

Vibrational Spectroscopic Features of a Novel Family of Amorphous Molecular Materials Containing an Oligothiophene Moiety as Color-Tunable Emitting Materials

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In this paper, we investigate the vibrational properties of a novel family of amorphous molecular materials containing an end-capped oligothiophene backbone of variable length, α,α' -bis-[4-[bis(4-methylphenyl)amino]phenyl]-oligothiophene, which function as color-tunable emitting materials for organic light-emitting diodes. The advantage of these amorphous oligothiophenes with respect to their crystalline parents is that the fluorescence quantum efficiencies as thin films are quite similar to those commonly found in solution. The thorough analysis of the infrared and Raman spectra of the neutral materials as solids has revealed the usefulness and selectivity of Raman spectroscopy to determine the efficiency of the π conjugation. Density functional theory B3LYP/3-21G* calculations rendered largely distorted conformations of the 4-[bis(4-methylphenyl)amino]phenyl groups with respect to the thiophene rings least-squares plane, in full accordance with the amorphous nature of the materials. The infrared and Raman spectra of the materials recorded at different temperatures between -170 and $+160$ °C did not show any substantial change, thus indicating that the materials have a high thermal stability, which has significance for their use as active components in optoelectronic devices.

Introduction

Organic light-emitting diodes (OLEDs) have attracted great attention in the past few years because of their potential application to full-color flat-panel displays. In applying emitting materials to practical applications, they may be used in the form of a solid film. Thus, color-tunable emission in the solid state is at present a subject of great interest. Both low-molecular-weight organic materials and polymers have been studied for use as materials in OLEDs. Oligothiophenes with well-defined structures, e.g., unsubstituted and alkyl- or silyl-substituted pentamer, hexamer, and heptamer, have also been studied for use as emitting materials in OLEDs; however, their performances are relatively poor.^{1–4} Oligothiophenes are crystalline in nature, and hence, they form polycrystalline films by a vacuum deposition or spin-coating method.^{5,6} The fluorescence quantum efficiencies of these oligothiophenes are significantly reduced in going from a solution to polycrystalline or Langmuir–Blodgett films.

One of us has reported on the synthesis of a series of amorphous molecular materials containing an oligothiophene central moiety of variable length, α,α' -bis-[4-[bis(4-methylphenyl)amino]phenyl]-oligothiophene (BMA-nT), which function as color-tunable emitting materials for organic light-emitting diodes (OLEDs).^{7–10} BMA-nT materials readily form stable amorphous glasses with relatively high glass-transition temperatures (T_g between 85 and 100 °C) when the melt samples are cooled.⁷ They also form uniform amorphous films by vacuum deposition. The fabrication and performances of both single-layer and double-layer OLEDs using this novel family of

amorphous molecular materials has been reported.^{8–10} Tuning of the emitting color from light blue to orange was achieved by varying the conjugation length ($n = 1–4$) of the oligothiophene chromophore.⁸

The ability of conjugated compounds as chromophores and electrophores is related to the efficiency of the intramolecular delocalization of π electrons along the molecular long axis. Thus, one of the main challenges of the oligomer approach¹¹ 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.

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 frequencies.¹² In particular, the Raman spectra of these materials show characteristic features directly related to the interaction between the successive conjugated units, whose interpretation has required the development in past years of new theoretical concepts.¹³

The aim of the present work is to analyze at the molecular level, by combining Fourier transform infrared and Raman (FT-IR and FT-Raman) spectroscopies with density functional theory (DFT) quantum chemical calculations, the efficiency of the π conjugation of these BMA-nT molecular materials in the neutral state as solids.

Experimental and Theoretical Details

The synthesis of the series of α,α' -bis-[4-[bis(4-methylphenyl)amino]phenyl] end-capped oligothiophenes has been previously reported^{7,8} (chemical structures are shown in Figure 1). FT-IR measurements were made with a Perkin-Elmer model

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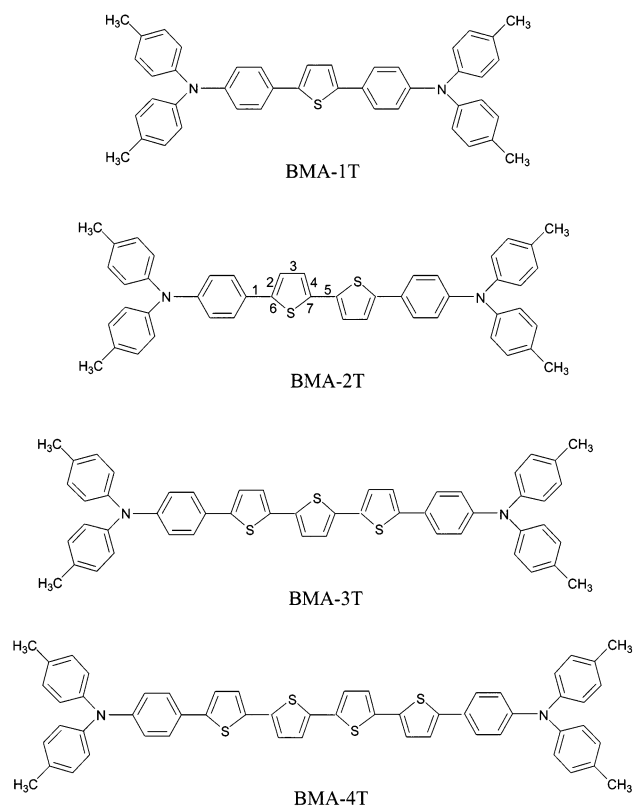


Figure 1. Chemical structures of the novel series of amorphous α,α' -bis-[4-[bis(4-methylphenyl)amino]phenyl] end-capped oligothiophenes studied in this work. The atom numbering for BMA-2T is to be used in Table 3.

1760 X spectrometer. Oligomers were ground to a powder and pressed into 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 collection. FT-Raman experiments were performed using a Bruker FRA106/S apparatus and a Nd:YAG laser source ($\lambda_{\text{exc}} = 1064\text{ nm}$). 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. A total of 1000 scans were averaged to optimize the signal-to-noise ratio, and spectra were plotted without smoothing or baseline corrections.

A suitable variable temperature cell Specac P/N 21525, with interchangeable pairs of NaCl or quartz windows for transmission studies, was used to record the FT-IR and FT-Raman spectra at different temperatures. The variable temperature cell consists of a surrounding vacuum jacket (0.5 Torr), which contains a combination of a refrigerant dewar and a heating block as the sample holder. It was equipped with a Copper-Constantan thermocouple for temperature monitoring purposes, and any temperature from -190 to $+250\text{ }^{\circ}\text{C}$ (83 – 523 K) can be achieved. The samples were inserted into the heating block part or the dewar/cell holder assembly in the form of KBr pellets. The spectra were recorded after waiting for thermal equilibrium at the sample, which required 20 min for every increment of $10\text{ }^{\circ}\text{C}$.

DFT calculations were carried out by means of the Gaussian 98 program¹⁴ running on an SGI Origin 2000 supercomputer. We used the Becke's three-parameter exchange functional combined with the LYP correlation functional (B3LYP).¹⁵ It has already been shown that the B3LYP functional yields similar geometries for medium-sized molecules as MP2 calculations

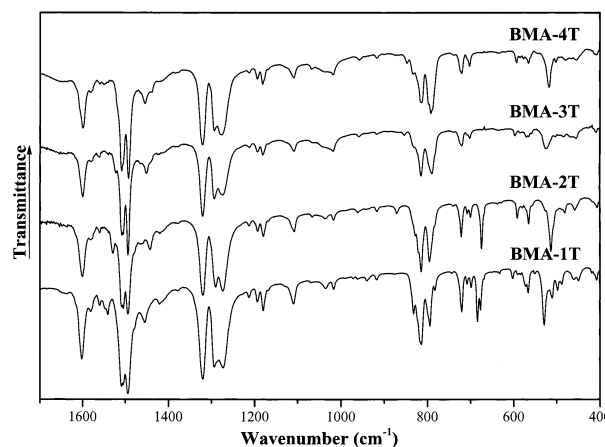


Figure 2. FT-IR spectra over probe energies of 1700 – 400 cm^{-1} of the BMA-nTs in neutral form (obtained as powdered samples in pressed KBr pellets).

do with the same basis sets.^{16,17} Moreover, the DFT force fields calculated using the B3LYP functional yield infrared spectra in good agreement with experiments.^{18,19} We also made use of the standard 3-21G* basis set.²⁰

Because of the required computer time, we restricted the calculations only to the shorter members of this novel series of oligothiophenes. Optimal geometries were determined on isolated entities. In each case, geometrical parameters were allowed to vary independently apart from planarity of the rings. On the resulting ground-state optimized geometries, harmonic vibrational frequencies and infrared and Raman intensities were calculated analytically with the B3LYP functional. In this work, we have used the often-practiced adjustment of the theoretical force fields in which frequencies are uniformly scaled down by a factor of 0.98, as recommended by Scott and Radom.¹⁸ This scaling procedure is often accurate enough to disentangle serious experimental misassignments. All quoted vibrational frequencies reported along the paper are thus scaled values.

Results and Discussion

A. Experimental Infrared and Raman Spectra. The FT-IR spectra of the α,α' -bis-[4-[bis(4-methylphenyl)amino]phenyl] end-capped oligothiophenes are shown in Figure 2. The complete assignment of the infrared absorption bands of each oligomer to particular vibrations is beyond the scope of this work because of the problems associated with identifying and assigning normal modes when there is an overlap of absorptions in a specific spectral region. Nonetheless, meaningful structural information can be gathered from the direct inspection of the spectra.

The first observation is that the infrared spectra of the various oligomers are virtually the same and show a negligible dependence on the chain length (see Table 1). The situation is opposite to the increasing simplicity of the spectral pattern with increasing molecular size found in many other families of linear α -oligothiophenes (i.e., the longer oligomers of a given series approach the optical selection rules of the corresponding polymer, because of the translational periodicity).^{21–27}

The strong absorptions at 1602 , 1509 , 1494 , 1320 , 1293 , and 1274 cm^{-1} are completely absent in the infrared spectra of the unsubstituted α -oligothiophenes^{23,23} and the α,α' -bis-alkyl substituted oligothiophenes,^{25,26} and they must be ascribed to characteristic vibrations of the 4-[bis(4-methylphenyl)amino]phenyl end groups as derived from the resemblance of the FT-IR spectra of these compounds with that of the tri-*p*-tolyl-amine

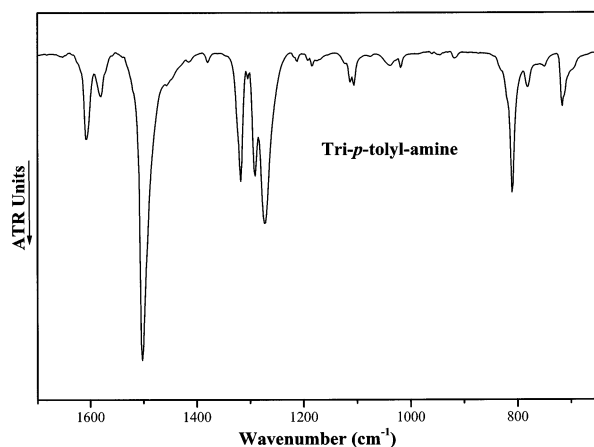


Figure 3. FT-IR spectrum of tri-*p*-tolyl-amine (purchased from Aldrich).

TABLE 1: Correlation between the Infrared Absorptions (in cm^{-1}) of the BMA-nTs in Neutral Form

BMA-1T	BMA-2T	BMA-3T	BMA-4T
1602	1600	1600	1599
1509	1508	1508	1509
1505	1505	1505	1505
1494	1494	1494	1493
1320	1320	1320	1321
1293	1290	1294	1293
1273	1274	1274	1276
1193	1193	1193	1194
1180	1179	1181	1181
1109	1108	1109	1109
1016	1017	1019	1018
814	815	815	815
794	795	790	792
720	722	720	720
684			
677	674		
530			
	526	525	518

depicted in Figure 3. BMA-1T and BMA-2T display some additional bands below 800 cm^{-1} as compared with BMA-3T and BMA-4T likely because of the coupling between the vibrations of both end groups. As a consequence, some of their in-phase and out-of-phase motions would not degenerate but split into different components.

The strong infrared activity of the end groups results from the lone pairs on the N atoms, which generate a negative charge density in the proximity of each nitrogen atom and sizeable fluxes of charge during their characteristic vibrations. Supposedly, as derived from the X-ray structures of some related compounds (such as the α,α' -dimethyl end-capped quaterthiophene²⁸ and the unsubstituted α -oligothiophenes²⁹), it can be assumed that sulfur atoms are located in an all-anti configuration with respect to the long molecular axis and that the oligothiophene central moiety retains a nearly coplanar conformation (probably the thiophene rings at both ends of the oligothiophene chain display a slight bend, of a few degrees, relative to the inner rings least-squares plane²⁸). With such a molecular structure, the oligothiophene moieties with an even number of rings are almost apolar (because of the existence of an inversion center in the middle of the chain), whereas those having an odd number of rings possess a low dipolar moment. Thus, the “bulk vibrations” of this new family of end-capped oligothiophenes are expected to be undetectable in the infrared as compared with the “end group vibrations”.

Figure 4 shows the FT-Raman scattering spectra of the neutral forms of the BMA-nT oligothiophenes. A dependence, common

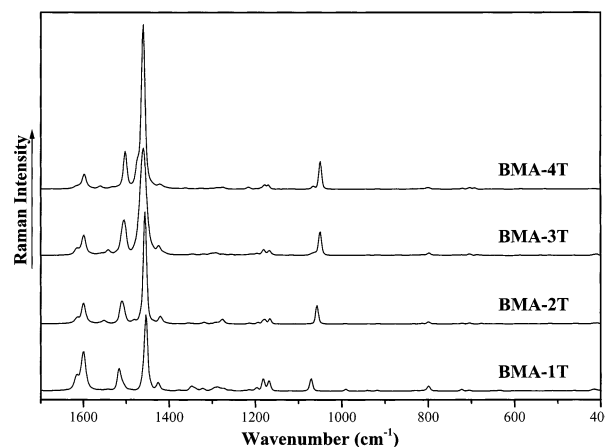


Figure 4. FT-Raman spectra of the of the BMA-nTs in neutral form (recorded on pure solids with a laser excitation wavelength of 1064 nm).

TABLE 2: Frequencies (in cm^{-1}) Measured for the Raman Lines of the BMA-nTs in Neutral Form

BMA-1T	BMA-2T	BMA-3T	BMA-4T
1615	1613	1614	1616
1600	1599	1599	1598
1516	1510	1505	1502
1454	1456	1460	1460
1425	1420	1424	1422
1182	1178	1180	1178
1168	1166	1167	1170
1071	1057	1050	1050
799	799	799	801

to many classes of π -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 some $\nu(\text{C}=\text{C})$ modes as the chain grows longer, because of the progressive extension of the π conjugation over the whole oligomer (see Table 2).^{12,22–27}

Another characteristic of the Raman spectra of neutral π -conjugated chain compounds is their surprisingly simple appearance, even for systems with complex chemical structures. The spectra usually consist of only four or five strong lines, despite the large population of Raman-active vibrations predicted by the optical selection rules.^{12,22–27} This general finding is also verified for the class of amorphous molecular materials studied in this paper; for example, 102 Raman-active normal modes are predicted by group theory for BMA-2T, whereas only a rather low number of Raman bands are experimentally observed with appreciable intensity. The enlarged profile of the Raman spectrum of BMA-2T plotted in Figure 5 illustrates more precisely how, particularly, the C=C stretching modes between 1600 and 1400 cm^{-1} and the line at 1060 cm^{-1} gain an overwhelming intensity with respect to the remaining Raman bands. This experimental finding strengthens the usefulness of Raman spectroscopy to analyze the relationship between the electronic properties and the chemical structure of any sort of π -conjugated materials independently of (i) the crystalline or amorphous nature of the material, (ii) the existence or absence of molecular symmetry, or (iii) the eventuality that the chromophore to be analyzed is in the form of a thin film or contained in a multicomponent matrix.

B. Optimized Geometries. Table 3 summarizes some selected skeletal bond lengths as derived from the gas-phase B3LYP/3-21G* minimum-energy structures of the neutral forms of three related end-capped bithiophenes, namely, α,α' -dimethylbithiophene (DMBT),²⁵ α,α' -bisphenyl-bithiophene (P2T),³⁰ and

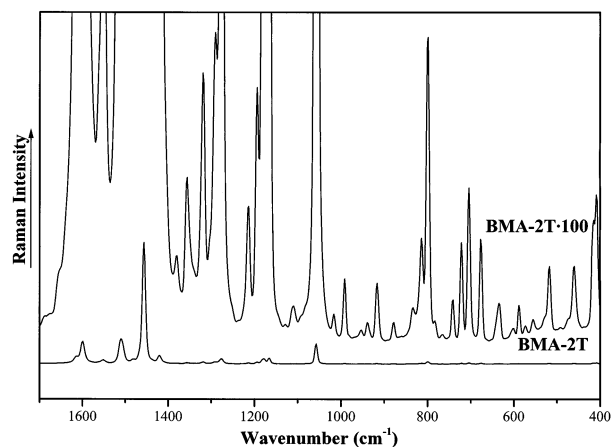


Figure 5. Enlarged profile of the FT-Raman spectrum of BMA-2T.

TABLE 3: Selected Bond Lengths (in Å) Derived from the B3LYP/3-21G* Optimized Geometries of the Neutral Forms of α,α' -dimethyl End Capped Bithiophene (DMBT), α,α' -Bisphenyl End Capped Bithiophene (P2T), and BMA-2T

bond ^a	DMBT	P2T	BMA-2T
1	1.505	1.466	1.463
2	1.371	1.381	1.381
3	1.428	1.418	1.422
4	1.379	1.383	1.383
5	1.446	1.444	1.442
6	1.748	1.756	1.755
7	1.759	1.752	1.755

^a See Figure 1 for bond numbering.

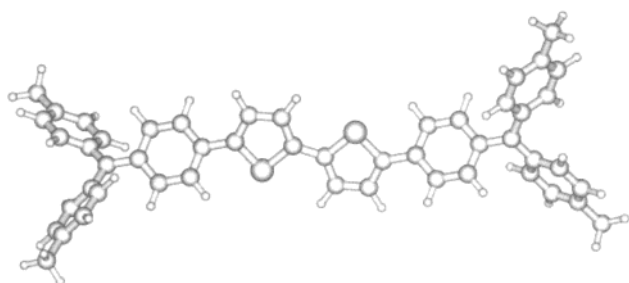


Figure 6. View of the optimized B3LYP/3-21G* structure (gas phase) of BMA-2T in neutral form.

BMA-2T. Upon substitution of the end α positions of the oligothiophene with phenyl or 4-[bis(4-methylphenyl)amino]-phenyl groups, the quinoid-like character of the molecule increases. Thus, the C=C bond lengths get longer as the C—C bond lengths get shorter. For example, the average C=C and C—C bond distances of the thiophene rings in P2T and BMA-2T amount to 1.380 and 1.417 Å, respectively, compared to 1.372 and 1.424 Å for DMBT. The bonds connecting the oligothiophene chain to the α substituents largely shrink from 1.498 to 1.465 Å on going from DMBT to P2T and BMA-2T, as a result of the involvement of the phenyl rings in the overall π -conjugation of the molecule.

Figure 6 displays a view of the optimized structure of the BMA-2T molecule as an isolated entity in the vacuum. The main structural information is the sizeable distortion of the 4-[bis(4-methylphenyl)amino]phenyl end groups with respect to the thiophene rings least-squares plane. In particular, the dihedral angle between the phenyl ring attached to the oligothiophene spine and the thiophene ring at each chain end amounts to 22°, in contrast with the nearly coplanar conformation theoretically found at the B3LYP/6-31G** level for a related

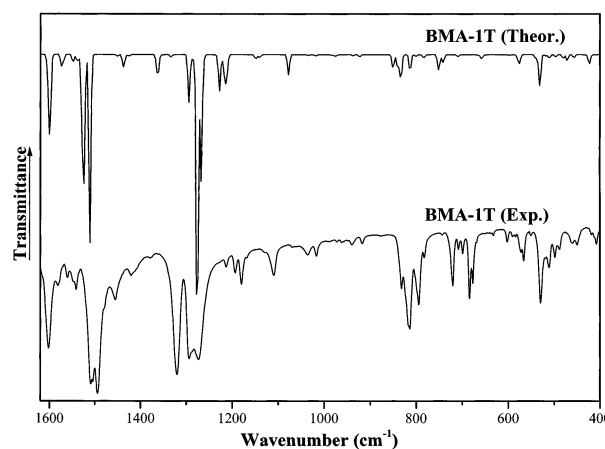


Figure 7. Comparison of the theoretical B3LYP/3-21G* infrared spectrum and the experimental one of BMA-1T in neutral form.

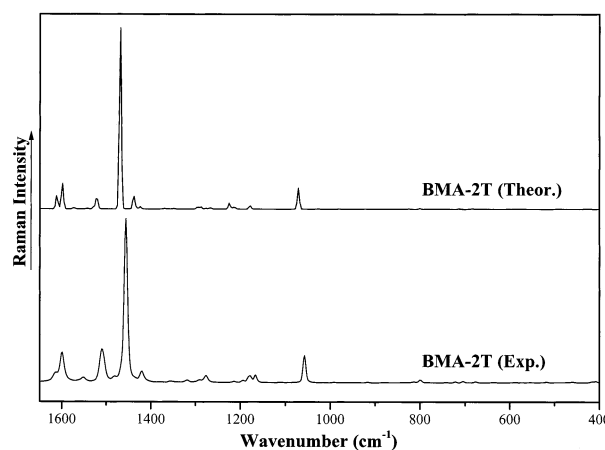


Figure 8. Comparison of the theoretical B3LYP/3-21G* Raman spectrum and the experimental one of BMA-2T in neutral form.

series of α,α' -bis-phenyl end-capped oligothiophenes.³⁰ On the other hand, the tolyl groups attached to the N atoms show a nearly perpendicular disposition with respect to the thiophene rings, and their contribution to the overall π conjugation must be negligible (at least in the neutral state). It is difficult to think that, in solid state, molecular packing could lead to a pronounced planarization of the bulky end groups. Thus, the results of our gas phase geometry optimizations fully agree with the amorphous nature of these molecular materials.

C. Theoretical Infrared and Raman Spectra. Figure 7 shows the great resemblance between the B3LYP/3-21G* infrared spectrum of BMA-1T and the experimental one. The analysis of the theoretical eigenvectors associated to the stronger infrared-active normal modes above 1000 cm^{-1} (available upon request to the authors) further confirms that the absorptions experimentally observed are due to “end group vibrations”. In particular, the bands measured at 1602 and 1509 cm^{-1} are due to out-of-phase $\nu(\text{CC})$ stretchings of the phenyl and of the tolyl groups, respectively. That at 1494 cm^{-1} can be described as an antisymmetric $\nu(\text{C}=\text{C})$ mode of the thiophene ring, although strongly coupled with motions of the phenyl groups. The 1320 cm^{-1} peak arises from a mixing of $\nu(\text{CC})$ stretchings of the tolyl groups with $\nu(\text{C}-\text{N})$ stretchings, whereas those at 1293 and 1274 cm^{-1} are due to pure $\nu(\text{C}-\text{N})$ stretchings.

Figure 8 shows, as a prototypical case, the comparison of the B3LYP/3-21G* Raman spectrum of BMA-2T and the experimental one. Table 4 summarizes the experimental and theoretical frequencies for the different Raman lines of BMA-

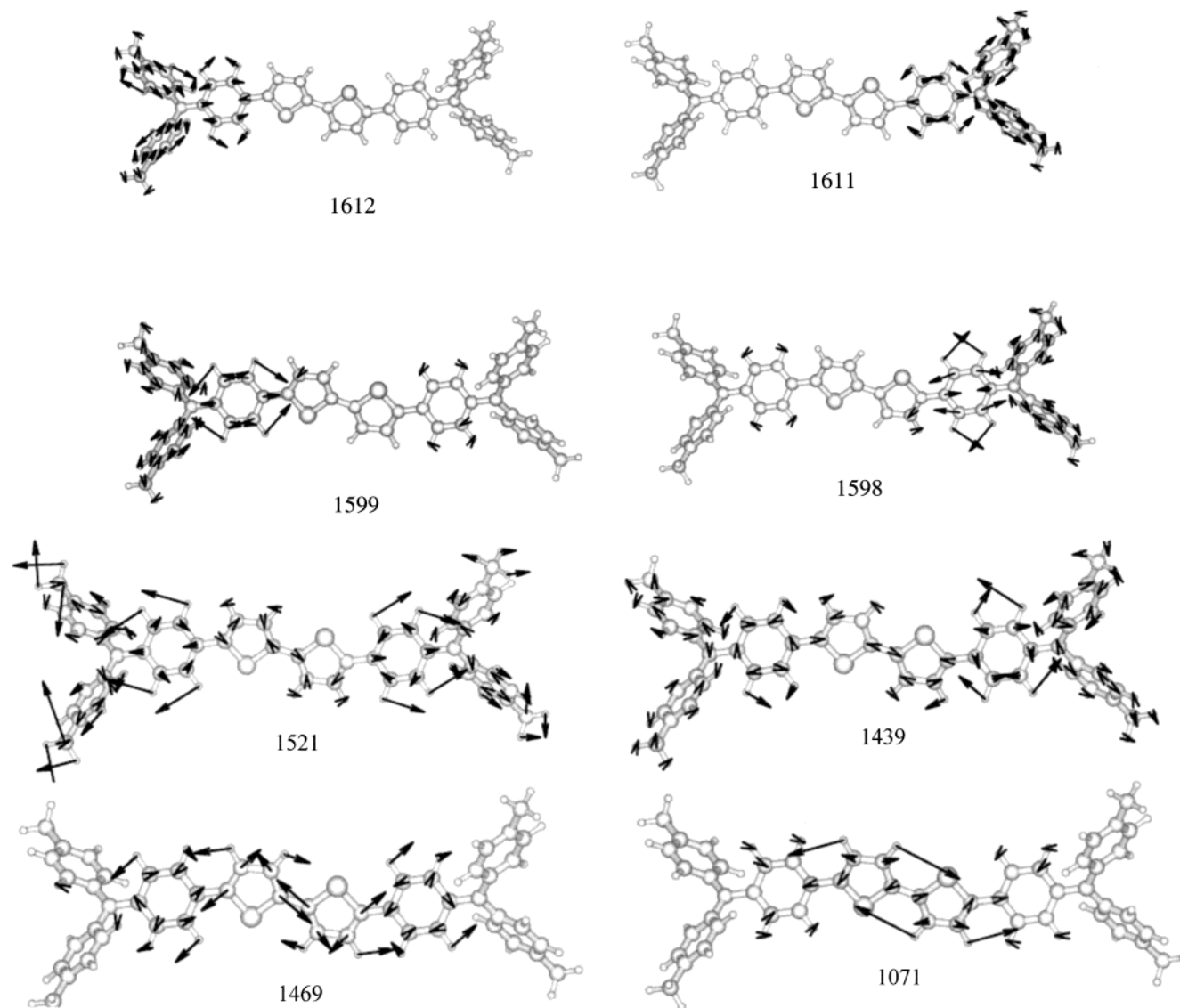


Figure 9. Schematic eigenvectors for the strongest Raman normal modes of the neutral form of BMA-2T, computed at the B3LYP/3-21G* level (scaled frequencies values are given in cm^{-1}).

TABLE 4: Correlation between the Experimental and Theoretical (B3LYP/3-21G*) Raman Frequencies of BMA-2T

ν_{theor}	ν_{exp}	assignment
1612	1613	$\nu(\text{C}-\text{C})$ phenyl+tolyl
1599	1599	$\nu(\text{C}-\text{C})$ phenyl
1521	1510	line A
1469	1456	line B
1439	1420	line C
1071	1057	line D

2T and the assignments derived from the B3LYP/3-21G* force field calculations, whereas the schematic eigenvectors for the main Raman-active normal modes of BMA-2T are plotted in Figure 9. The actual Raman spectral pattern is nicely reproduced, both in peak positions and relative intensities, by the calculations.

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 developed by Horovitz et al.,³¹ 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.^{12,13} The latter model reformulates the concept of

amplitude mode, applied to polyacetylene by Horovitz, in terms of classical molecular dynamics parameters (i.e., internal coordinates and force constants) to explain the Raman spectra of undoped π -conjugated polymers and the IR absorption spectra of doped and photoexcited polymers. In the past couple of years, the ECC model has allowed for the interpretation of the vibrational spectra of many π -conjugated polymers.^{32–37}

As mentioned above, the Raman spectra of this novel series of amorphous end-capped oligothiophenes resemble the usual appearance of many other families of π -conjugated oligomers (see Figure 4), and meaningful information can be gathered from the inspection of the spectra about the dependence of the π conjugation on the chain length and chemical structure.^{22–27} The Raman features of these materials are in full agreement with the predictions of the ECC theory,³⁸ even when the oligomers lack molecular symmetry because of the sizeable distortions of the bulky end groups from coplanarity with the oligothiophene backbone.

In particular, the lines measured at 1503, 1463, and 1051 cm^{-1} of BMA-4T undergo a selective enhancement with increasing number of thiophene units in the chain, and they arise from “bulk vibrations” strongly coupled with the π -conjugated system. More precisely, these Raman lines appear almost at the

same frequencies as those in the unsubstituted oligothiophenes of the same length.^{22,23} This observation suggests that the electronic interaction between the central oligothiophene spine and the phenyl rings at both side ends decreases as the chain grows longer. This result is supported by another two observations: (i) the negligible frequency dispersion and quick disappearance with increasing molecular size of the bands associated to the $\nu(\text{CC})$ stretchings of the phenyl rings (i.e., this lattice dynamical behavior is characteristic of end groups scarcely coupled with the bulk of an one-dimensional chain)²¹ and (ii) the weak intensity of the line measured around 1425 cm^{-1} . This line arises from a characteristic vibration of the oligothiophene backbone, which is usually termed as *line C* (whereas lines at 1503 , 1463 , and 1051 cm^{-1} are denoted as *lines A*, *B*, and *D*, respectively).^{25–27,38} The general behavior of these four Raman lines and the precise data for the compounds studied in this work are as follows:

(i) Line A undergoes an unquestionable dispersion toward lower frequency values with increasing conjugation length. In addition, its intensity (relative to the strongest band around 1460 cm^{-1}) weakens and becomes almost unobservable for relative long chain lengths (i.e., for the octamer).^{23,38} For the series of BMA-*n*T oligothiophenes studied in this paper, line A disperses 15 cm^{-1} giving 1518 cm^{-1} (BMA-1T), 1512 cm^{-1} (BMA-2T), 1507 cm^{-1} (BMA-3T), and 1503 cm^{-1} (BMA-4T). The theoretical eigenvectors calculated for various series of oligothiophenes^{26,27,39} indicate that line A arises from an in-phase antisymmetric $\nu(\text{C}=\text{C})$ vibration that is mostly localized on the outer thiophene rings of the oligothiophene chain (see Figure 9).

(ii) Line B is always very strong and dominates the whole Raman spectrum, even for very short conjugation lengths (i.e., for the trimer). Although it largely downshifts in the oligopyrroles and oligofuranes, for the oligothiophenes, its peak position is almost independent of the chain length and quickly meets saturation.³⁸ When the end α or β positions of the oligothiophene are substituted by alkyl groups, line B experiences a sizeable upshift with respect to the unsubstituted oligothiophene of the same length. However, within each class of compounds, it is almost invariably strong and only slightly shifted. In the case of the BMA-*n*T oligothiophenes, line B is measured at 1456 cm^{-1} (BMA-1T), 1457 cm^{-1} (BMA-2T), 1462 cm^{-1} (BMA-3T), and 1462 cm^{-1} (BMA-4T), upshifting by 6 cm^{-1} from the monomer to the tetramer.

The theoretical eigenvectors demonstrate that the bulk thiophene rings greatly contribute to this normal vibration, which should be described as a fully in-phase symmetric $\nu(\text{C}=\text{C})$ stretching spreading over the whole oligothiophene chain.^{26,27,39} The motions of the CC bonds are necessarily coupled with the in-plane bending of the C–H bonds, in which the H atoms recoil with a large displacement which opposes that of the C atoms (see Figure 9). This normal mode corresponds to the collective *Y* coordinate of the ECC theory.^{12,13}

(iii) Line C is clearly observed at the lower energy side of line B only for the class of the α and/or β end-capped oligothiophenes,^{26,27} whereas its intensity is almost negligible for the unsubstituted oligothiophenes.^{22,23} The experimental data so far collected support the hypothesis that the strong enhancement of line C upon substitution of the end α and/or β positions is a consequence of the electronic interaction between the π -conjugated backbone and the end groups.⁴⁰ It has also previously reported that in the α,α' -dialkyl end-capped oligothiophenes, line C slightly upshifts and becomes stronger, tending to converge with line B, as the oligomer grows up.^{26,27}

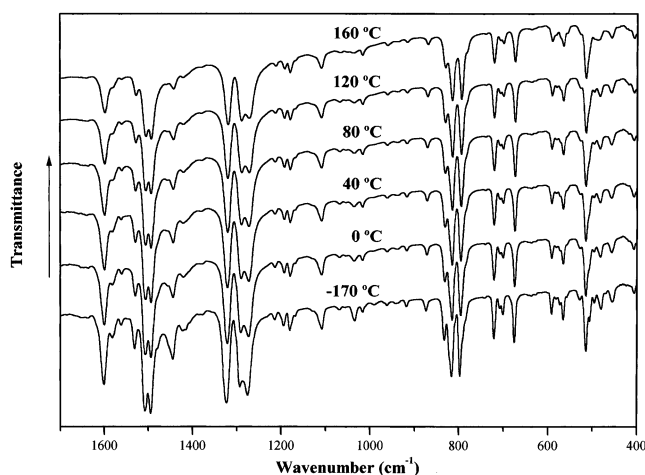


Figure 10. FT-IR spectra of BMA-2T at various intermediate temperatures between -170 and $+160\text{ }^{\circ}\text{C}$.

Line C has been found to arise from a collective symmetric $\nu(\text{C}=\text{C})$ mode, mostly localized on the “bulk” thiophene rings of the chain, but where, opposite to line B, the motions of the successive units take place in complete out-of-phase.^{26,27,39}

As for the BMA-*n*Ts, line C is measured at 1428 cm^{-1} (BMA-1T), 1422 cm^{-1} (BMA-2T), 1426 cm^{-1} (BMA-3T), and 1424 cm^{-1} (BMA-4T) and displays a very weak intensity, comparable to that of the unsubstituted oligothiophenes.^{22,23} This finding contrasts with the strong Raman activity showed by line C in the α,α' -bis-phenyl end-capped oligothiophenes.³⁰ The intensity pattern, and the similar peak positions of lines A–D in the BMA-*n*Ts and the unsubstituted oligothiophenes, further supports the result that the end groups interact very little with the oligothiophene moiety.

The diminished interaction between the 4-[bis(4-methyl-phenyl)amino]phenyl end groups and the π -conjugated oligothiophene backbone can be in part attributed to the distortion of the phenyl rings from coplanarity. However, it has been previously demonstrated that in polyaromatics and polyheteroaromatics the conformational flexibility is an additional, but not the most relevant, factor in determining the degree of π conjugation.³⁸ The phenomenon of the delocalization of the p_z electrons along the molecular chain is competitive with the confinement of the p_z electrons within the rings. A large intraring confinement occurs for benzene (due to its full aromaticity), whereas the introduction of a heteroatom reduces the aromaticity of the monomer and the intra-ring confinement potential (pinning potential), thus favoring the inter-ring conjugation.³⁸

(iv) Line D appears for all of the oligothiophenes as a sharp band (sometimes as a doublet) of medium-strong intensity around $1050\text{--}1080\text{ cm}^{-1}$. The frequencies for our BMA-*n*Ts are the following: 1058 cm^{-1} (BMA-2T), 1051 cm^{-1} (BMA-3T), and 1051 cm^{-1} (BMA-4T). The relative intensity of line D as compared with that of the line at 1597 cm^{-1} increases on going from the dimer to the tetramer.

In view of the theoretical eigenvectors, line D has to be assigned to the fully in-phase symmetric bending vibration of the C–H bonds attached to the different β positions of the inner part of the molecule.^{26,27,39} Along this normal mode, a slight recoiling of the C_β atoms effectively takes place. Thus, we must conclude that lines B and D derive directly from the dynamics associated to the collective *Y* coordinate.^{12,13}

D. Thermal Dependence of the Infrared and Raman Spectra. The variable-temperature FT-IR and FT-Raman spectra of BMA-2T are shown in Figures 10 and 11, respectively. The

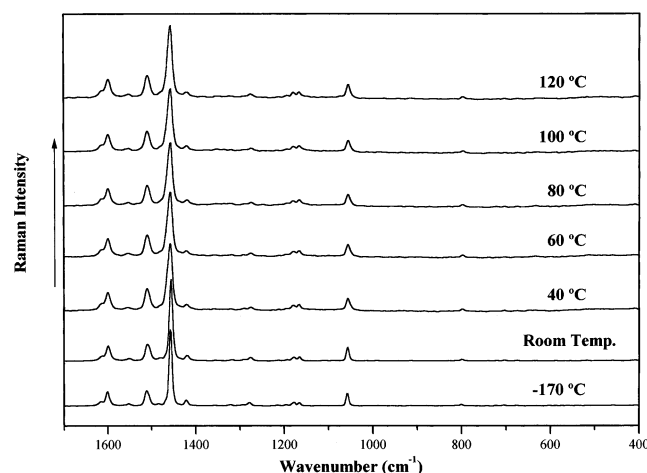


Figure 11. FT-Raman spectra of BMA-2T at various intermediate temperatures between -170 and $+120$ °C.

range studied was from -170 °C to $+160$ °C (103 to 433 K); intermediate points at about 0, $+40$, $+80$, and $+120$ °C and the room temperature (around $+20$ °C) were analyzed. The melting points of the compounds (close to $+230$ °C as determined from DSC)⁷ were not reached in any case.

The spectra displayed in Figures 10 and 11 exhibit rather systematic trends which are common to all the oligomers of the series. No dramatic changes are noticed in the infrared and Raman spectra before the maximum temperature is reached, and the spectra reversibly recover their profiles throughout the full temperature range examined. We also observe that at low temperatures the widths of the infrared bands neither substantially narrow nor split into well-resolved components, as expected for crystalline systems.

An opposite thermal behavior was previously found for a crystalline series of α,α' -dimethyl end-capped oligothiophenes: (i) the infrared absorptions of the dimer and trimer became broad in the proximity of their melting points as a consequence of both the disappearance of the crystal order and the lowering of molecular symmetry caused by rotations around the inter-rings C—C bonds and (ii) some absorption bands at low temperatures clearly resolved into sharp peaks as being due to the hindered internal rotation and also to the well-ordered intermolecular interactions induced by the close molecular packing.⁴¹

Thus, the temperature dependence of the FT-IR and FT-Raman spectra of the BMA-nT oligomers is consistent with the amorphous nature of these molecular materials and reveals that they can be used as active components in nonlinear optical (NLO) devices, which must be thermally stable at continuous working temperatures of about $+80$ °C.^{42,43}

Conclusions

In this work, we have performed a combined theoretical and vibrational study on a novel series of amorphous π -conjugated molecular materials. These compounds contain a central oligothiophene spine of variable length, with its two end α -positions capped by 4-[bis(4-methylphenyl)amino]phenyl groups, and they function as color-tunable emitting chromophores for organic light-emitting diodes. Tuning of their color emission from blue to orange can be achieved by varying the conjugation length ($n = 1-4$) of the oligothiophene moiety. The advantage of these amorphous oligothiophenes with respect to the crystalline ones is that the fluorescence quantum efficiencies in the form of thin films are quite similar to those found in solution.

This study has revealed the usefulness and selectivity of Raman spectroscopy to analyze the efficiency of the π conjugation in this class of materials. In fact, while the infrared absorptions of these compounds arise almost exclusively from vibrations of the bulky end groups due to the existence of lone pairs on the nitrogen atoms, the Raman bands are mainly related to particular skeletal $\nu(\text{C}=\text{C})$ stretching vibrations largely involved in the π conjugation.

Geometry optimizations performed on isolated molecules with DFT methods rendered largely distorted conformations of the 4-[bis(4-methylphenyl)amino]phenyl groups with respect to the thiophene rings least-squares plane, which is in full accordance with the amorphous nature of the materials.

The comparison of the Raman spectral patterns of these compounds with those previously collected for many families of unsubstituted and substituted oligothiophenes indicates that the phenyl rings directly attached to the oligothiophene spine contribute very little to the overall π conjugation. This is not only a consequence of the sizeable distortions from coplanarity of the end substituents but mainly of the different aromaticity of benzene and thiophene so that π electrons are less pinned over the oligothiophene chain than in the phenyl rings.

Regarding the analysis of the thermal stability of these new materials at the molecular level, no dramatic changes are noticed in the infrared and Raman spectra from -170 to $+160$ °C, which has significance for their use as active components in optoelectronic devices.

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