituents.

Vis-NIR electronic absorption and IR and Raman vibrational spectroscopies are among the early techniques most widely used over the last 15 years to study very many classes of electrically conducting polymers and π-conjugated oligomers. Raman spectroscopy has been shown to be particularly useful in: (i) estimating the degree of π-conjugation in neutral state [9–11], (ii) characterizing different types of conjugational defects in doped materials [12], and (iii) analyzing the efficiency of the intramolecular charge transfer in push–pull π-conjugated NLO-phores [13,14]. The usual observation of rather a few and overwhelmingly strong Raman scatterings, even for molecular materials with complex chemical structures, has been successfully explained, in the framework of the effective

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conjugation coordinate (ECC) theory [15], in terms of the occurrence in these quasi one-dimensional systems of a rather effective electron-phonon coupling taking place over the whole π-backbone path. In polyaromatic and polyheteroaromatic π-conjugated systems, the so-termed as *collective ECC vibrational coordinate* can be analytically defined as the linear combination of skeletal C=C/C–C stretching oscillations mostly pointing towards the structural evolution occurring in the system in passing from the benzenoid form (usually that of the ground state) to the quinonoid form (namely, that corresponding to the electronically excited state or the charged species). ECC theory states that, upon increasing conjugation length (CL), totally symmetric vibrational normal modes of the neutral system largely involved in the lattice dynamics of the ECC coordinate (namely, those giving rise to the few selectively enhanced Raman scatterings experimentally observed) undergo sizeable dispersions both in frequency and intensity. Thus, changes in the peak positions and relative intensities of the Raman features with increasing chain length are particularly useful in evaluating the *mean conjugation length* for the members of a given homologous series of neutral oligomers. On the other hand, when π-conjugated α-linked oligomers, and particularly aromatic non-polar oligothiophenes, become oxidized (either chemically or electrochemically), various types of quinonoid-like charged defects are created [16]. These structural modifications also induce a significant redshift of the Raman lines associated to the π-conjugated backbone (i.e. due the softening of the C=C bonds). Thus, the Raman spectral changes between the neutral and doped forms of a given system can provide valuable information to elucidate the nature of the charged carriers induced by chemical or electrochemical doping [9–12].

We report herein on a comparative study, by means of FT-Raman spectroscopy and DFT quantum chemical calculations, of three different types of oligothiophenes: (i) a p-type 5,5′-dimethyl end-capped bithiophene (**DMBT**), (ii) a n-type 5,5′-bis(dicyanomethylene)-5,5′-dihydro-2,2′-bithiophene (**Th2CN4**) and (iii) a push–pull 5-dimethylamino-5′-cyano-2,2′-bithiophene (**Me$_2$N–T$_2$–CN**) NLO-phore. The main aim of this work is to derive useful information about the conjugational properties of these systems from their Raman features with the help of DFT//B3LYP/6-31G** molecular dynamics calculations and upon the light of the concepts developed in the ECC theory.

2. Experimental and computational details

FT-Raman spectra were recorded on pure solids in sealed capillaries in a back scattering configuration with the FRA 106/S modulus of a Bruker Equinox 55 FT-IR interferometer, operating upon a 1064 nm Raman excitation from an infrared diode pumped Nd-YAG laser. Signal detection was carried out by means of a germanium detector working at liquid nitrogen temperature.

DFT calculations were performed with the GAUSSIAN 98 program [17] running on a SGI Origin 2000 supercomputer. Molecular geometry optimizations were performed with the B3LYP functional and the 6-31G** standard basis set [18,19]. All geometrical parameters were allowed to vary independently apart from planarity of the rings. Symmetry constraints were imposed for the two non-polar end-capped molecules (i.e. **DMBT** and **Th2CN4**). On the resulting ground-state minimum-energy structures, we also computed analytically with the B3LYP functional the harmonic force fields from which normal vibrational frequencies, intensities and the corresponding vibrational atomic displacements in the 3*N* Cartesian coordinates are derived. In molecular dynamics calculations it is customary to use however internal vibrational coordinates *R*, were *R* represents a set of bond stretching, angle bending or torsional coordinates [20–23]. For finite molecules local (three branches) and cyclic redundancies usually occur and can be completely removed by defining a new set of 3*N*-6 symmetry or group coordinates *S* orthogonal to the redundancy conditions. In this paper we follow the method proposed by Pulay et al. [24] to remove systematically all redundancies occuring in our systems.

In matrix notation the linear transformations between coordinates are $\mathbf{R}=\mathbf{Bx}$ and $\mathbf{S}=\mathbf{UR}$. Then the potential energy in Cartesian coordinates:

$$2\mathbf{V} = \mathbf{x}^t\mathbf{F}_x\mathbf{x}$$

can be re-expressed in terms of the S coordinates as:

$$2\mathbf{V} = \mathbf{S}^t\mathbf{U}^{-1t}\mathbf{B}^{-1t}\mathbf{F}_x\mathbf{B}^{-1}\mathbf{U}^{-1}\mathbf{S}$$

For the solution of the vibrational problem for finite molecules we follow the Wilson's method [25] and solve the eigenvalue equation:

$$\mathbf{G}_S\mathbf{F}_S\mathbf{L}_S = \mathbf{L}_S\Lambda$$

Where $\mathbf{G_S}$ is the kinetic energy matrix, and contains information about the atoms which constitute the molecule and their equilibrium positions, $\mathbf{F_S}$ is the matrix of the Pulay force constants, $\mathbf{L_S}$ is the matrix of the vibrational amplitudes and Λ is the diagonal eigenvalue matrix. The normal frequencies λ_i, in cm^{-1}, can be obtained from eigenvalues, ν_i, through the relation $\nu_i=(\lambda_i/4\pi^2c^2)^{1/2}$.

It is known that semiempirical or ab initio quantum chemical methods overestimate the vibrational frequencies and force constants, especially the diagonal stretching terms. It is customary to introduce a set of scaling factors, acting on the force constants, to reduce the discrepancies between calculated and experimental data. We have made use in the past [25] of the scaling method of harmonic force fields proposed by Pulay et al. [26], but in the present work force constants were not scaled. Nonetheless, to improve the comparison between the experimental and theoretical