Exploration of the electronic structure of dendrimerlike acetylene-bridged oligothiophenes by correlating Raman spectroscopy, electrochemistry, and theory

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A series of radial thiophene-based structures consisting of a central benzene or thiophene ring surrounded by acetylene-bridged terthienyl arms has been investigated by physical and theoretical methods. Fourier transform Raman spectroscopy of the neutral solids shows that the terthiophene arms are weakly coupled across the core (benzene plus acetylene groups) likely due to cross-conjugation or meta-conjugation effects that may prevent full delocalization. By increasing the number of arms around the central ring, the electronic structure of the molecules seems to be affected only at the core, whereas the outer terthiophene arms remain almost unaltered. Raman spectroelectrochemistry and quantum chemical calculations provide further insight into the charge delocalization of the oxidized species. There is no evidence to suggest that these oxidized forms, obtained upon electrochemical doping of the molecules, show charge delocalization across the core. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1755665]

I. INTRODUCTION

Multichromophore dendrimers are able to transfer energy rapidly and efficiently to a central core. To understand energy flow in these molecules, one must identify the relevant light-absorbing and emitting units and determine their electronic coupling. This is relatively straightforward for well-separated chromophores, but more difficult for conjugated supermolecules such as conjugated dendrimers.[1]

The successful use of benzene-core dendrimers in materials science is well reported owing to their potential liquid-crystalline behavior and to their ability to self-assemble and to form supramolecular architectures.[2,3] The understanding of the electronic structure of these macromolecules from the standpoint of the electronic interactions between their building conjugated blocks is needed since, for example, they mainly govern the mechanisms of charge transfer from the peripheral groups to the core (antennae systems), or because they are responsible for the mechanisms in which optical excitations efficiently convert into charge-separated states (photonic materials in solar cells). The precise understanding of the structure-property relationships in molecular materials are of primary importance since the optimization of their electronic properties will mainly depend on how the electronic structure is related with the molecular structure or with

the chemical functionalization. A useful and practical strategy for investigating these relationships is the systematic variation of the number of repeat units or varying substitution patterns in a particular type of molecule. In this regard, it is desirable to deal with systems of conjugated molecules of this type which allow the use of spectroscopic techniques, electrochemical methods, and quantum chemistry.[3,4]

Pappenfus *et al.* have recently prepared a series of molecules that can be viewed as models of the first generation of larger dendrimers. These molecules consist of a central benzene or thiophene ring surrounded by three, four or six acetylene-bridged terthiophenes (herein denoted as arms).[5] This strategy is attractive since it combines the excellent optical and electronic properties of oligothiophenes with the physical properties of dendrimers.[6(a)] It is also noted that these systems could be explored as organic electroluminiscent materials with potential applications in light-emitting devices since they may render materials with stable amorphous morphologies, and because of the high concentration of functional groups (hole-transporting units) which may be beneficial to the physical performance of the potential device.[6(b)] Furthermore, charge transport or energy flow from the peripheral groups to the core are many times associated with charged separated states. In a first approach, one can reasonably model these states with the analysis of the fully ionized (anionic or cationic) species. Accordingly, to achieve molecular materials with enhanced hole-transporting properties or improved electrochromic behavior, it is necessary to

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understand the electronic structure of the charged species.

In this work, we explore the electronic structure of the neutral and the oxidized species of a series of radial oligothiophenes with different substitution patterns. This study focuses on the interactions between the peripheral groups and the core, and on the role played by the acetylene groups by means of spectroscopy, electrochemistry, and quantum chemistry. FT–Raman spectroscopy is the guide method used in this study to analyze the electronic features since it is perfectly suited, in combination with the effective conjugation coordinate (ECC) theory,[7] for dealing with the evaluation of the π-conjugational properties of virtually any polyconjugated molecule. The methodology of the work will consist first on the assignment of the Raman bands both in the neutral and in the charged compounds. Second, we will analyze the wave number changes of the Raman lines as a function of the substitution pattern, i.e., those mostly related, within the framework of the ECC model, with the degree of involvement of each moiety in the overall π-electron conjugation. In all the cases theoretical calculations on model compounds will be carried out in order to support the experimental findings.

II. EXPERIMENTAL AND THEORETICAL DETAILS

The synthesis of these acetylene bridged oligothiophenes has been reported elsewhere.[5] A representative chemical structure for the molecules is displayed in Fig. 1. FT–Raman spectra were measured using an FT–Raman accesory kit (FRA/106-S) of a Bruker Equinox 55 FT–IR interferometer. A continuous-wave Nd–YAG laser working at 1064 nm was employed for Raman excitation. A germanium detector operating at liquid nitrogen temperature was used. Raman scattering radiation was collected in a back-scattering configuration with a standard spectral resolution of 4 cm^{-1}. In order to avoid possible damage to the samples upon laser radiation, especially regarding the oxidized species, the laser beam was loosely focused on the sample and its power was kept at a level lower than 100 mW and 500 scans were averaged for each spectrum.

Full geometry optimizations were performed in the framework of the density functional theory by means of the B3LYP functional, using the A.7 revision of the GAUSSIAN 98 program package running on a SGI Origin 2000 computer.[8,9] The 3-21G* basis set was chosen to reduce the high dimension of the problem.[8,10] Due to the large molecular size of the compounds studied in this work, quantum chemical calculations for the neutral systems were carried out on two model systems built up from a central benzene ring surrounded by three and six acetylene thiophene groups [Ph(AlT)$_3$ and Ph(AlT)$_6$]. A benzene ring surrounded by two α-acetylene, α'-phenyl terthiophene groups in *para* positions, denoted as *para* Ph(A3TPh)$_2$, was used to model the effects of ionization. As usual, the effect of the doping was mimicked by considering the radical cationic or dicationic species of *para* Ph(A3TPh)$_2$. Geometry optimizations were performed on isolated entities in the vacuum. The neutral and dicationic species were treated as closed-shell systems (B3LYP procedure), while for the radical cations (open-shell systems) optimizations were carried out using spin unrestricted wave
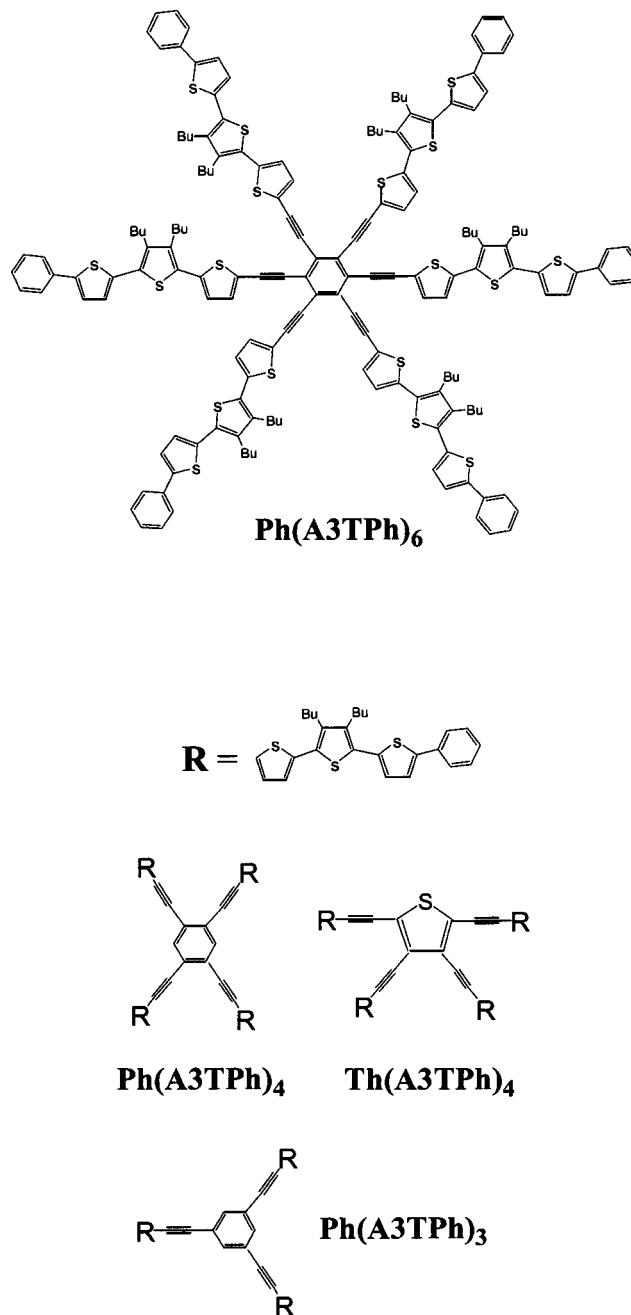

FIG. 1. Representative chemical structures and nomenclature used for the studied compounds.

functions (UB3LYP). The model systems were considered without butyl groups, being confident that these alkyl side chains have minimal effects on the conjugated path. All geometry parameters (i.e., bond lengths, bond angles, and dihedral angles) were allowed to vary independently along the molecular optimizations. For the ionized species, negative counterions were not considered.

Electrochemical studies (cyclic voltammograms) were obtained with a BAS 100B electrochemical analyzer using a glassy carbon working electrode. For the Raman spectroelectrochemical studies, thin solid films were obtained by casting on a Pt working electrode from a CH$_2$Cl$_2$ dispersion of the solid. The film of the compound on the Pt working electrode was then immersed in a 0.1 M tetrabutyl ammonium
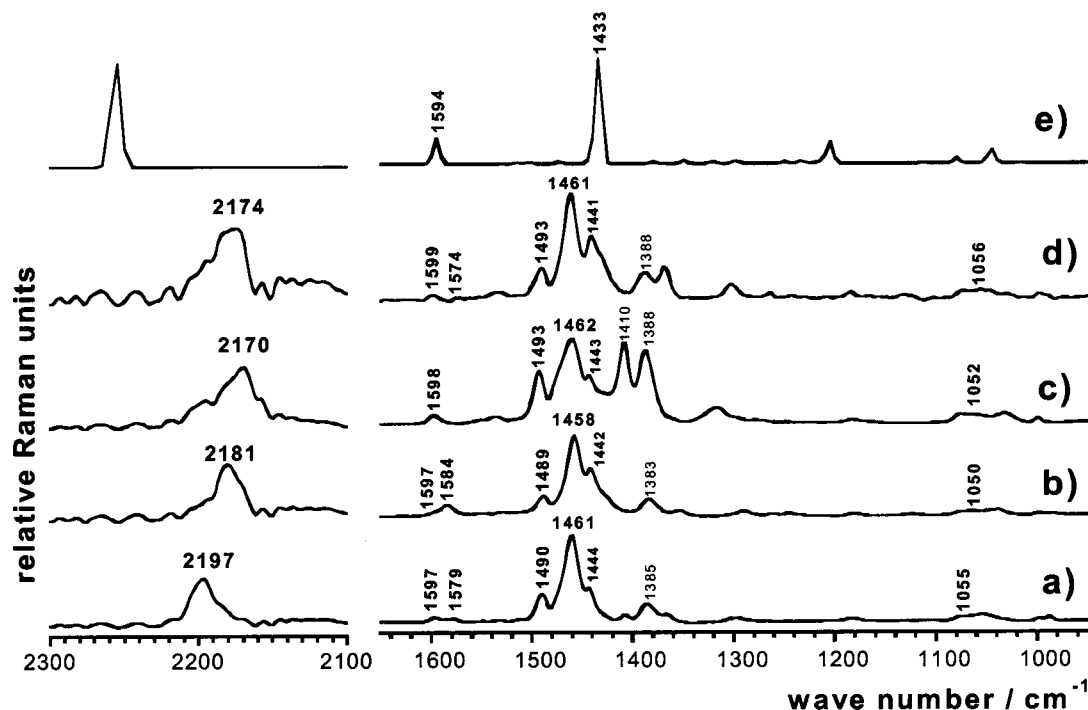
FIG. 2. FT–Raman spectra of (a) Ph(A3TPh)$_3$, (b) Ph(A3TPh)$_4$, (c) Th(A3TPh)$_4$, and (d) Ph(A3TPh)$_6$. The spectrum labeled as (e) corresponds to the calculated B3LYP/3-21G* Raman spectrum of the *para* Ph(A3TPh)$_2$ model in neutral state.

hexafluoro phosphate (TBAPF$_6$) solution in acetonitrile. A 1×1 cm^2 Pt electrode and a Ag/AgCl electrode were used as the auxiliary and reference electrodes, respectively. Oxidation of the films, using a chronoamperometric technique for 50 s, was run up to 2 V to avoid for solid state hysteresis processes that could diminish the real potential in the solid–electrode interface, thus ensuring for the complete oxidation of the thin films.

III. VIBRATIONAL CONSIDERATIONS

A. ECC theory, Raman spectra and π-electron conjugation

The Raman spectrum of a given molecule, or a series of molecules, can be theoretically explored by group theory on the basis of the optical selection rules for the Raman scattering process. It is well known from many x-ray diffraction studies that oligothiophenes usually display a full planar or nearly planar molecular conformation in solid state.[4(b)] Therefore, one may reasonably consider that in solid phase, the molecules subject of the present investigation are fully or almost planar. Under this assumption, for example, Ph(A3TPh)$_4$ belongs to the D_{2h} symmetry point group and, since it has 240 atoms (N), there exists 714 modes (3N-6) of vibration of which 357 are Raman active. More precisely, the normal modes distribution among the various symmetry species of the D_{2h} point group is the following: $120(A_g) + 58(B_{1g}) + 119(B_{2g}) + 60(B_{3g})$.

The experimental solid state Raman spectrum of Ph(A3TPh)$_4$ in Fig. 2 displays however only 10–12 well-resolved bands, which is in principle unexpected. This contradiction can be justified as follows: (a) when Franck–Condon scattering is predominant, totally symmetric modes

(A_g) are found to be selectively enhanced, while B_g (B_{1g}, B_{2g}, and B_{3g}) modes become weak or almost undetectable; (b) there exists a nonuniform distribution of Raman intensity among the different totally symmetric modes. This phenomenon can be accounted for by the existence of a very large electron–phonon coupling between the electronic structure of the system and the nuclear motions for a given vibration (generally the normal mode that mostly mimics the geometrical evolution from the ground electronic state to the first excited state). Consequently, as for the α,α'-linked oligothiophenes (or any other five-member ring polyconjugated molecule), this vibration consists of a collective C$=$C/C–C stretching mode in which all the C$=$C and C–C bonds shorten and lengthen in phase, respectively. It is usually termed as the ECC mode in the effective conjugation coordinate theory.[7] Furthermore, the electron–phonon coupling gives rise to a selective enhancement of the C$=$C/C–C stretchings of the conjugated path.

For low band-gap polyconjugated oligomers, the ECC mode strongly couples with π electron delocalization. Thus, the C$=$C/C–C stretching vibrations that compose the ECC mode give information about the π-electron conjugation. At the level of the molecular geometry parameters an increment of π-electron conjugation or π-electron delocalization in a given oligothiophene series can be described by the lowering of the overall BLA parameter (i.e., the average difference between the conjugated C$=$C and C–C bond lengths) because of the continuous weakening of the double bonds and the strengthening of the single bonds. This is a consequence of the loss of aromaticity of the five-membered rings at the expense of gaining quinoid character within the structure. At the level of the molecular force field which determines the wave numbers of the Raman lines, the increasing contribu-
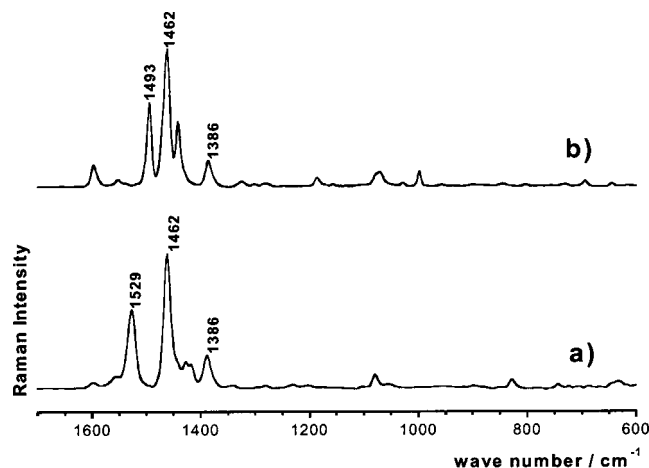
FIG. 3. FT–Raman spectra of (a) 3T and (b) Ph3TPh.

tion of the quinoid form to the electronic structure of the system gives rise to a lower value or softening of the force constants associated to the ECC mode. Consequently the increased π-electron conjugation along a homologous series of compounds can be followed by a wave number downshift of some of the strong C═C/C–C stretching vibrations appearing in the Raman spectrum.[7]

B. Assignment of the Raman spectra

Figure 2 displays the FT–Raman spectra of the four radially branched oligothiophenes. For comparison purposes, the Raman spectrum of 3T (terthiophene with the two innermost β positions substituted with butyl groups) and the spectrum of Ph3TPh are shown in Fig. 3.

A well resolved Raman peak is recorded in each case around 2200 cm^{-1} due to the fully in-phase C≡C stretching vibration, ν_s(C≡C), measured at 2197 cm^{-1} in Ph(A3TPh)$_3$, 2181 cm^{-1} in Ph(A3TPh)$_4$, 2174 cm^{-1} in Ph(A3TPh)$_6$, and 2170 cm^{-1} in Th(A3TPh)$_4$.[11] These bands are quite intense, in some cases even more than those at 1460 cm^{-1} due to the thienyl vibrations. Owing to its sp hybridization, acetylide bonds can be viewed as weak electron-accepting or withdrawing groups relative to their sp^2 counterparts. According to the theoretical calculations performed for the model systems, the triple C≡C bond accumulates a total negative charge (sum of the Mülliken atomic charges of the two sp carbon atoms) of $-0.1730e$ in Ph(A1T)$_6$ versus $-0.1172e$ in Ph(A1T)$_3$. At the same time, the C≡C bond distances lengthen by 0.001 Å upon hexa substitution. One may argue that, upon increasing branching of the core, the electron-accepting acetylene bridges induce an increasing confinement of the π electrons in their surrounding and, likely due to the repulsion of the accumulated charge, loosing triple bond character and shifting its ν_s(C≡C) associated Raman to lower wave numbers.[11] In Th(A3TPh)$_4$ with a much more polarizable thienyl core, the attraction of the π electrons by the triple bonds should be even more pronounced.

The bands associated with the skeletal C═C stretching vibrations, ν(C═C), of the phenyl groups appear in the 1600–1570 cm^{-1} spectral region.[11] The ν(C═C) stretching

of the phenyl end caps of Ph3TPh has been previously assigned to the bands at 1597 cm^{-1}, which clearly correlates with the lines at 1597 cm^{-1} in Ph(A3TPh)$_3$ and Ph(A3TPh)$_4$, at 1599 cm^{-1} in Ph(A3TPh)$_6$ and at 1598 cm^{-1} in Th(A3TPh)$_4$.[12] Quite small wave number differences for this Raman scattering are observed among the series of compounds which is consistent with the negligible changes of the electronic and molecular structures of these outer phenyl groups in the series.

Bands at 1579 cm^{-1} in Ph(A3TPh)$_3$, 1584 cm^{-1} in Ph(A3TPh)$_4$ and 1574 cm^{-1} in Ph(A3TPh)$_6$ are likely due to ν(C═C) stretching of the central phenyl ring.[11] The lowest wave number corresponds precisely to the most radially branched compound which reveals that this is the most electron-deficient phenyl ring in the series. B3LYP/3-21G* Mülliken atomic charges from calculations also provide evidence of the increased positive charge over the central phenyl ring with the increasing number of periphirical electron-withdrawing acetylenic groups: $+0.09344e$ in Ph(A1T)$_3$ versus $+0.18761e$ in Ph(A1T)$_6$. Additional data were derived from a molecule related to Ph(A3TPh)$_3$, but lacking of the acetylene bridges: its solid-state Raman spectrum displays a band at 1589 cm^{-1} associated to ν(C═C) of its central phenyl core, whereas it is measured at 1579 cm^{-1} in Ph(A3TPh)$_3$.[11,13]

Most Raman bands corresponding to thienyl vibrations appear in the 1550–1000 cm^{-1} spectral region.[7,12,14] The characteristic Raman spectral features of the 3T moiety is easily recognized in the spectra of all the radial compounds for which they dominate the whole Raman fingerprint. In particular, bands at 1490, 1460, 1440, 1385 cm^{-1}, and 1070–1050 cm^{-1}, associated to various oligothienyl vibrational modes, are clearly observed.

Lines at 1490 cm^{-1} in Ph(A3TPh)$_3$, 1489 cm^{-1} in Ph(A3TPh)$_4$, 1493 cm^{-1} in Ph(A3TPh)$_6$, and 1493 cm^{-1} in Th(A3TPh)$_4$ correspond to that usually termed as line A in the Raman spectra of α-linked oligothiophenes and the corresponding vibration can be described as a in-phase C═C antisymmetric oscillation of the outermost thienyl rings of the chain.[7,12,14] As in the present compounds, the line A generally shows a little dependence on the number of conjugated units in the chain: thus, it appears at 1503 cm^{-1} in α,α'-diphenyl thiophene, 1499 cm^{-1} in α,α'-diphenyl bithiophene, and 1496 cm^{-1} in α,α'-diphenyl terthiophene.[12]

Line B is always the strongest band of the Raman spectra of oligothiophenes.[7,12,14] While it largely downshifts with the increasing chain length in oligopyrroles and oligofurans, in oligothiophenes its peak position is quite little dependent on the chain length. For the molecules under study, line B, which corresponds to a in-phase C═C symmetric vibration spreading over the whole terthienyl backbone, can be assigned to the bands at 1461, 1458, 1462, and 1461 cm^{-1}, respectively, in Ph(A3TPh)$_3$, Ph(A3TPh)$_4$, Ph(A3TPh)$_6$, and Th(A3TPh)$_4$. Owing to its large intensity for all the compounds, this scattering can be reasonably assigned to the ECC mode.[7,12,14]

Close to line B also the so-called line C is distinguished at 1444, 1442, 1443, and 1441 cm^{-1}, respectively, in Ph(A3TPh)$_3$, Ph(A3TPh)$_4$, Ph(A3TPh)$_6$, and Th(A3TPh)$_4$. Its associated vibration can be described as the out-of-phase symmetric C=C stretching of the inner thienyl rings of the chain.[7,12,14] As for Th(A3TPh)$_4$, the intense line at 1410 cm^{-1} can arise from a stretching mode of the central thiophene which can be related with the Raman lines at around 1415 cm^{-1} in oligothiophenes bearing a full quinoid structure for their thiophene rings (dicationic species). In this sense, one could think in the appearance of a quinoidlike structure for this thiophene core due again to the effect of the surrounding acetylene groups.[15]

Near to this band at around 1385 cm^{-1} medium-intense scatterings are observed for all the samples. These bands are absent for the nonbutylated terthiophenes and always appear after alkylation of the β positions of the central thiophene.[12] Therefore, it can be assigned to a vibration composed by ν(C–C) and β(CH$_2$) modes of the butyl side chains extensively coupled to the ECC mode in a similar way as line D does. Line D appears at 1055, 1050, 1052, and 1056 cm^{-1}, respectively, in Ph(A3TPh)$_3$, Ph(A3TPh)$_4$, Ph(A3TPh)$_6$, and Th(A3TPh)$_4$ and corresponds to the in-phase C–H deformation vibration, δ(C–H), of the aromatic CH bonds that are extensively coupled with the dynamics of line B since the C$_\beta$ atoms of the thiophenes in the ν(C=C) motions leads to recoil the CH bonds giving rise to a mechanical coupling and the subsequent activity enhancement of the δ(C–H) Raman lines.[7,12,14]

C. Density functional theory calculations

At this point of the analysis we have observed that Raman wave numbers arising from the outer phenyl and terthiophene units do not change significantly within the series of compounds. This seems to indicate that the arms are minimally affected by the branching pattern around the central core. Accordingly, the choice of the Ph(A1T)$_3$ and Ph(A1T)$_6$ models in which each arm is replaced by one thiophene ring could be sufficient to simulate the structural and electronic effects on the core. Calculations at the B3LYP/3-21G* level carried out for Ph(A1T)$_3$ and Ph(A1T)$_6$ show negligible differences since the larger CC bond length changes found for the β,β' thienyl bonds do not exceed from 0.0003 Å, whereas the Mülliken atomic charges of the β' atoms of the thiophene rings are also nearly the same: $+0.017\,262\,e$ in Ph(A1T)$_3$ and $+0.017\,268\,e$ in Ph(A1T)$_6$. In contrast, the calculated B3LYP/3-21G* CC bond lengths for the central phenyl core of Ph(A1T)$_3$ and Ph(A1T)$_6$ amount to 1.4066 and 1.4233 Å, respectively, and the CC bonds connecting the acetylene bridge to the central phenyl ring and to the thiophene arms shorten, respectively, by 0.089 and 0.036 Å in passing from Ph(A1T)$_3$ to Ph(A1T)$_6$. These theoretical data seemingly give support to the progressive attenuation of electronic and structural modifications upon increasing branching of the central phenyl core at the level of the first thiophene rings of the model.

D. UV–Vis complementary data

The behavior of the wavelength maximun of the π–π* electronic absorption within the series: 400 nm in Ph(A3TPh)$_3$, 417 nm in Ph(A3TPh)$_4$, 458 nm in Ph(A3TPh)$_6$, and 402 nm in Th(A3TPh)$_4$ represents one of the few cases where no saturation of the wavelength of this transition with the increasing number of thiophene rings is observed.[5] For most linear oligothiophenes the wavelength of the maximun of the π–π* absorption meets saturation at the level of 10–12 thiophene units, however we call the attention that in Ph(A3TPh)$_6$ there are present up to 18 thiophene rings.[16] Since, upon increasing branching, the electronic and structural differences mainly affect to the central core, one would in principle expect that the whole position of the π–π* band could not depend, at least linearly, on the number of thiophene rings of the macromolecule.

We would like also to mention that the electronic spectra of neutral 3T, Ph3TPh, Ph3TASiMe$_3$ (SiMe$_3$ denotes the trimethyl silyl group) and Ph(A3TPh)$_3$ display the maximun of their respective π–π* bands at 336, 384, 383, and 400 nm. This agrees with the fact that the absorbing units in these systems mainly consist of a phenyl–terthienyl moiety, only slightly affected by the presence of the core. Moreover, the homologue molecule of Ph(A3TPh)$_3$ without acetylene groups shows the π–π* band maximun at 396 nm which further reveals the minimal involvement of the triple bonds regarding the HOMO–LUMO transition placed at the phenyl–terthienyl arms.

For the general discussion of the results, it is convenient to review the literature for explanations of similar spectroscopic phenomena of acetylene-bridged compounds. In the case of some oligothiophenes made up with terthiophene groups bridged by a triple bond, the authors invoked the participation of resonance structures consisting of cumulated double bonds. These cumulated bonds could induce conformational and π-electronic cloud distortions which could preclude for full conjugation between the two terthienyl groups.[17] But these molecules could also be viewed as cross-conjugated systems in the sense that there exist double or triple bonds that are in conjugation but not in a linear disposition.[18] In contrast to linear conjugated chromophores, cross-conjugated molecules generally display a reduced π-electron conjugation.

IV. CHARGED SPECIES

The electrochemical properties of these radially branched oligothiophenes have been previously investigated.[5] The cyclic voltammogram of Ph3TASiMe$_3$ in 0.1 M CH$_2$Cl$_2$ TBAPF$_6$ is displayed in Fig. 4. This oligomer displays much more stable oxidation processes than the previously investigated Ph3TAH homologue and consisting of two one-electron processes associated to the successive generation of the radical cation and dication. Figure 5 also displays the cyclic voltammogram of Ph(A3TPh)$_3$ in which the first and second processes at 0.93 and 1.00 V likely involve the formation of cation radicals on each arm while the third process at 1.41 V could be assigned to the formation of the tricationic species followed by the generation of higher oxi-
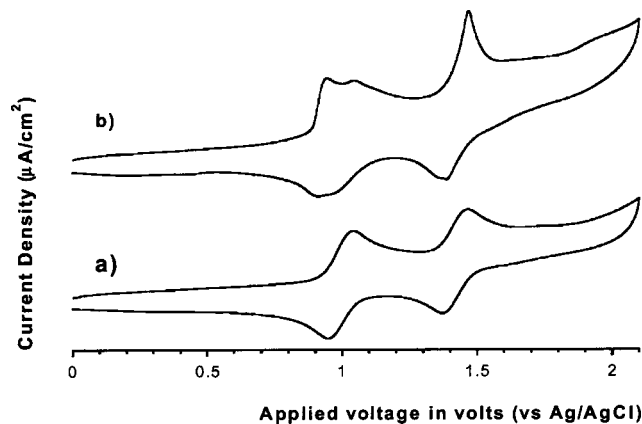
J. Chem. Phys., Vol. 120, No. 24, 22 June 2004

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FIG. 4. Cyclic voltammetries of (a) Ph3TASiMe$_3$ and (b) Ph(A3TPh)$_3$ recorded in 0.1 M TBAPF$_6$ in CH$_2$Cl$_2$.

FIG. 6. FT–Raman spectrum of the radical cation of Ph3TASiMe$_3$.

dation species to which the large peak current for the return of the third anodic wave can be due as a consequence of their precipitation. The first oxidation peak at 0.99 V in Ph3TASiMe$_3$ can be related with the first oxidation process of Ph(A3TPh)$_3$ at 0.93 V. The difference in oxidation potentials may be more indicative of a Coulombic effect rather than any significant electronic effect. The electrochemical data are consistent with the Raman analysis which reveals that the various arms interact very little across the core. In addition to the oxidation processes, it is noticeable to mention that for Ph(A3TPh)$_4$ its CV shows a reversible reduction in the cathodic branch at −1.49 V.[5] The existence of reversible oxidations and reductions in oligothiophenes is rare and offers attractive prospects for applications. In this regard, the quantum chemical calculations well justify the stabilization of anionic species since the central phenyl ring displays an important electron deficient character which can reasonably facilitate the incorporation of new electrons in the electrochemical experiment.

As for the oxidized samples (which absorb in the Vis–NIR spectral region) FT–Raman spectroscopy working with
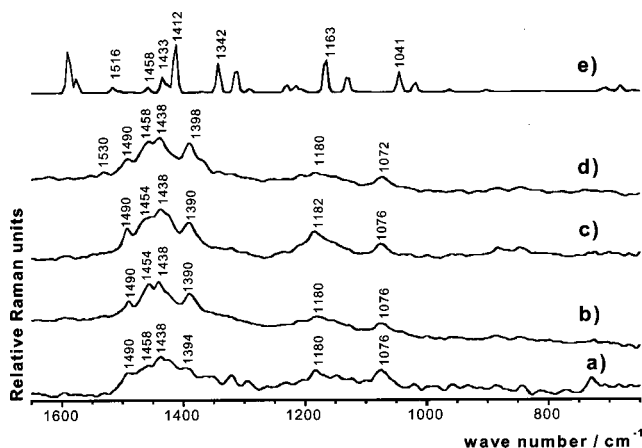

FIG. 5. FT–Raman spectra of (a) Ph(A3TPh)$_3$, (b) Ph(A3TPh)$_4$, (c) Th(A3TPh)$_4$, and (d) Ph(A3TPh)$_6$ obtained after exhaustive electrochemical oxidation at 2 V (vs Ag/AgCl). The spectrum labeled as (e) corresponds to the calculated B3LYP/3-21G* Raman spectrum of the *para* Ph(A3TPh)$_2$ model in dicationic state.
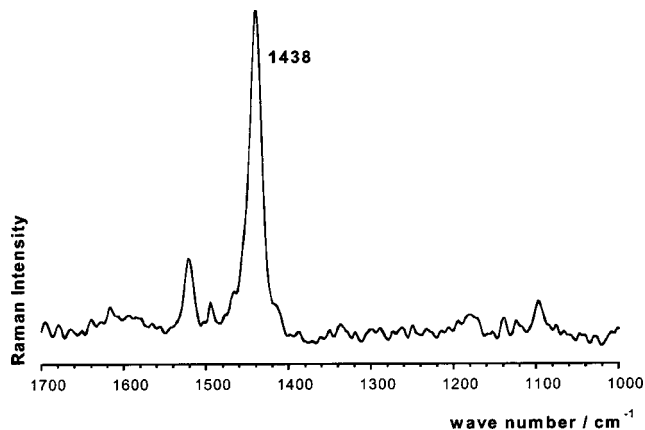
a 1064 nm laser excitation can provide very useful and selective vibrational information because of the gaining in sensibility of the technique when resonance or preresonance conditions between the exciting laser radiation and the real electronic transition are reached.[19] Figure 5 shows the Raman spectra collected after exhaustive electrochemical oxidation of all the radial molecules in solid state. The spectra, recorded in the 0–2 V potential range, are characterized by the disappearance of the Raman bands of the neutral molecules and the appearance of two intense bands at around 1450 and 1440 cm^{-1}. As an aid to the discussion which follows, Fig. 6 shows the Raman spectrum of the radical cation of Ph3TASiMe$_3$ which is dominated by the presence of a strong and sharp band at 1438 cm^{-1}. The spectral profile of this charged species is clearly distinguished in the Raman spectra of all the oxidized forms of the acetylene-bridged oligothiophene compounds. On the other hand, the component near 1450 cm^{-1} is absent in the spectrum of the fully oxidized species of the homologue molecule of Ph(A3TPh)$_3$ lacking of acetylene groups and, therefore this Raman line must be associated with vibrational modes of the acetylene spacers.[13]

Accounting that, in view of their chemical structures, the most feasible structure for the oxidized species of these radial molecules could consist of one positive charge on each arm, one could reasonably think that theoretical calculations using a model like *para* Ph(A3TPh)$_2$ could be representative of the structural modifications occurring after doping. Thus, optimized molecular geometries, charge distribution, and theoretical Raman features for the neutral and dicationic species of *para* Ph(A3TPh)$_2$ have been obtained at the B3LYP/3-21G* level of theory.

The Raman spectra of the models reproduce the main tendencies of the features collected during the spectroelectrochemical Raman experiment: the strongest Raman bands of the neutral species, measured around 1455–1460 cm^{-1}, can be correlated with that calculated at 1433 cm^{-1} in *para* Ph(A3TPh)$_2$. Furthermore the downshift of around 20 cm^{-1} (to 1438 cm^{-1}) observed in the Raman spectra of all the fully electrochemically oxidized samples is nicely predicted by the theory since the strongest band downshifts by 21 cm^{-1} on going from the neutral to the dicationic species of *para*

Ph(A3TPh)$_2$. Others experimental Raman bands like those around 1522, 1490, 1454–1458, 1180, and 1070–1080 cm^{-1} can also be correlated with the theoretical features at 1516, 1458, 1433, 1163, and 1041 cm^{-1}. Consequently, it seems reasonable to use these models to assess insight about the trend of the variation of the molecular parameters taking place in the real molecules upon *p*-doping or oxidation.

Theory predicts the molecular structure *para* Ph(A3TPh)$_2$ in neutral state to be fully planar while the successive introduction of one and two positive charges makes the two outer phenyl rings to deviate from the coplanarity by 2 and 15 degrees, respectively, likely to mitigate electrostatic repulsion between the positive charges over the phenyl end rings and their nearest sulphur atoms which also bear a partial positive charge. The terthienyl moieties display an aromaticlike structure for the neutral species that is still preserved in the radical cation but subsequently evolves to a quinoidlike structure for the dication with a reversal of the C≡C/C–C bond length alternation pattern. As for the acetylene spacer, the triple bond lengthens from 1.2170 Å in the neutral species, to 1.2213 Å in the radical cation, and 1.2258 Å in the dication, at the same time that the CC bonds connecting the triple bond with the terthiophene and the central phenyl ring shortens by around 0.0228 Å in passing from the neutral form to the dication. It is noteworthy that these two CC distances are quite close to those typical of π-conjugated double bonds: 1.3744 and 1.3939 Å.

Regarding the Mülliken atomic charges, one observes that the oligothienyl segments mainly store the positive charge upon ionization $+0.6410e$ and $+1.2280e$ on passing from the neutral to the radical cation and dication, respectively. The outermost phenyl groups are much more affected by the full ionization because of the electrostatic repulsion between the two positive charges. Finally, and as a consequence of its high electron-deficient character, the acetylene spacers are much less perturbed, hence the sum of the Mülliken atomic charges over the two Csp atoms are $-0.0949e$ in the neutral species, $-0.0430e$ in the radical cation, and $+0.003e$ in the dication.

V. CONCLUSIONS

The Raman spectra of a series of radial compounds consisting of a central benzene or thiophene ring surrounded by three, four and six α-acetylene, α'-phenyl terthienyl arms have been analyzed, assigned and interpreted in order to extract relevant information of their electronic structure. For the neutral solids, regarding the π-conjugational properties, the outermost phenyl terthienyl arms are weakly electronically coupled to the central phenyl or acetylene moieties. By increasing the branching pattern, the electronic structure of the molecules seems to be only affected at the level of the central phenyl core and of the acetylene bridges, whereas the outermost phenyl terthienyl moieties remain almost unaltered.

The combination of the electrochemical data, the Raman spectra of the oxidized species and the theoretical calculations on two model systems has been able to give us molecular details of the p-doped species. Each arm is capable of

accommodate cation radicals what leads us to postulate the formation of hexacation radicals in the largest radial molecule. If these charged species could resemble the electronic structure of the excited states, this study shows how the active sites (hole transporting or light absorbing units) are located at the periphery of the molecule and are weakly connected or electronically coupled to the central core. The description of the electronic feature for these acetylene-bridged oligothiophenes, as models of dendrimer-like structures, can be of interest in order to understand the striking mechanisms of energy flow and charge transport in dendrimer materials and in the latter design of new materials.

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