I. INTRODUCTION

Molecular electronics promises to use single molecules as the basic operational elements of future computational architectures.1,2 The transition from semiconducting bulk arrays to single molecule-based systems may increase the performance of present electronic devices by several orders of magnitudes.3,4 To set the stage for molecular electronics research, it is important to perform precise experiments and computations on single molecules to determine their optical, electrical and electronic properties.5

Oligomeric materials with conjugated \( \pi \)-electron systems have attracted considerable interest during recent years because of their promising electronic properties.6,7 Oligothiophenes are perhaps the most thoroughly investigated and for example as light emitting diodes and field-effect transistors.10–15 Furthermore, the use of oligomeric systems solve the problem of the low solubility and processability of their parent polythiophenes as well as offers large freedom in term of designing materials with well-defined conjugation length and substitution patterns.6

It is at present well-documented that: (i) bulk conjugated organic materials can be semiconducting or even conducting when doped,6 (ii) rigid rod conjugated oligomers derived from thiophene orient themselves on gold surfaces,16 and (iii) electronic conduction is recorded through single undoped conjugated molecules that are end-bound onto a metal probe surface.17 The characterization of the electronic structure alterations produced by the moiety that allows the connection of a single molecular system (oligothiophenes) to a macroscopic interface, usually a metallic tip or a nanoscale cluster, is of fundamental importance in order to design molecular circuits, self-assembled monolayers, etc. The majority of systems studied so far use thiol-terminated molecules as connectors, because of sulfur’s ability to bond to metal surfaces.18–20 Recent works have shown that the surface bonding can be strong enough to distort the electronic structure of the molecule, thus substantially affecting the contact
Vibrational spectroscopy is one of the most useful tools for deriving information at a molecular level (i.e., intramolecular and electronic structures, conformational properties, etc.).

Effective conjugation coordinate (ECC) theory states the suitable formulation of the amplitude mode theory in terms of classical molecular parameters (i.e., internal coordinates, force constants, etc.) and provides a framework for interpreting the Raman spectra of conjugated molecules under the assumption of the existence of an effective π-electron delocalization or conjugation. In other words, intramolecular electronic interactions in conjugated molecules as a function of chain length and/or substituent can be inferred from the analysis of the Raman spectra. Central concept in the ECC theory is the definition of the ECC coordinate or mode. This coordinate can be described as a collective mode made up of ring C=C/C—C stretching vibrations which involves the major vibrational spectroscopic aspects of polycoujugated molecules because it describes all the important structural and electronic changes occurring upon chain elongation, doping or photoexcitation, etc. In heteroaromatic systems, when π-electron delocalization increases (HOMO-LUMO energy gap decreases) the aromatic character of the π-electron system decreases, that is to say, the strength of the C=C double bonds decreases while that of the CC single bonds increases. Therefore, from a vibrational point of view, the frequencies associated to C=C stretching vibrations downshift. Also, any conformational or structural factor that could affect the electronic delocalization gives rise to modifications in intensity and wave number of the bands associated to the ECC mode.

Density functional theory (DFT) has proved to be a very effective method to estimate the ground-state geometry as well as the vibrational frequencies and intensities of many classes of oligothiophene molecular materials. In this paper, we will analyze the vibrational features of a novel series of α,ω-bis(mesitylthio)oligothiophenes, both experimentally and theoretically, taking as reference a previously studied series of α,ω-methyloligothiophenes in order to derive information about the type of electronic interaction between the end mesityl groups (as model of macroscopic surface) and the central oligothiophene moiety (as a molecular wire model) through the α,ω-sulphur bonds (as surface connectors).

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

The α,ω-bis(mesitylthio)oligothiophenes and the ethylendioxy derivatives were synthesized following the procedure described elsewhere. Figure 1 depicts the chemical structures of these compounds.

Infrared measurements were made with a Bruker Equinox 55 FT-IR spectrometer fitted with a Golden Gate single reflection ATR accessory kit from Specac. All spectra were collected using a resolution of 2 cm⁻¹, and the mean of 50 scans was averaged. FT-Raman measurements were performed using the FRA 106/S modulus of the Bruker Equinox 55 spectrometer. A Nd:YAG laser source (λexc = 1064 nm) was used for Raman excitation, with an operating power of 100 mW. 500 scans were averaged in order to improve the signal–noise ratio. Raman spectra were typically acquired in a back-scattering configuration. Raman spectra of the solutions were carried out in fresh 1,2-dichloromethane of analytical grade purchased from Aldrich.

DFT calculations were carried out with the GAUSSIAN 98 program using a SCI Origin 2000 supercomputer. We used the Becke’s three-parameters exchange functional combined with the LYP correlation functional (B3LYP). It has already been shown that the B3LYP functional yields similar geometries and vibrational properties for medium size molecules as MP2 calculations do with the same basis set. We also made use of the 6-31 G** basis set, which includes...
a set of six second-order (d-type) Gaussian primitive functions for the description of each heavy atom and a single set of Gaussian p-polarization functions for hydrogens. Molecular optimizations were carried out on isolated identities in the vacuum. All geometrical parameters were allowed to vary independently apart from planarity of the rings and keeping the all-anticonfiguration for the central oligothiophene backbone. The harmonic vibrational frequencies and the infrared and Raman intensities were calculated analytically on the resulting ground-state optimized molecular geometries. The theoretical frequencies were uniformly scaled down by a factor of 0.96. All quoted vibrational frequencies reported along the paper are thus scaled values.

III. THEORETICAL OPTIMIZED MOLECULAR GEOMETRIES

No x-ray diffraction data or crystalline structures are available for the compounds studied here. To overcome the absence of structural data, theoretical vibrational spectra for different molecular conformations were compared with the experimental solid-state spectra, to decide about the more probable molecular structure. Figure 2 compared the experimental infrared spectrum of MesS₂T with the theoretical B3LYP/6-31G** spectra obtained on two different conformations: (i) on the fully coplanar molecule (i.e., with the two mesitylthio groups and the bithiophene spine in the same plane) and (ii) on the minimum energy conformation (with the two end-capping mesitylthio groups twisted from the central bithiophene least square plane). The experimental spectra pattern better agrees with that of the nonplanar conformation, thus suggesting the twisted molecular structure as the more probably one in the solid state.

Figure 3(a) depicts the B3LYP/6-31G** optimized geometry of MesS₂T and shows that the mesityl groups are nearly perpendicular to the central bithiophene moiety, likely due to the close contact between the methyl groups, the β hydrogens of the thiophene rings and the lone electron pairs of the sulphur atoms at the α,ω-positions in the fully coplanar structure. Furthermore, the bonds between the mesityl groups and the α,ω-sulphur atoms are also in the same plane that the π-conjugated bithiophene spine, so that only the α,ω-sulphur atoms have the right geometry to electronically interact with the bithienyl spine but not the mesityl groups.

As mentioned above, no crystallographic data were obtained for these samples since they are amorphous in nature, and appear as powdered solid samples at room temperature. In this regard, the largely twisted molecular structure obtained from the B3LYP/6-31G** theoretical calculations is fully consistent with this experimental fact, since it precludes for a suitable packing of the molecules in a well-ordered crystal lattice. As large fluorescence and phosphorescence quantum yields and other optical properties seem to be related with the amorphous nature of organic thin films (glasses molecules), the twisted conformation of these mesitylthiooligothiophene materials could be useful in their practical application in electroluminescence or optoelectronic devices.

As another result, we observe that the B3LYP/6-31G**
distances of the α-ω C—S bonds are too large as compared with those of an α-ω-bis(propylthio)quaterthiophene (DPTQtT): 1.779 Å in MesS1T and 1775 Å in MesS2T versus 1.765 Å in DPTQtT. The steric repulsion between the mesityl groups, the thiophene rings and the lone pairs of the sulphur atoms are probably responsible for these relatively long distances. We also observe that as the oligothiophenyl chain gets longer, the B3LYP/6-31G** distances of the α-ω C—S bonds slightly shorten from 1.779 Å (MesS1T) to 1.773 Å (MesS4T), due to the increasing participation of the α-ω-S atoms in the overall π-conjugation of the system. The variations of the average C—C and C—C ring bond lengths on going from MesS2T (1.376 and 1.422 Å, respectively) to MesS4T (1.380 and 1.419 Å) also reflects the increasing π-conjugation of the system as the oligothiophenyl chain gets longer. On the other hand, the average values of the C—C and C—C ring bond lengths obtained for an α-ω-bis(methyl)bithiophene (DMBT) at the same level of calculation (1.372 and 1.424 Å, respectively) reveal that DMBT is less conjugated than MesS2T. Contrarily, the comparison between the average B3LYP/6-31G** C—C and C—C ring bond lengths for MesS4T and the α-ω-bis(propylthio)quaterthiophene mentioned above (i.e., 1.380 Å and 1.419 Å, respectively, in MesS4T versus 1.388 Å and 1.418 Å in DPTQtT) indicates that the attachment of mesityl groups to the α-ω-S atoms partially lower the overall π-conjugation of the system with respect to the case of the alkylthio α-ω-side chains. This simple analysis of the theoretical molecular geometries suggests that the π-conjugation in the α-ω-bis(mesitylthio)oligothiophenes is larger than in the α-ω-bis(alkyl)oligothiophenes, but lower than in the α-ω-bis(alkylthio)oligothiophenes.

IV. INFRARED SPECTRA

The FT-IR spectra of the neutral forms of the α-ω-bis(mesitylthio)oligothiophenes in solid state are plotted in Fig. 4, whereas the wave number values for the main infrared absorptions are summarized in Table I. The band due to the antisymmetric C—C stretching vibration of the mesityl groups appears near 1600 cm⁻¹. The constant peak position of this vibration along the series of compounds shows that the mesityl groups are not conjugated with the oligothiophene backbone, likely due to the sizeable deviation of the end-capping rings from coplanarity.

Infrared absorptions at 1499 cm⁻¹ (MesS1T), 1499 cm⁻¹ (MesS2T), 1494 cm⁻¹ (MesS3T), and 1492 cm⁻¹ (MesS4T) must be assigned to an antisymmetric C—C stretching vibration of the thiophene rings, ν̃(C—C). This bond correlates quite well with the theoretical one at 1497 cm⁻¹ in the B3LYP/6-31G** infrared spectrum of MesS4T. On the other hand, bands at 1433 cm⁻¹ (MesS1T), 1426 cm⁻¹ (MesS2T), 1426 cm⁻¹ (MesS3T), and 1425 cm⁻¹ (MesS4T) are to be compared with the theoretical feature at 7422 cm⁻¹ in the B3LYP/6-31G** infrared spectrum of MesS4T, and they arise from an out-of-phase symmetric C—C stretching mode of the thiophene rings, νs(C—C). Eigenvectors for these theoretical vibrations are available upon request to the authors. In the α-ω-bis(methyl)oligothiophenes, the corresponding νs(C—C) mode appeared at around 1445 cm⁻¹, and it scarcely shifted with increasing chain length. The appearance of the ν̃(C—C) and νs(C—C) vibrations at lower frequency values in the mesitylthio-series than in the methyl-series of end-capped oligothiophenes could be explained in terms of the extra-conjugation of the α-ω-sulphurs lone pairs with the oligothiophenyl backbone, which should induce a certain weakening of the ring C—C bonds.

Weak IR bands recorded at 950 cm⁻¹ (MesS1T), 994 cm⁻¹ (MesS2T), 990 cm⁻¹ (MesS3T) and 987 cm⁻¹ (MesS4T) are in good agreement with the B3LYP/6-31G** vibrations at 993 and 977 cm⁻¹ in MesS2T and MesS4T, respectively. These infrared absorptions correspond to the out-of-phase stretching mode of the C—S bonds at the end α-ω-positions of the π-conjugated backbone, ν(C—S). The wave number value for this vibration is lower in MesS1T than in the other three oligomers, what is consistent with the longer α-ω C—S bonds for this compound. As the chain length of the oligothiophene moiety increases, the lone pairs of the α-ω sulphur atoms more extensively contribute to the overall π-conjugation of the system, and this the C—S bond become shorter and higher the wavenumbers of their associated stretching vibrations.

Let us finally mention another interesting feature related to the infrared intensities. The out-of-plane deformation vibrations of the C—H bonds, γ(CH), at the β-positions of the thiophene rings are usually recorded as an overlap of very strong absorptions centered at 795 cm⁻¹. In addition, the γ(CH) vibrations have a marked local character, being fully decoupled from the other vibrational motions of the
oligothienyl backbone. Thus, the characteristic γ(CH) peak may be used, at a first glance, as an internal reference for comparing the relative intensities of other infrared absorptions among several series of oligothiophenes.22 In this regard, we observe that the band associated to the \( v_{\text{anti}}(C\equiv C) \) and \( v_{\text{sym}}(C\equiv C) \) vibrations display a stronger intensity in the mesitylthio compounds under study than in the \( a,\nu \)-bis(mesitylthio)oligothiophene series.34 A possible explanation is that extra-conjugation by the \( a,\nu \)-sulphur atoms gives rise to larger charge fluxes during the vibrational motions of the oligothiophene backbone and stronger IR-activities.

V. RAMAN SPECTRA

Figure 5 shows the Raman spectra of the \( a,\nu \)-bis(mesitylthio)oligothiophenes, while the theoretical B3LYP/6-31G** spectra of MesS1T, MesS2T, and MesS4T are shown in Fig. 6. Figure 7 displays the eigenvectors associated to the most relevant Raman bands of MesS4T. Vibrational calculations account for the main experimental features, and satisfactorily agree with the simple appearance of the Raman spectral profiles notwithstanding the very large number of vibrational degrees of freedom predicted by the optical selection rules.

TABLE I. Correlation between the infrared absorptions (in cm\(^{-1}\)) of the \( a,\nu \)-bis(mesitylthio)oligothiophenes in neutral form as solids.

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<th>MesS1T</th>
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The weak band recorded around 1600 cm\(^{-1}\) for all the compounds must be correlated with the theoretical vibration at 1593–1592 cm\(^{-1}\) in the B3LYP/6-31G** Raman spectrum of MesS4T. The associated eigenvectors show that the experimental band arises from a totally symmetric C\(=\)C stretching mode of the mesityl groups, \(\nu_{\text{mes}}(C=C)\). The fact that this vibration is recorded almost at the same wave number value for all the oligomers, together with its quick disappearance with increasing chain length, further confirms that the mesityl end-caps do not electronically interact with the oligothiophene backbone.

The Raman spectra of any series of oligothiophenes (in the neutral state) show a typical dependence between the peak positions of the stretching vibrations of the conjugated C\(=\)C bonds and the number of repeating units in the chain. These experimental observations were accounted for by the ECC theory 15 years ago.\(^{23,24}\) In this regard, we observe that the strongest Raman band of MesS1T is recorded at 1408 cm\(^{-1}\), being its peak position rather similar to that in 3-methylthiophene and unsubstituted thiophene, while the other bands in the 1600–1000 cm\(^{-1}\) spectral region display much less intensity.\(^{36}\) Contrarily, the longer oligomers show the characteristic Raman profile already found in many series of oligothiophenes, with two main \(\nu(C=C)\) stretching vibrations at 1549 and 1438 cm\(^{-1}\) (MesS2T), 1526 and 1454 cm\(^{-1}\) (MesS3T), 1515 and 1454 cm\(^{-1}\) (MesS4T). The line at higher energy undergoes a sizeable downward dispersion as the oligomeric chain grows longer (due to the softening of the \(\pi\)-conjugated backbone), while the peak position of the second line scarcely shifts from one member to another along a given series of compounds.

The strong lines at 1549 cm\(^{-1}\) (MesS2T), 1526 cm\(^{-1}\) (MesS3T), and 1515 cm\(^{-1}\) (MesS4T) are to be correlated with the vibrations on MesS2T and MesS4T calculated at 1544 and 1513 cm\(^{-1}\), respectively (which are predicted with a great accuracy at the B3LYP/6-31G** level). The theoretical eigenvector for this Raman mode corresponds to a antisymmetric C\(=\)C stretching vibration (if one looks at the individual chemical units), being mainly centered on the outer rings of the oligothiophene chain, along which the vibrational displacements of the symmetry-equivalent atoms take place in-phase. This characteristic Raman line is usually termed as line A, and its chain length dispersion is strongly related to the efficiency of the \(\pi\)-electrons degree of freedom.\(^{37}\) For example, line A has been measured at 1546 cm\(^{-1}\) in \(\alpha,\omega\)-bis(methyl)thiophene (DMTT), 1533 cm\(^{-1}\) in \(\alpha,\omega\)-bis(methyl)quaterthiophene (DMQqT) and 1525 cm\(^{-1}\) in \(\alpha,\omega\)-bis(methyl)quethiophene (DMQqT). By comparing both series of oligothiophenes, we observed that line A is measured at close wave number values in MesS2T and DMTT, and in MesS3T and DMQqT, what could be accounted for in terms of the extra-conjugation of the lone pairs of the \(\alpha,\omega\)-sulphur atoms in the mesitylthio derivatives.

The very strong Raman scatterings at 1438 cm\(^{-1}\) (MesS2T), 1454 cm\(^{-1}\) (MesS3T), and 1454 cm\(^{-1}\) (MesS4T) must be related to the theoretical vibration of MesS4T at 1439 cm\(^{-1}\), which is predicted to have the strongest activity among all the Raman-active normal modes. The eigenvector associated to this skeletal vibration highlights its marked collective character: it spreads over the whole \(\pi\)-conjugated backbone of the molecule, and could be described as a symmetric C\(=\)C stretching mode (if one looks at each chemical unit) along which all the thiophene rings of the chain vibrate in-phase and with similar amplitudes. This line is usually termed as line B in the Raman spectra of the oligothiophenes.\(^{37}\) It has already been reported that line B experiences a large downshift with increasing conjugation length in oligopyrroles and oligofurans, however it scarcely shifts for the \(\alpha\) or \(\beta\) substituted oligothiophenes.\(^{37}\) For example, in the \(\alpha,\omega\)-bis(methyl)oligothiophenes, line B appears at 1492 cm\(^{-1}\) in DMBT, 1488 cm\(^{-1}\) in DMTT, 1492 cm\(^{-1}\) in DMQqT, 1481 cm\(^{-1}\) in DMQqT, and 1477 cm\(^{-1}\) in DMSxT. Thus, line B appears at lower wave numbers in the \(\alpha,\omega\)-bis(mesitylthio)oligothiophenes. On the other hand, the peak position of line B in MesS4T (i.e., a tetramer) is nearly coincident with that previously reported for unsubstituted 5T or 6T (i.e., a pentamer or hexamer).\(^{37}\) Moreover, we also observe that line B is recorded at even lower wavenumber values in MesS2T (1438 cm\(^{-1}\)) and MesS3T (1454 cm\(^{-1}\)) than in 5T and 6T (around 1460 cm\(^{-1}\)), what suggests that the extra-conjugation of the lone pairs of the \(\alpha,\omega\)-sulphur atoms mainly affects the outermost thiophene rings of the oligothienyl chain, and consequently the electronic properties of the shorter oligomers of the mesitylthio series.

The medium-weak Raman bands at 1426 cm\(^{-1}\) in MesS3T and 1427 cm\(^{-1}\) in MesS4T correlate with the theoretical vibrations of MesS4T at 1423–1422 cm\(^{-1}\). These Raman scatterings also correspond to a characteristic Raman-active normal mode commonly found in many classes of oligothiophene, which is usually terms as line C.\(^{37}\) The associated eigenvectors also show, as in the case of line B, their marked collective character: these normal modes can be described as a totally symmetric C\(=\)C stretching vibration along which the successive thiophene rings of the \(\pi\)-conjugated chain vibrate in fully out-of-phase and with similar amplitudes. This vibration is logically absent in the
Raman spectra of MesS1T and MesS2T, for which it should display a strong intensity only in the IR spectrum.

Weak Raman bands at 1300 cm\(^{-1}\) (MesS1T), 1336 cm\(^{-1}\) (MesS2T), 1354 cm\(^{-1}\) (MesS3T), and 1353 cm\(^{-1}\) (MesS4T) are due to a symmetric C—C stretching vibration of the thiophene rings, \(v\),(C—C), which in the B3LYP/6-31G** Raman spectrum of MesS4T is predicted to appear 1371 cm\(^{-1}\). The upshift of this \(v\),(C—C) mode with increasing chain length is consistent with the shortening of the aromatic C—C bonds as the \(\pi\)-electron delocalization increases.

Finally a medium-weak Raman intensity band is observed around 1055 cm\(^{-1}\) for the four compounds. This experimental feature correlates with the theoretical band at 1071 cm\(^{-1}\) in the B3LYP/6-31G** spectrum of MesS4T, and it is due to a totally symmetric in-plane \(\delta\)(C—H) deformation mode which spreads over the whole \(\pi\)-conjugated backbone. This line is usually termed as line D and it is strongly coupled with line B.\(^{37}\)

Figure 8 shows the Raman spectra of the \(\alpha,\omega\)-bis(mesitylthio)oligothiophenes recorded in 1,2-dichloromethane solution. Spectral differences between solutions and solids are small. This means that no relevant conformational distortions from coplanarity of the thiophene units take place upon solution with respect to the solid sample, and that \(\pi\)-conjugation is the driving force which determines the minimum energy molecular conformation either in the solid state or in solution.

VI. RAMAN SPECTRA OF THE EDO DERIVATIVES

The effects on the \(\pi\)-electrons conjugation of the attachment of electron donating groups at the \(\beta\)-positions of the thiophene rings have been also analyzed. In this regard we have recorded the solid state Raman spectra of an \(\alpha,\omega\)-bis(mesitylthio)terthiophene and an \(\alpha,\omega\)-bis(mesitylthio)quaterthiophene in which both \(\beta\)-positions of each outermost thiophene ring of the central moiety are connected through an ethylenedioxy bridge (compounds hereafter referred to as MesSEDO3T and MesSEDO4T, respectively. See Fig. 1 for chemical structures). Figure 9 shows the comparison between the Raman spectra of MesSEDO3T and MesSEDO4T and those of MesS3T and MesS4T.

As mentioned above, the peak position of the characteristic line A is quite sensitive to the degree of \(\pi\)-conjugation along a given series of oligothiophenes. As for MesSEDO3T and MesSEDO4T, line A can be assigned to the Raman band at 1492 and 1489 cm\(^{-1}\), respectively. Thus, line A is measured at substantially lower wave number values in the \(\beta,\beta'\)-ethylenedioxy derivatives than in the corresponding \(\beta\)-unsubstituted \(\alpha,\omega\)-bis(mesitylthio)oligothiophenes. According to the statements of the ECC theory, the large downshift (i.e., 34 cm\(^{-1}\) in the case of MesSEDO3T with respect to MesS3T and 26 cm\(^{-1}\) in the case of MesSEDO4T with respect to MesS4T) results from a more efficient \(\pi\)-conjugation upon the attachment of oxygen atoms at the \(\beta\)-positions of the oligothienyl backbone.

Figure 10 compares the experimental Raman spectrum of MesSEDO1T with the theoretical B3LYP/6-31G** one calculated on the optimized molecular structure [see Fig. 3(b)]. The satisfactory agreement between the experimental and theoretical vibrational spectra let us derive reliable infor-
formation from the molecular parameters calculated at the B3LYP/6-31G** level for the MesSEDO1T model system. The bonds between the α,ω-sulphur atoms and the thiophene ring are shorter than in MesS1T (i.e., 1.770 versus 1.779 Å). We also observe that the nearest distance between the oxygens of the EDO group and the hydrogens of the methyl groups, 2.90 Å, is of the order of those commonly found for the hydrogen bond-type interactions. Thus, attractive intramolecular forces can be anticipated to occur, from the B3LYP/6-31G** geometrical calculations, between the mesityl end-capping groups and the β,β'-ethylenedioxy bridge. In this regard, the angle defined by the two C=S bonds at each α-position goes from 105.8 degree in MesS1T to 101.2 degree in MesSEDO1T, what implies that the mesityl groups are more fold over the oligothiienyl spine that in the series of the α,ω-bis(mesitylthio)oligothiophenes [please compare Figs. 3(a) and 5(b)].

We notice in the Raman spectra of MesSEDO3T and MesSEDO4T the presence of a weak-medium band around 1500 cm\(^{-1}\), which becomes stronger with increasing chain length. This band could arise from a C==C ring stretching vibration mixed with the stretchings of the C=O bonds connecting the EDO bridges to the π-conjugated backbone. The selective enhancement of this vibration among all the Raman-active normal modes suggests that the oxygens of the EDO side groups contribute to some extent to the overall π-conjugation of the system. Although the oxygen lone pairs can overlap with the π-system through the C=O bonds, the π-HOMO of the oligothiophenes are usually calculated to have its largest atomic orbital coefficients at the C\(_a\) and moderately smaller contributions from the C\(_\beta\) ones. There exists another possibility to account for the contribution by the oxygens to the conjugational properties of the material: the noncovalent intramolecular interactions between the oxygens and the ring sulphur atom of the adjacent thiophene rings.

Finally, Raman spectroscopy seems to be a suitable tool to discriminate the contributions to the overall π-conjugation of the different constituting parts of the molecule. On going from the mesitylthio series to the EDO derivatives, there coexist in the π-conjugated spine two types of thiophene rings with different chemical environment: with and without β,β’-ethylenedioxy groups. This structural difference is nicely featured in the Raman spectra, since the well-resolved doublet at 1430 and 1448 cm\(^{-1}\) in the spectrum of MesSEDO3T is to be correlated with the single peak at 1454 cm\(^{-1}\) in MesS3T. Thus, the characteristic Raman line of the oligothiophene chains denoted as line B (which has a strong collective character, spreading over all the π-conjugated units) splits into two different components upon the attachment of EDO bridges to some of the thiophene rings.

### VII. CONCLUSIONS

We have performed a combined theoretical and vibrational study on a novel series of conjugated oligothiophenes with potential applications as molecular wires. These compounds are made up of a central oligothiophene spine of variable length, with their end α-positions capped with mesitylthio groups, and some of them also have ethylenedioxy groups attached at the β positions of the thiophene rings. These molecular materials can be viewed as conjugated oligomers bearing a thioether, –SR substituent, where the “substituent” R can play the role of the metal surface to which molecular wires should be connected in the “real” device. In this context, we address the study of how electronic properties of the conjugated spine are altered by sulfur-containing end groups.
The infrared and Raman vibrational features of these mesitylthiooligothiophenes have been studied with the help of accurate DFT/B3LYP/6-31G** quantum chemical calculations. The analysis of the data shows that the use of sulphur atoms as the strategy to link oligothiophenes to the metal surface or cluster is not justified only by the well known propensity of thiols to self-assemble onto gold surfaces but also by the possibility of conjugation of the sulphur lone pairs with the oligothienyl moiety giving rise to richer electronic systems. The evolution of the vibrational properties along the series of materials has been related with the conformational properties and the degree of π-electron conjugation of the oligothiophene spine.

Upon solution, the electronic properties of these mesitylthiooligothiophenes remain almost unchanged with respect to the solid state. This fact has been related with the role played by the π-electron delocalization in this class of systems, which is strong enough to determine the molecular structure almost independently on the intermolecular forces and/or solvent effects.

Finally, we have also analyzed the degree of π-conjugation in a related series of α,ω-bis(mesitylthio)oligothiophenes with some of the β,β’-positions connected through ethylenedioxy bridges. The π-conjugation in this second series of materials is somewhat more effective than in their β-unsubstituted homologues. This Raman spectroscopic observation has been attributed to the participation of the oxygen lone pairs, besides of that by the sulphur lone pairs at the α,ω-positions, in the overall π-conjugation of the system.

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