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FT-Raman spectroscopic study, aided by quantum chemical DFT calculations, of a series of oligothiophenes end-capped by nitriles

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Abstract

We report on the FT-Raman spectroscopic characterization, aided by DFT model chemistry calculations, of a bunch of α,ω-dicyano end-capped oligothiophenes, ranging in length from the dimer to the hexamer, which have been previously shown to display quite promissing amphoteric redox properties for their potential use in new technological applications. The attention is mainly focused to the role played by the CN···H hydrogen bonding interactions between adjacent molecules on various molecular properties, such as the minimum-energy geometry, atomic charges equilibrium distribution,topologies/energies of the frontier molecular orbitals and the Raman scattering spectral profile. To this end we have performed to two sets of quantum chemical calculations, at the DFT//B3LYP/3-21G* level, on: (a) a single terthiophene in the vacuum and (b) a suited dimeric model with a fully coplanar array of the two terthienyl segments interacting through the cyano end-caps.

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

1. Introduction

We investigate herein by means of FT-Raman spectroscopy and DFT model chemistry some α,ω-dicyano end-capped oligothiophenes, which have been previously found to display a interesting amphoteric redox behavior for new technological applications [1]. Oligothiophenes have received great attention over the last decade for their potential use in a variety of molecular electronic and photonic devices, including nonlinear optics [2], Schottky diodes [3], organic light-emitting diodes (OLEDs) [4], and thin-film effect transistors (FETs) [5].

The Raman spectral features of these α,ω-dicyano end-capped oligothiophenes are analyzed with the help of DFT//B3LYP/3-21G* calculations, with the purpose of deriving information about the role played by the CN···H intermolecular interactions on different properties, such as optimal geometry, equilibrium charge distribution, topologies/energies of the frontier molecular orbitals around the gap and the Raman scattering vibrational spectrum from the comparison between the DFT//B3LYP/3-21G* quantities computed for a single terthiophene in the vacuum and for a dimeric model with the fully coplanar array of the two terthenyl mioeties most suited to favour the CN···H intermolecular interactions.

2. Experimental and computational details

The FT-Raman spectra were recorded either on pure solids or dilute solutions in sealed capillaries in a back scattering configuration by means of 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

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was carried out by using a germanium detector working at liquid nitrogen temperature.

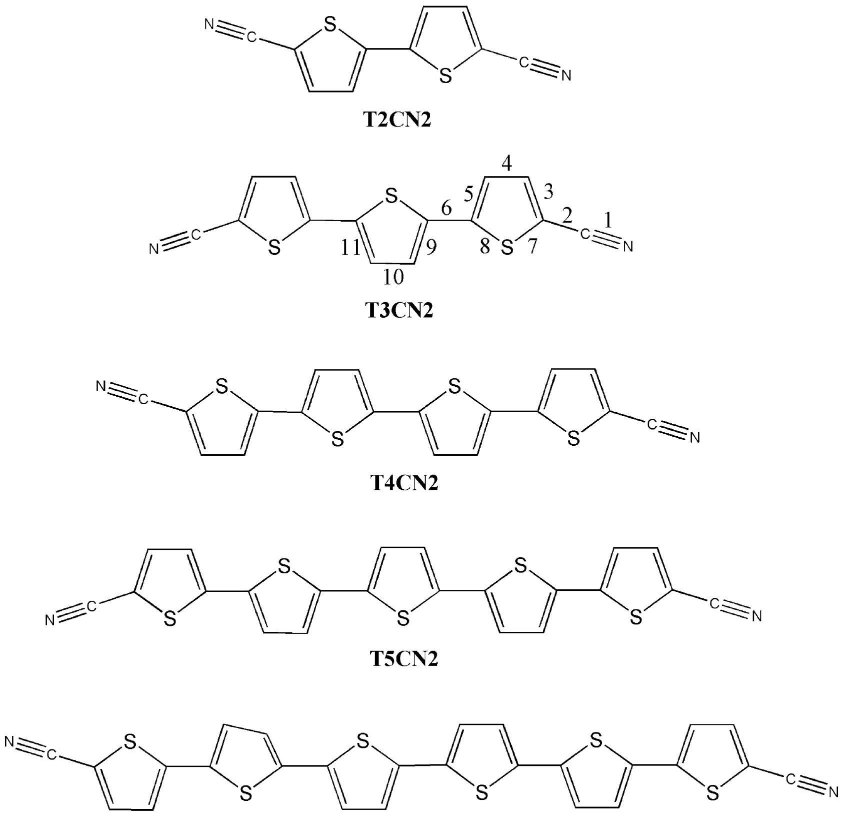
DFT calculations were carried out with the GAUSSIAN 98 program [6] running on a SGI Origin 2000 supercomputer. Molecular geometry optimizations were performed with the B3LYP functional and the 3-21G* standard basis set [7,8]. All geometrical parameters were allowed to vary independently apart from planarity of the rings. On the resulting ground-state molecular geometries, the harmonic vibrational frequencies and intensities were computed analytically with the same functional. We followed the nowadays rather usual adjustment of theoretical force fields in which 3-21G* theoretical frequencies are uniformly scaled down by a factor of 0.98, as recommended by Scott and Radom [9]. This quite simple scaling procedure, however, is often accurate enough to disentangle serious experimental misassignments. All quoted vibrational frequency values reported along the paper are thus the scaled ones. Theoretical spectra were plotted by convoluting the scaled frequencies with Gaussian functions (10 cm^{-1} width at the half-height). The relative heights of the Gaussians were determined from the DFT//B3LYP/3-21G* Raman activities.

3. Results and discussion

3.1. Optical absorption data

The chemical structures and abbreviate notation of the homologous series of α,ω-dicyano end-capped oligothiophenes studied in this article are depicted in Fig. 1. The synthesis of the oligomers has been reported elsewhere [10].

Table 1 lists the maxima ($\lambda_{\max}$) of the strong absorption band of each α,ω-dicyano end-capped oligothiophene in the visible spectral region, measured both in CH_2Cl_2 and DMSO solutions. The peak position of this visible absorption, which is attributable to the one-electron π–π* transition, largely redshifts with increasing chain length of the oligomer; the optical absorption data also show that these π-conjugated materials are characterized by a smaller HOMO–LUMO separation than their unsubstituted oligothienyl counterparts. In this regard, the attachment of a pair of electron-withdrawing cyano groups to the end α,ω-positions of the terthienyl induces a bathochromic shift of ≈50 nm. A similar, but larger effect has been previously observed upon dinitro substitution of terthiophene, the redshift being mainly caused by the sizeable stabilisation of the LUMO frontier orbital upon end-capsulation of



T2CN2

T3CN2

T4CN2

T5CN2

T6CN2

Fig. 1. Chemical structures and abbreviate notation of the various α,ω-dicyano end-capped oligothiophenes under study (the bond numbering of the trimer is to be used in Table 3).