A Combined Spectroscopic and Theoretical Study of a Series of Aminomethyl End-Capped Oligothiophenes with Potential Applications in Thin Film Devices

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In this article, we investigate the vibrational properties of a series of π-conjugated α,α'-bis(aminomethyl)-oligothiophenes, in the pristine state, as solids. The FT-IR and FT-Raman spectra have been studied in relation to the effective conjugation length of the compounds. We have used ab initio calculations, at the B3LYP/6-31G** and RHF/6-31G** levels, as a support of the experimental analysis. Our study reveals that the aminomethyl end groups easily undergo a protonation process upon reaction with atmospheric moisture, although this does not affect the electronic structure of the π-conjugated spine. This structural characteristic of these oligothiophenes brings new practical applications for possible technological developments.

I. Introduction

Π-conjugated polymers are low band gap systems having attractive optical and electrical properties.[1] The controlled synthesis of oligomers with well-defined substitution patterns and chain lengths is receiving considerable attention since it constitutes the most straightforward procedure to establish the precise structure−property relationships of these materials.[2] The detailed study of these oligomers can stimulate advances in attempts to put the technology of electronic materials on a firm structural basis and to achieve fine-tuning of their fascinating properties by simple modification of their chemical structures.

The ability of conjugated materials as chromophores and electrophores is related to the degree of intramolecular delocalization of π-electrons along the molecular long axis. Thus, one of the main challenges of the oligomers research is to systematically investigate the relevant properties of extensively conjugated chains as a function of the "effective conjugation length", qualitatively defined as the length of the molecular domain over which delocalization takes place.

Among π-conjugated materials, oligothiophenes have gained importance for their contributions to the development of molecular electronics[3−5] or electro-optics.[6] Most oligothiophenes possess an all-anti arrangement of the rings which avoids for the steric interactions between the β-hydrogen atoms of adjacent units. Reliable structural data currently available have shown that these oligomers are essentially planar with a fully conjugated carbon skeleton.[7,8]

Much work has been devoted in past years to β-substituted oligothiophenes to obtain soluble materials easy to characterize and process.[9−14] In comparison with the β-substitution, the α,α'-disubstitution has the advantage of inducing only very small conformational distortions of the outermost rings, thus preserving the conjugation and the electronic properties of the materials.[15−19] Moreover, the synthetic strategy of appending substituents at the end α positions facilitates the investigation of stable and soluble radical cationic and dicationic model systems, which can provide insight into the conducting mechanism of doped polythiophene. Contrarily, in the unsubstituted or β-substituted oligothiophenes, the research of charged species is only possible for longer members, since shorter oligomers are inherently reactive and udergo follow-up reactions.

Vibrational spectra of π-conjugated chain compounds constitute a very rich source of information on their structure and properties if the analysis goes beyond the traditional correlations with the tabulated group wavenumbers. In particular, the Raman spectra of these systems show peculiar and characteristic features, which are directly related to the distance of interaction between the successive chemical units and whose interpretation has required the development in past years of new theoretical aspects.

Because of their structural variability and stability, end-capped oligothiophenes connected in α-positions are ideal materials for technological applications. The precise aim of this work is to analyze at the molecular level, by using both infrared and Raman spectroscopies and ab initio and DFT quantum chemical calculations, how the chemical modification of the end groups can affect the conjugational properties of three α,α'-bis(aminomethyl) oligothiophenes with increasing chain length. The substitution by aminomethyl groups at both molecular ends constitutes a suitable functionalization of the π-conjugated backbone to fabricate thin films by direct evaporation of the oligomer onto the substrate.[20]

II. Experimental and Theoretical Details

The α,α'-bis(aminomethyl) oligothiophenes were synthesized following the procedure described in a previous publication[21] (chemical structures are shown in Figure 1). FT-IR measurements were made with a Perkin-Elmer model 1760 X spectrometer. Oligomers were ground to a powder and pressed in a KBr pellet. All spectra were collected using a resolution of 2 cm^{-1}, and the mean of 50 scans was obtained. Interference from atmospheric water vapor was minimized by purging the instrument for 10−15 min with dry argon before beginning data

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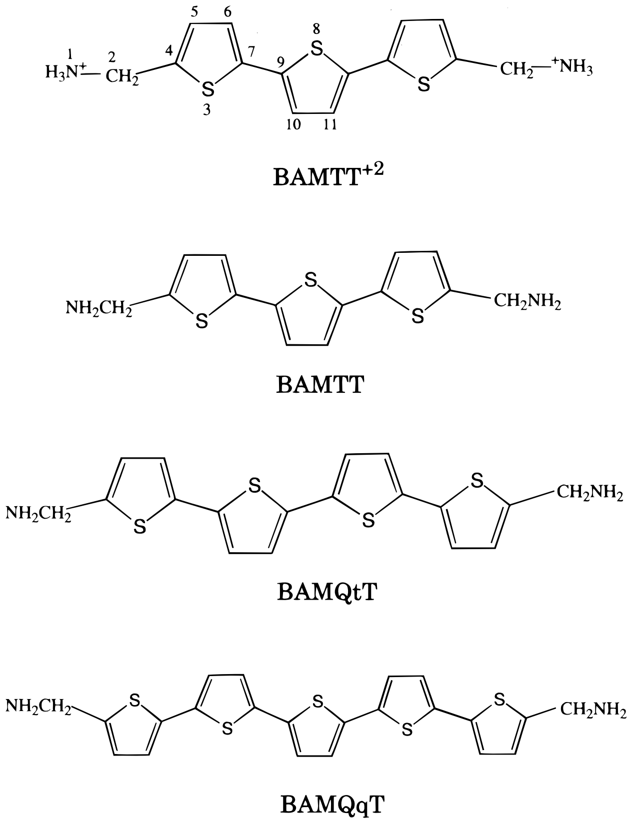

Figure 1. Chemical structures of the α,α′-bis(aminomethyl) oligothiophenes studied in this work.

collection. FT-Raman experiments were performed using a Bruker FRA106/S apparatus and a Nd:YAG laser source (λ_{exc} = 1064 nm). Data were typically acquired in a backscattering configuration. Operating power for the exciting laser was 100 mW in all experiments. Samples were analyzed as pure solids in sealed capillaries. 1000 scans were averaged to obtain adequate signal-to-noise ratios, and spectra were plotted without smoothing or baseline corrections.

Ab initio Restricted Hartree−Fock (RHF) and Density Functional Theory (DFT) calculations were carried out by means of the Gaussian 94 program[22] running on SGI Origin 2000 and CRAY-YMP supercomputers. As for the DFT method, we have used the Becke's three-parameter exchange functional combined with the LYP correlation functional (B3LYP),[23] as implemented in Gaussian 94. 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.[24,25] Moreover, the DFT force fields calculated using the B3LYP functional yield infrared spectra in very good agreement with experiments.[26,27] We also made use of the standard split valence 6-31G(d,p) basis set.[28]

We have investigated aminomethyl end-capped oligothiophenes up to the pentamer. The optimal geometries of the oligomers were determined on isolated entities. Only all-anti planar conformations were treated throughout due to the large cost of calculations and since the X-ray diffraction patterns demonstrate that the compounds comprise a well-defined molecular layered structure.[20] Oligomers with an even number of units are characterized by C_{2h} symmetry, while those with an odd number of rings present C_{2v} symmetry. On the ground-state optimized geometries, harmonic vibrational wavenumbers and infrared intensities were calculated analytically with the B3LYP functional. We recall however that Gaussian 94 does not provide the Raman activities for DFT calculations. This is because the Raman spectra have been calculated by using the RHF methodology. In this work, we have used the often-practiced adjustment of the theoretical force fields in which wavenumbers are uniformly scaled down by a factor of 0.96 for DFT and 0.90 for RHF calculations, as recommended by Scott and Radom.[26] This scaling procedure is often accurate enough to disentangle serious experimental misassignments. All quoted vibrational wavenumbers reported along the paper are thus scaled values.

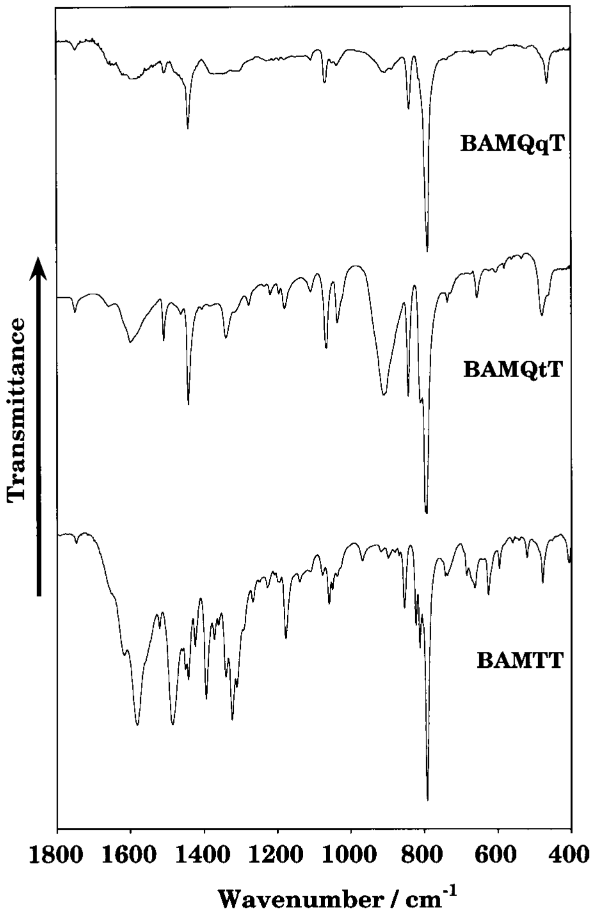

Figure 2. FT-IR spectra over probe energies of 1800−400 cm^{-1} of the α,α′-bis(aminomethyl) oligothiophenes in neutral form (obtained as powdered samples in pressed KBr pellets).

III. Results and Discussion

A. Infrared Spectra. The FT-IR spectra of the α,α′-bis(aminomethyl) oligothiophenes are shown in Figure 2 [the nomenclature used denotes for BAMTT = α,α′-bis(aminomethyl) terthiophene, BAMQtT = α,α′-bis(aminomethyl) quaterthiophene and BAMQqT = α,α′-bis(aminomethyl) quinquethiophene]. The complete assignment of the infrared bands of each oligomer to particular vibrations is beyond the scope of our analysis because of the problems associated with identifying and assigning normal modes when there is a overlap of absorptions in a specific spectral region. The situation is particularly complex for BAMTT. Nonetheless, meaningful structural information can be gathered from the direct inspection of the spectra.

The end-capped trimer shows a wealth of bands in the whole spectral region. For this short chain oligomer, it is expected to occur an intensive coupling between the characteristic vibrations of the two aminomethyl groups. As a consequence, some of their in-phase and out-of-phase motions would not degenerate but split into different components.

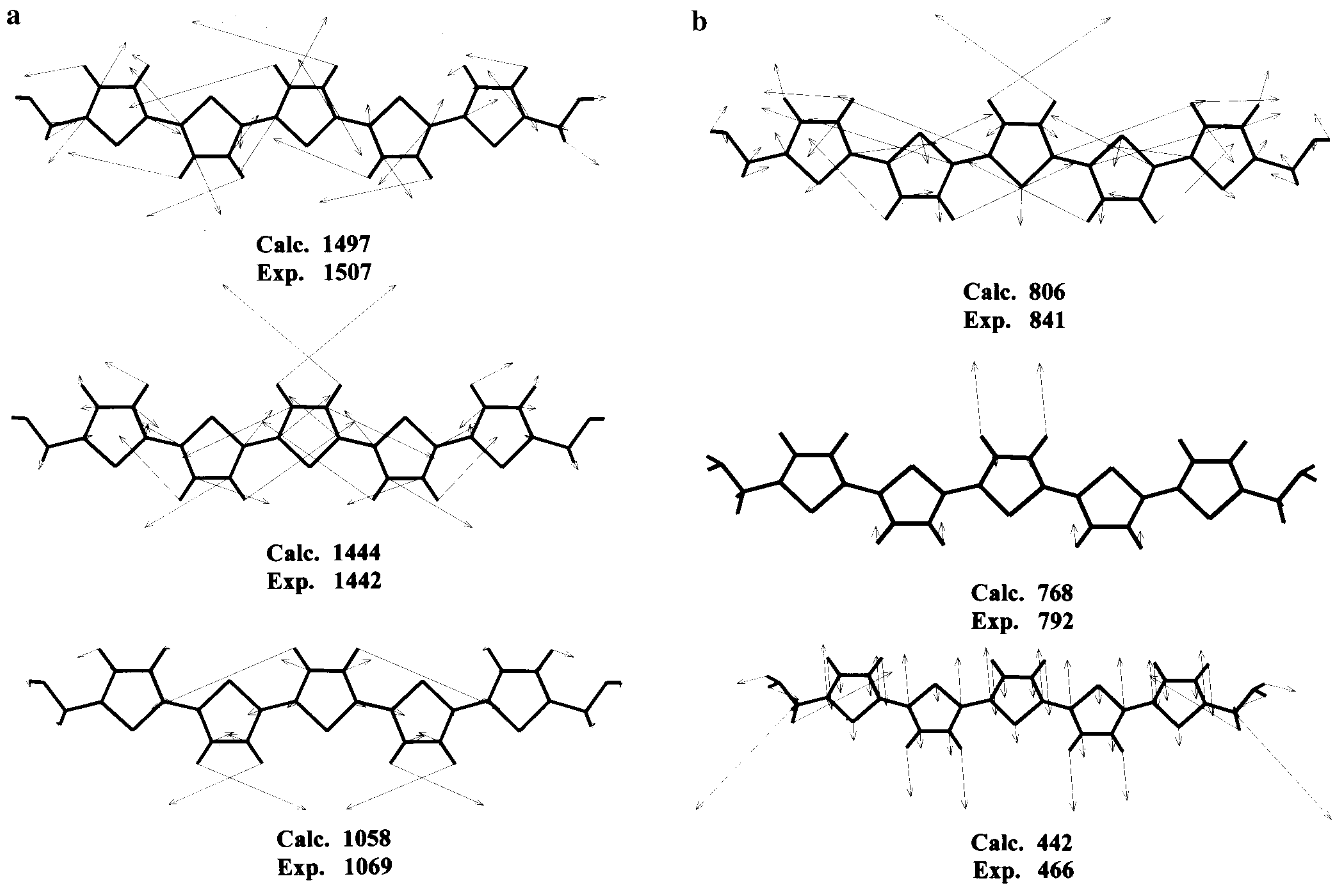

Figure 3. Schematic eigenvectors for the main infrared-active vibrations of α,α′-bis(aminomethyl)quinquethiophene, calculated at the B3LYP/6-31G** level (scaled and experimental wavenumber values are given in cm^{-1}).

Note, however, that the pentamer displays only a few and sharp absorptions. The increasing simplicity of the spectral pattern with increasing molecular size is consequence of the translational periodicity, thus approaching the optical selection rules of the polymer. The infrared bands measured at 1507, 1442, 1069, 841, 792, and 466 cm^{-1} can be roughly assigned to vibrations of the "bulk" rings, because of the quick extinction of the remainder absorptions with increasing chain length (see Figure 2).

Figure 3 displays the atomic vibrational displacements for the main infrared bands of α,α′-bis(aminomethyl) quinquethiophene, calculated at the B3LYP/6-31G** level. The theoretical results support the assignment of the bands at 1507 and 1442 cm^{-1} as an aromatic antisymmetric, ν_{as}(C=C), and symmetric, ν_s(C=C), stretching modes, respectively. The absorption at 1069 cm^{-1} is due to an in-plane δ(C−H) deformation mode. Finally, the three peaks at 841, 792, and 466 cm^{-1} arise from an symmetric ν_s(C−S) ring stretching mode, an out-of-plane γ(C−H) bending vibration, and an out-of-plane γ_{ring} folding mode, respectively.

As can be seen in Figure 2, the spectrum of BAMTT displays a considerable overlap of bands, particularly in the 1600−1300 cm^{-1} range. The absorptions at 1520, 1443, 1059, 855, 792, and 479 cm^{-1} are related to the normal vibrations of the π-conjugated backbone of the pentamer, assigned in the preceding paragraph. We observe that the antisymmetric ν_{as}-(C=C) vibration undergoes a softening, by about 13 cm^{-1}, as the chain length grows longer: 1520 cm^{-1} (BAMTT), 1510 cm^{-1} (BAMQtT), and 1507 cm^{-1} (BAMQqT). Contrarily, the chain length dispersion of the symmetric ν_s(C=C) vibration is vanishing: 1443 cm^{-1} (BAMTT), 1443 cm^{-1} (BAMQtT), and 1442 cm^{-1} (BAMQqT).

The broad absorptions centered at 1580, 1483, 1394, and 1323 cm^{-1} are completely absent in the infrared spectra of the unsubstituted α-oligothiophenes[29] and the α,α′-dimethyl end-capped oligothiophenes,[30] while all the bands attributable to vibrations of the π-conjugated backbone have a counterpart in both series of compounds. The strong intensity and broad appearance of the above bands make us suspect that they are related to motions of charged atoms. A likely explanation may be that the aminomethyl end groups suffer from a chemical modification (i.e., a protonation process after reaction with atmospheric moisture), which however does not substantially affect the electronic structure of the π-conjugated spine. The quick dissappearance of these broad absorptions in going to the pentamer further supports their assignment as end group vibrations. The protonation of the NH_2 group generates a positive charge density in the proximity of the N atom, thus transmitting very large infrared intensity to the characteristic vibrations of the end groups. The infrared spectral pattern of the protonated α,α′-bis(aminomethyl) terthiophene is however quite different from the FT-IR spectra of oligothiophenes radical cations.[31] This observation indicates that the positive charges are highly localized on both the $CH_2NH_3^+$ end moieties and do not extend so much toward the middle of the molecule. Thus, the CH_2 groups seem to act as effective electronic spacers, being the aminomethylation of the end α-positions an appropriate functionalization of the π-conjugated backbone to make thin films whithout damaging the electronic properties of the oligothiophene.

To gain a deeper insight into the effects of the protonation on the geometry, the atomic charge distribution, and the infrared spectrum, we have extented the B3LYP/6-31G** study to the diprotonated α,α′-bis(aminomethyl) terthiophene. Main bond

TABLE 1: Comparison of the Main Bond Lengths (in Å) between the Diprotonated Trimer and the Unprotonated One[a]

bond[b]	BAMTT^{+2}	BAMTT	bond[b]	BAMTT^{+2}	BAMTT
C_2-N_1	1.514	1.475	C_7-S_3	1.759	1.762
C_2-C_4	1.499	1.512	C_7-C_9	1.447	1.445
C_4-S_3	1.744	1.752	C_9-S_8	1.753	1.759
C_4-C_5	1.373	1.367	C_9-C_{10}	1.381	1.379
C_5-C_6	1.421	1.424	$C_{10}-C_{11}$	1.412	1.416
C_6-C_7	1.378	1.377			

[a] Results derived from DFT geometry optimizations at the B3LYP/6-31G** level of calculation. [b] See Figure 1 for atom numbering.

TABLE 2: Mulliken Atomic Charges (with Hydrogens Summed into Heavy Atoms) for the Diprotonated Trimer and the Unprotonated One, Calculated at the B3LYP/6-31G Level**

atom[a]	BAMTT^{+2}	BAMTT	atom[a]	BAMTT^{+2}	BAMTT
N_1	0.588	−0.108	C_6	0.062	0.006
C_2	0.269	0.132	C_7	−0.152	−0.157
S_3	0.337	0.224	S_8	0.322	0.261
C_4	−0.182	−0.142	C_9	−0.150	−0.149
C_5	0.017	0.055	C_{10}	0.051	0.007

[a] See Figure 1 for atom numbering.

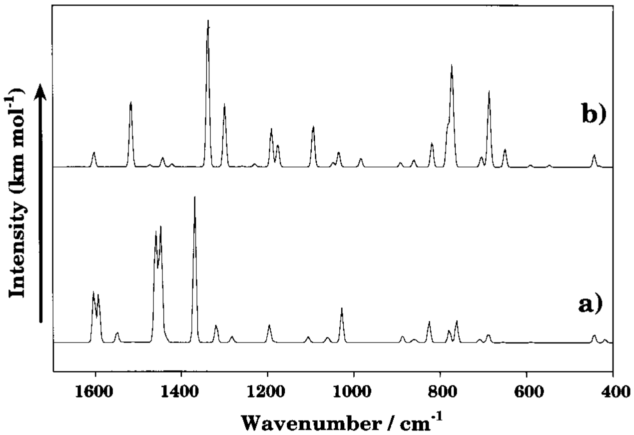

Figure 4. Comparison between the B3LYP/6-31G** theoretical infrared spectra of a) diprotonated α,α′-bis(aminomethyl)-terthiophene and (b) unprotonated trimer.

lengths for the diprotonated trimer are correlated to those of the unprotonated trimer in Table 1, while Table 2 summarizes the atomic charges (with hydrogens summed into heavy atoms) for both the systems. Comparatively, the geometry of each system is essentially the same, the main difference being the elongation by about 0.04 Å of the C−N bond distance upon protonation. It is worthwhile to notice that protonation of the NH_2 groups does not lead to large changes in the atomic charges of the C atoms of the π-conjugated backbone. On the contrary, the charge densities over the sp^3-C and N atoms greatly vary upon protonation by + 0.14*e* and + 0.70*e*, respectively. We also observe that the positive atomic charge over the S atoms of the outermost rings increases by + 0.12*e* in the diprotonated trimer, while this change is lower for the S atom of the middle ring. This result can be rationalized by the ease of the sulfur atom to vary its electron density and the likelihood of resonance interactions with substituents in the α-positions of the thiophene ring.[32]

Figure 4 compares the B3LYP/6-31G** theoretical infrared spectra of the diprotonated trimer and the unprotoned one, and Figure 5 shows the eigenvectors for the vibrations which give rise to the stronger absorptions of the diprotonated trimer. The B3LYP/6-31G** spectrum of the diprotonated system displays the upsurge of a few infrared absorptions in the 1600−1300 cm^{-1} spectral range with exceedingly large intensities, in good correspondence with the experimental observations. The analysis of the theoretical data in terms of characteristic group vibrations let us assign these absorptions as follows. The bands calculated at 1604 and 1593 cm^{-1}, which are to be compared with the broad band centered at 1580 cm^{-1}, are due to in-plane $\delta_{as}(NH_3^+)$ deformation modes, of B_2 and B_1 symmetry, respectively. The broad absorption measured at 1483 cm^{-1} should be correlated with the theoretical multiplet of bands at 1460, 1453, and 1447 cm^{-1}. The component at 1460 cm^{-1} is due to the overlapping of three degenerate vibrations: (i) two in-plane combinations of $\delta(CH_2) + \delta_s(NH_3^+)$ deformations, of A_1 and B_2 symmetries, and (ii) a pure $\delta(CH_2)$ deformation of B_2 symmetry. As for the components at lower wavenumbers, there is a coupling of the motions of the end groups with aromatic ν(C=C) strechings. In particular, the component at 1453 cm^{-1} is predicted to arise from a mixture of in-plane $\delta(CH_2) + \delta_s(NH_3^+)$ deformations with the ν_s(C=C) stretching of the outermost rings, with an overall A_1 symmetry. Finally, the component at 1447 cm^{-1} results from the coupling of in-plane $\delta(CH_2) + \delta_s(NH_3^+)$ deformations with the ν_{as}(C=C) stretching of the middle ring, with a B_2 symmetry. The absorption measured at 1394 cm^{-1} must be compared with the band calculated at 1369 cm^{-1}, being a pure CH_2 wagging of B_2 symmetry. On the basis of the calculations, we find it reasonable to assign the structured band centered at 1323 cm^{-1} to combinations of the aromatic $\nu(C_\beta\text{-}C_\beta)$ stretchings with stretchings of the two $C_\alpha-C_{sp^3}$ bonds, with different phases.

In summary, this comparative theoretical study suggests that the strong and broad infrared absorptions observed in the spectra of the α,α′-bis(aminomethyl) oligothiophenes, which were absent in other families of oligothiophenes, are likely due to the protonation of the NH_2 groups after reaction with atmospheric moisture.

B. Raman Spectra. Figure 6 shows the FT-Raman scattering spectra of the undoped forms of the α,α′-bis(aminomethyl) oligothiophenes. A dependence, typical of conjugated chain compounds, appears between the frequencies of the C=C stretching modes and the number of repeat units; there indeed occurs a significant red shift or softening of the higher ν(C=C) modes as the chain grows, due to the progressive extension of the π-delocalized system.

Another characteristic of the Raman spectra of neutral π-conjugated chain compounds is their extremely simple appearance, even for systems with complex chemical structures. The spectra usually consist of very few and strong lines, despite the large number of vibrational degrees of freedom. The enlarged profiles depicted in Figure 7 show more precisely how the C=C stretching modes between 1600 and 1400 cm^{-1} and the line at about 1060 cm^{-1} gain an overwhelming intensity with respect to the remaining Raman-active normal modes. The chain length dependence of the Raman spectral patterns is nicely reproduced by the theoretical RHF/6-31G** Raman spectra plotted in Figure 8.

Two main theoretical models have been proposed for the explanation of the seeming simplicity of the Raman spectral pattern of π-conjugated materials: (i) the amplitude mode (AM) theory proposed by Horovitz et al.,[33] which turned out to be inapplicable to systems with complex chemical structures, and (ii) the effective conjugation coordinate (ECC) theory developed by Zerbi et al.[34] The latter model reformulates the concept of *amplitude mode*, first applied to polyacetylene by Horovitz, in terms of classical molecular dynamics parameters (i.e., internal

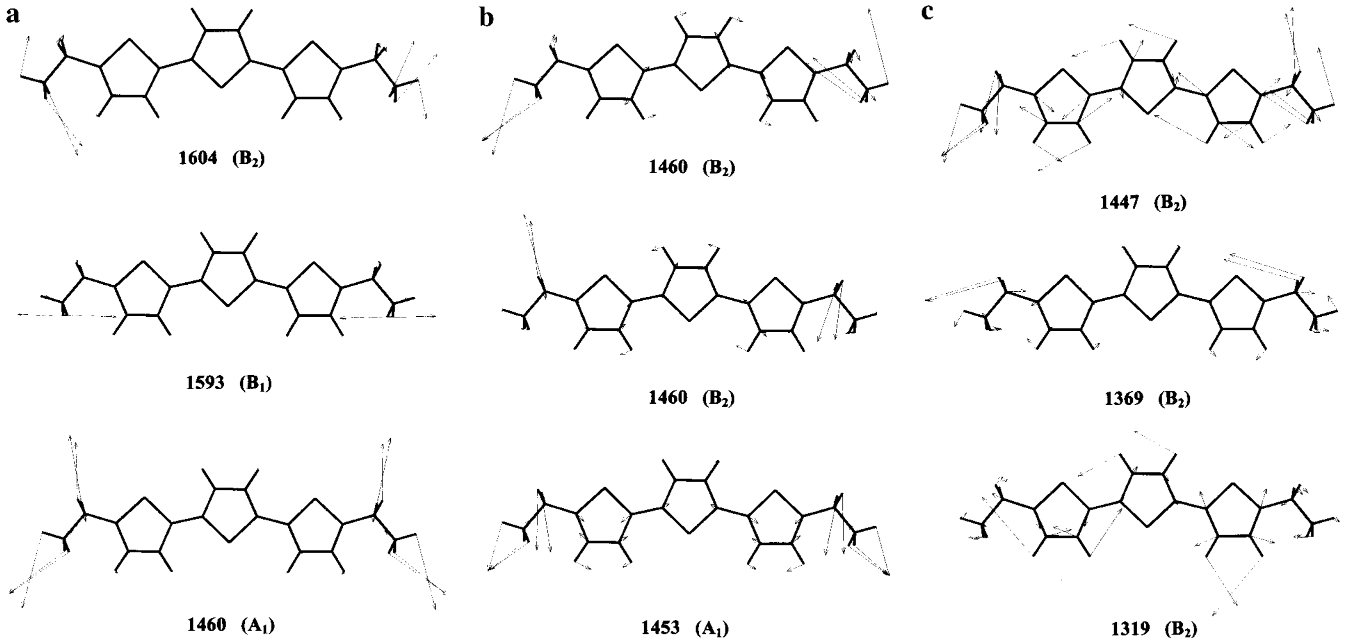

Figure 5. Schematic eigenvectors for the strongest infrared normal modes of the diprotonated α,α′-bis(aminomethyl)terthiophene, computed at the B3LYP/6-31G** level (scaled wavenumber values are given in cm^{-1} and symmetry species in parentheses).

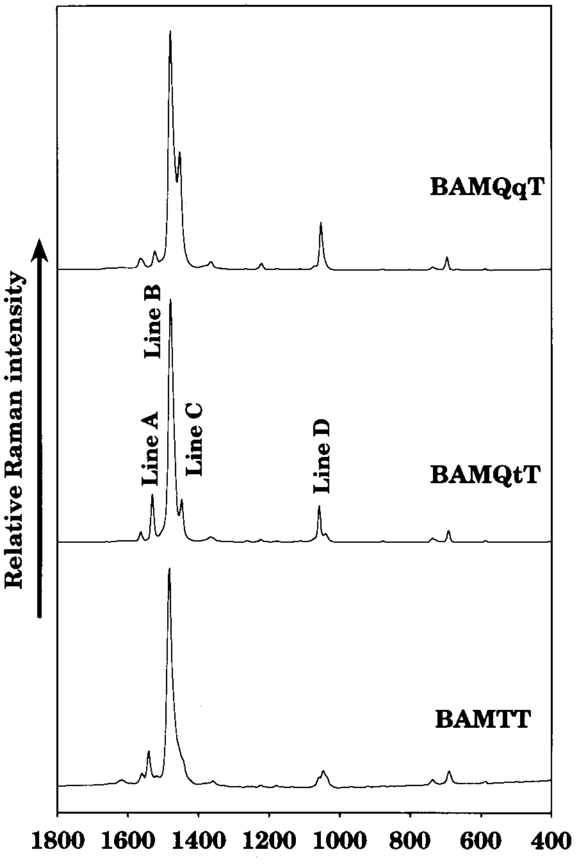

Figure 6. FT-Raman spectra of the α,α′-bis(aminomethyl) oligothiophenes in neutral form (recorded on pure solids with an excitation wavelength of 1064 nm).

coordinates and force constants) to explain the Raman spectra of undoped π-conjugated polymers and the IR absorption spectra of doped and photoexcited polymers. Over the past years, the ECC model has allowed for the interpretation of the vibrational spectra of many π-conjugated polymers.[35−40]

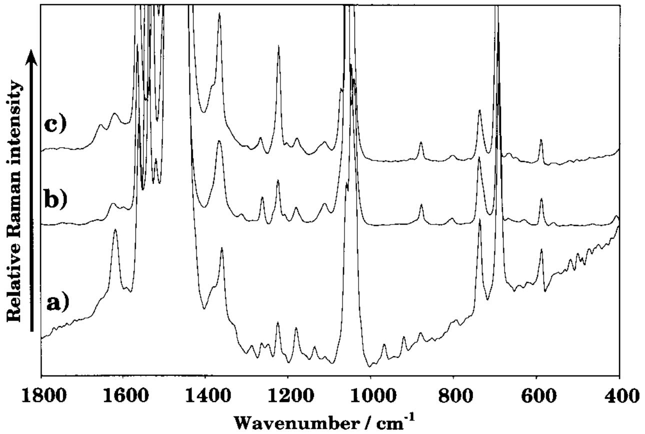

Figure 7. Enlarged profiles of the FT-Raman spectra of (a) BAMTT, (b) BAMQtT, and (c) BAMQqT.

The Raman spectra of this novel class of oligothiophenes resemble the usual appearance, both in band positions and relative intensities, of many other families of oligothiophenes,[29,30,41] and they are in full agreement with the predictions of the ECC theory. Thus, the Raman data confirm that the π-conjugated backbone is not affected by the protonation of the end groups.

IV. Conclusions

We have investigated the vibrational properties of a series of medium-sized α,α′-bis(aminomethyl) oligothiophenes. The FT-IR and FT-Raman spectra of the undoped compounds have been analyzed in relation to the effective conjugation length. This study reveals that an effective electron−phonon interaction occurs in these systems. The intramolecular delocalization of π-electrons accounts for the large wavenumber dispersions (sometimes accompanied by noticeable intensity enhancements) of a few Raman and IR-active normal modes with the molecular size, particularly in the aromatic C=C stretching region.

The aminomethyl end groups easily undergo a protonation process upon reaction with atmospheric moisture, although this

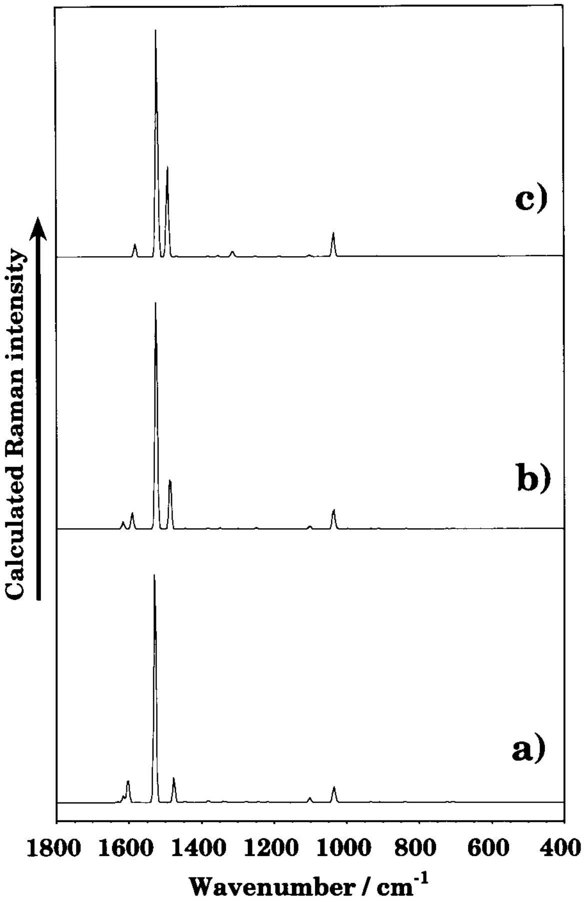

Figure 8. Theoretical evolution with chain length of the Raman spectra of the α,α′-bis(aminomethyl) oligothiophenes in neutral form, at the RHF/6-31G** level: (a) BAMTT; (b) BAMQtT; (c) BAMQqT.

does not affect the electronic structure of the π-conjugated spine. This is because the terminal NH_2 groups are attached to the thiophene chain through the electronically inert CH_2 groups. This structural characteristic of these oligomers brings new practical applications for the class of oligothiophenes, as the possibility of making thin films and soluble ionic salts which could retain the electronic properties of the undoped oligomer.

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