Structural implications of ring shape, dimension, and metal atom insertion in nanosized cyclic oligothiophenes: Joint Raman and density functional theory study

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This paper reports on a combined spectroscopic and density functional theory study on a series of cyclo(diacetylenes-oligothiophenes) with different shapes and dimensions. The case of a macrocycle fragmented by the insertion of Pt metallic atoms is illustrated as well. The analysis covers the neutral and oxidized samples. A full assignment of the spectra has been proposed, supported by BP86/cc-pVQZ theoretical calculations. Ring shape and molecular dimension have been related with the C—C/C—C structural parameters and Raman wave numbers. Platinum atom insertion within the acetylene spacer seems to soften ring strain owing to the rupture of the strained circular shape. Oxidation causes an overall downshift of the Raman wave numbers likely due to the skeletal relaxation of CC conjugated path, while the ring shape of each macrocycle is conserved upon oxidation. © 2006 American Institute of Physics. [DOI: 10.1063/1.2217746]

I. INTRODUCTION

The field of nanosized and shaped persistent cycles is growing rapidly.1,2 Recently, the first series of macrocyclic structures, cyclo(diacetylenes-oligothiophenes) and cyclo[n]thiophenes, have been synthesized. These systems might be considered themselves as a new area in the field of polyconjugated materials with properties half-way between those of discrete oligomers and long chain polymers.3–5 Other relevant characteristics of these macromolecules are the strong propensity to physisorb on graphitic substrates and to form highly ordered two-dimensional self-assembled monolayers (very important for thin film electronic devices), generating channels and nanotubes in analogy with the case of self-assembled peptides.6 The nanoscale structure of these assemblies is further controlled by molecular features such as the shape, conformation, and dimension of the macrocycles. Moreover, the existence of a peripheral CC π-electron delocalization circuit is of great interest since it constitutes the basis for the electronic and linear and nonlinear optical actuations (namely, intramolecular electron-hole migration is intimately related with the efficiency of π-electron delocalization).7 In this scenario, one wonders to what extent ring shape, macrocycle dimension, or insertion/combination with metallic centers enhances or disrupts this peripheral cyclic π-electron delocalization.

The uncommon appearance of the Raman spectra of π-conjugated molecules is the result of the existence of an intensive coupling between some particular atomic motions and the electronic structure of the conjugated path, or electron-phonon mechanism in solid state terminology.8 Intuitively, these motions outline the structural deformation through which the π electronic cloud is easiest perturbed. Conversely, it can be stated that the projection over the vibrational space of this CC deformation results in the normal modes that carry out the largest changes of the molecular polarizability and, consequently, give rise to few and stronger lines of the Raman spectrum.9,10 For this reason, Raman spectroscopy becomes a very useful technique to address the electronic properties of π-conjugated systems and to establish relevant property-structure relationships.9 The understanding of the physical properties contained in the Raman spectra, further complemented with the information provided by other physicochemical techniques, is a source of information of great importance to extract suitable property-structure correlations.

This paper tries to bring new insights on the electronic structure of the cyclothiophenes depicted in Fig. 1 by means of the analysis of the information provided by Raman spectroscopy, absorption and fluorescence data, electrochemistry, and density functional theory (DFT) quantum chemical calculations. Interesting points such as the effects on the peripheral π-electronic delocalization of ring shape, macrocyclic dimension, and insertion of metallic (platinum) atoms will be analyzed. The insertion of Pt within the macrocycle illustrates the case of intervalence charge transfer processes, where interaction between carbon π electrons and metal or-
bital orbitals might come into play. This study concerns the cyclo(diacetylene-oligothiophenes) derivatives both in the neutral and oxidized states.

II. EXPERIMENTAL AND THEORETICAL DETAILS

The synthesis of the macrocycles (Fig. 1) was already reported. Chemical oxidation was carried out with I₂ using a solid/gas procedure. Fourier transform (FT)-Raman spectra were measured using a FT-Raman accessory kit (FRA/106-S) of a Bruker Equinox 55 Fourier transform infrared (FTIR) interferometer. A continuous-wave Nd:YAG (yttrium aluminum garnet) laser working at 1064 nm was employed for excitation. A germanium detector operating at liquid nitrogen temperature was used. Raman scattering radiation was collected in a backscattering configuration with a standard spectral resolution of 4 cm⁻¹. In order to avoid possible damage of the oxidized samples upon laser radiation, its power was kept at a level lower than 100 mW, and 1000–3000 scans were averaged for each spectrum.

In recent years, density functional theory methods have become very popular. It is clear that DFT methods have many advantages; they scale well with system size, implicitly include electron correlation effects, and their accuracy is comparable to correlated ab initio procedures, such as MP2, which do not scale as well with molecular size. Also the suitability of DFT methods for determining the electronic structure of molecular ions has recently been assessed. Overall, these methods are ideal low-cost computational procedures to analyze conjugated molecules in which electron correlation effect plays a significant role. DFT is also very successful in describing vibrational properties in large molecules (for example, see Ref. 14 and quoted references for the frequencies and transition strengths of the infrared active vibrations in C₆₀). Consequently, the ground-state total energies, equilibrium geometries, eigenfrequencies, and normal coordinates for our macrocycles were calculated within the DFT framework. Calculations were carried out by means of the GAUSSIAN 98 package of programs. The computational method used is the Becke exchange correction combined with the Perdew86 correlation functional (BP86). The correlation-consistent polarized valence double zeta (cc-pVDZ) basis sets were considered. Particular details of the modelization are as follows: (i) optimal geometries were determined on isolated entities and neither solvent nor counterion effects were taken into account. (ii) The molecules studied in this work display an all-cis conformation of the successive rings (i.e., with a C₂ᵥ molecular symmetry). (iii) Butyl groups are omitted in these models assuming that the conjugated backbone is scarcely affected by the alkyl chains (i.e., these were only included to facilitate the synthesis by improving their solubility). (iv) Harmonic vibrational frequencies and Raman intensities in the ground-state optimized geometries were calculated analytically with the BP86 functional. (v) Ab initio calculations often yield vibrational frequencies with an accuracy of about 10% compared to the respective experimental values. Only to improve the numerical comparison, calculated harmonic vibrational frequencies are uniformly scaled down by a single scaling factor of 0.97. All reported theoretical vibrational frequencies are thus scaled values. (vi) Radical cations were treated as open-shell systems and were computed using the spin-unrestricted UBP86 wave functions. The maximum value obtained for $S^2$
was 0.7509, very close to the 0.75 theoretically expected for a doublet,\textsuperscript{18} showing that spin contamination is almost absent.

The time-dependent DFT (TD-DFT) approach is now being widely applied in both chemistry and condensed matter physics to describe electron excitations.\textsuperscript{19} Although TD-DFT is not as accurate for excitations as the ordinary DFT is for ground electronic state properties, this theory has considerable predictive power for excited states and is computationally quite tractable. Therefore, vertical electronic excitation energies and oscillator strengths were computed by using the TD-DFT approach at the same BP86/cc-pVDZ level of theory. At least the lowest 30 energy electronic excited states were computed for all the molecules.

III. SPECTROSCOPIC-STRUCTURE RELATIONSHIPS IN NEUTRAL SPECIES
A. Optical spectra

UV-Vis spectra of C(DA-3T)$_2$ in CH$_2$Cl$_2$ are shown in Fig. 2. The absorption spectrum displays a strong band at 401 nm and a weak-broad feature at 480 nm. TD-DFT calculations for C(DA-3T)$_2$ reproduce the presence of two intense transitions at quite similar energies and oscillator strengths ($f$), 493 nm ($f=0.99$) and 472 nm ($f=1.12$), whose overlap might result in the strong experimental feature around 400 nm. These theoretical lines are assigned to the $1\text{Ag} \rightarrow 2\text{Bu}$ and $1\text{Ag} \rightarrow 2\text{Au}$ excitations, which are described by double monoelectronic promotions, $H-1 \rightarrow L+H \rightarrow L+1$ and $H-2 \rightarrow L+H \rightarrow L+2$, respectively. The shoulder at 377 nm is separated from the maximum of the band by 1587 cm$^{-1}$, likely constituting part of the vibronic structure of this absorption further supported by the presence of intense Raman bands in the 1450–1600 cm$^{-1}$ region. The $1\text{Ag} \rightarrow 1\text{Bg}$ excitation (i.e., the one-electron $H \rightarrow L$ promotion) is predicted to appear at 944 nm, corresponding to a $C_{2h}$ symmetry forbidden band ($f=0$). TD-DFT//BP86/cc-pVDZ calculations also reproduce a group of weak lines in the 600–660 nm range, which are respectively assigned to the following excitations: $1\text{Ag} \rightarrow 2\text{Au}$ at 590 nm with $f=0.010$, $1\text{Ag} \rightarrow 1\text{Au}$ at 656 nm with $f=0.004$, and $1\text{Ag} \rightarrow 1\text{Bu}$ at 666 nm with $f=0.002$. This latter theoretical band corresponds to the antisymmetric combination of the same terms (i.e., $H-1 \rightarrow L$ and $H \rightarrow L+1$ one-electron promotions) involved in the strong band measured at 401 nm and presumably accounts for its low oscillator strength. This set of bands, likely receiving extra intensity by vibronic coupling due to ring strain, can support the occurrence of the weak and broad features spreading from 430 to 550 nm (i.e., maximum around 480 nm) in the spectrum of C(DA-3T)$_2$ in CH$_2$Cl$_2$. The absorption spectra of the bigger macrocycles show an intense feature at 422 nm in C(DA-3T)$_1$ at 420 nm in C(DA-3T)$_4$, and at 431 nm in C(DA-3T)$_2$.\textsuperscript{20} However, the weak band at 440 nm in the smallest system is not clearly visible in the macrocycles with more than two terthienyl units, therefore confirming the vibronic intensity released by ring strain in C(DA-3T)$_2$.

Very recently, Bednarz et al.\textsuperscript{21} have reported a comparative study between the absorption spectra of linear and cyclic ring-shaped oligothiophenes by means of the Frenkel exciton theory. Within this approach, they show that the selection rules for linear oligothiophenes determine that most of the oscillator strength is accumulated in the lowest state of the exciton band, meaning that the absorption spectra of linear oligothiophenes are dominated by the optically allowed transition from the ground electronic state to the lowest excited state ($S_0 \rightarrow S_1$, described by the one-electron $H \rightarrow L$ promotion). In contrast, the selection rules for the cyclic symmetry makes the $S_0 \rightarrow S_1$ excitation to be a dipole-forbidden transition with the oscillator strength concentrated in higher energy excitations compared to the linear case. Our calculations agree with the Frenkel exciton theory data, since TD-DFT predicts the strongest band of the cyclic C(DA-3T)$_2$ compound to be a superposition of two one-electron excitation ($H-1 \rightarrow L+H \rightarrow L+1$), neither of them involved in the $S_0 \rightarrow S_1$ ($H \rightarrow L$) excitation whose oscillator strength is predicted to be zero.

The luminescence spectrum with excitation at 430 nm of C(DA-3T)$_2$, (Fig. 2) consists of a broad fluorescence band starting at 500 nm, which extends up to 800 nm, and two well resolved peaks at 550 and 590 nm. Assuming that emission occurs from a quinoidal state, quinoidization implies a concerted strengthening/weakening of the $C-C/C=C-C$ bonds of the whole conjugated cyclic path of the aromatic ground electronic state, a process that is somehow impeded by ring strain. As a result, a medium-large Stokes shift (i.e., 4545 cm$^{-1}$) is measured for this molecule. To get insights into the influence of the cyclic geometry and ring strain in the photophysical properties, linearly connected $\alpha$-oligothiophenes show considerably minor Stokes shifts, or 3672 cm$^{-1}$ for terthiophene and 3015 cm$^{-1}$ for sexithiophene (i.e., the comparison is more representative for the six unit member).\textsuperscript{20} In this sense, large Stokes shifts are distinctive of ring strain.\textsuperscript{20,22} Due to the structural relaxation prior to photon emission from the $S_1$ state, other phenomena can interfere fluorescence, thus resulting in a rather low fluorescence quantum yield (i.e., $\approx 1\%$) for C(DA-3T)$_2$. For the bigger macrocycles ring strain is mitigated, and expectedly, fluorescence quantum yields increase, such as is observed. Interestingly, these macrocycles show a redshifting of the fluores-
cence band on going from C(DA-3T)$_2$ (i.e., 550 nm) to C(DA-3T)$_1$ (i.e., 571 nm) followed by an isochromic displacement for C(DA-3T)$_4$ (i.e., 549 nm) and C(DA-3T)$_3$ (i.e., 546 nm). A comprehensive understanding of these photophysical properties is beyond the scope of the present work, however, the dependence of the luminescence behavior in C(DA-3T)$_2$ with respect to the other macrocycles likely outlines the interesting physical phenomena that might emerge when ring shape and ring strain come into play. Similar photophysical features have been observed in alkyyl derived oligomers and polymers, which reveal the relevant role of the acetylene groups in terms of photophysics. This is consistent with an emissive state extended over the whole molecule that might suppose a slight quinoidization of the thiophene rings and a cumulization of the acetylene spacers.

The absorption and emission spectra of C(Pt-DA-3T)$_2$ are similar to those of C(DA-3T)$_2$. A rather small bathochromic shift of around 0.08 eV in the Pt derivative [namely, 384 and 410 nm in C(Pt-DA-3T)$_2$ versus 377 and 401 nm in C(DA-3T)$_2$] are measured. No metal→ligand charge transfer bands are observed, and the origin of the electronic absorption features in the Pt derivative is likely the same in C(DA-3T)$_2$, adding a minimal participation of the Pt atomic orbitals on the low lying π excited states.

B. Raman spectra: Assignment and cis-trans isomerism

Raman wave numbers and theoretical vibrational eigenvectors can be taken as microscopic proofs of the molecular and electronic structures, and their comparison within a family of samples allows the assessment of particular structural details. Figure 3 compares the experimental Raman spectrum of C(DA-3T)$_2$ with the DFT//BP86/cc-pVDZ Raman spectrum of its model C(DA-3T)$_2$ (i.e., without butyl chains).

The weak band at 1546 cm$^{-1}$ is calculated at 1552 cm$^{-1}$ and arises from an antisymmetric C=C ring stretching vibration [i.e., $\nu_s$(C=C)], mostly spreading over the external thiophenes or those connected to the acetylene spacers. This feature is usually named line A in the literature of Raman spectroscopy of linear all-trans oligothiophenes. In this regard, the last paragraph of this section will describe the consequences on the Raman spectra of oligothiophenes of cis→trans structural isomerization motivated by the all-cis conformation of the successive thiophene rings in our macrocycles.

The strongest Raman line of C(DA-3T)$_2$, line B or effective conjugation coordinate (ECC mode), is measured at 1471 cm$^{-1}$ and computed at 1473 cm$^{-1}$. Its associated eigenvector (insert of Fig. 3) shows that this vibration is due to a in-phase ring C=C symmetric stretching [i.e., $\nu_v$(C=C)] predominantly located at the internal thiophene ring and coupled with the respective $\nu_s$(C=C) modes of the external thiophenes. This ECC mode best represents the projection over the vibrational space of the skeletal changes associated with the evolution from the geometry of the ground electronic state to the geometry of the first excited state. The large intensity of this line indicates that its atomic displacements (lengthening/shortening of the C=C bonds and shortening/lengthening of the C=C) mostly outline the structural changes that the molecule undergoes upon optical excitation. In terms of solid state physics, this mode mostly carries out the electron-phonon coupling mechanism. On the low energy side of line B, a medium-weak intensity band is recorded (line C) at 1438 cm$^{-1}$, which might be related to the theoretical feature at 1436 cm$^{-1}$, whose dynamics is very similar to that of line B but with the motions of the adjacent rings taking place out of phase.

A medium intensity band at 1391 cm$^{-1}$, not reproduced by theory, is measured in the spectrum of C(DA-3T)$_2$. This band is missing in the case of linear α-tertiophene$^{21}$ (i.e., 3T without side chains); however, butyl substitution of the β
positions of the central ring of 3T gives rise to the appearance of a medium intensity Raman line around 1390 cm$^{-1}$. In this energy range, only a weak line is computed at 1367 cm$^{-1}$, mostly arising from an intraring $C_β$--$C_β$ stretching mode [i.e., $\nu(C-C)$]. Taking these two facts into account, the experimental line at 1391 cm$^{-1}$ might emerge from skeletal $C_β$--$C_β$ vibrations somehow mixed with the butyl CH$_2$/CH$_3$ deformation vibrations (usually appearing around 1380 cm$^{-1}$), which explains reasonably well the presence of this line with similar intensity around 2200 cm$^{-1}$.

Theoretical calculations of DA-3T either in all-cis or all-trans conformation of their ground electronic states in contrast to the all-trans isomer. This theoretical splitting almost falls within the spectral resolution of the experimental band at 2120 cm$^{-1}$. Its associated eigenvector [i.e., $\nu(C\equiv C)$] appears. It is worth to point out that the movements of the carbon atoms along with the ECC mode make the H atoms at $\beta$ positions recoil in opposite directions originating a mechanical coupling at the origin of the detection of this nonskeletal $\beta(C-H)$ mode.

As already mentioned, these macrocycles display an all-cis conformation in their ground electronic states in contrast to the all-trans disposition in the case of linear oligothiophenes. This fact motivates the discussion of the implications of cis--trans isomerization in the Raman spectrum of oligothiophenes. To this goal, theoretical calculations of DA-3T either in all-cis or all-trans conformation of their consecutive thiophene rings have been performed. In Fig. 4 the following is found: (i) Almost twice Raman activity is predicted for the all-trans isomer. (ii) The $\nu(C\equiv C)$ mode around 2200 cm$^{-1}$ (vide infra) and line A at 1503 cm$^{-1}$ scarcely move upon isomerization of the oligothiophene backbone. This is likely due to the cylindrical geometry of the acetylene group and to the localization on the terminal thiophene rings of line A. (iii) In the theoretical spectra, line B shifts by 8–10 cm$^{-1}$ from one to another and splits into a few components in the all-cis isomer. This theoretical splitting almost falls within the spectral resolution of the experimental line B broadening, which thus becomes the main difference between the Raman spectra of all-cis macrocycles (i.e., line B is a broad band with a few components) and the spectra of the all-trans linear parents (i.e., line B appears as a sharp line).

C. Raman spectra: Macroyclic shape and dimension

The theoretical spectrum of C(DA-3T)$_2$ shows one intense Raman line around 2150 cm$^{-1}$ that relates with the experimental band at 2120 cm$^{-1}$. Its associated eigenvector (Fig. 3) displays that this mode corresponds to a CC stretch of the diacetylene moiety [i.e., $\nu(C\equiv C/C\equiv C)$]. This vibration spreads over the entire spacer, justifying the occurrence of only one overwhelming Raman band associated with the DA group (i.e., a very weak satellite line is observed in the theoretical spectrum, which is rather undistinguishable in the experimental measurement). Another interesting feature is the relatively large intensity of this $\nu(C\equiv C/C\equiv C)$ line compared with the 1550–1400 cm$^{-1}$ thienyl vibrations. This fact indicates a rather efficient polarization or $\pi$-electron conjugation within the spacer. Let us closely examine the structure of the diacetylene moiety.
The x-ray crystalline structures of C(DA-3T)\textsubscript{2} and C(DA-3T)\textsubscript{4} have been already established.\textsuperscript{3-5} These crystallographic analyses show that (i) C(DA-3T)\textsubscript{2} has a nearly perfect circular shape versus a rounded rectangular form in the case of C(DA-3T)\textsubscript{4}. And, as a consequence, (ii) the diacetylene moieties of C(DA-3T)\textsubscript{2} form concavely bowed units revealing considerable ring strain, which results in an averaged angle between each two consecutive CC bonds of the DA moiety of 164° and a bond length alternation pattern (BLA, averaged distances between the consecutive CC bonds) of 0.187 Å. The biggest macrocycle is quite planar i.e., much less strained. This x-ray crystalline structures of C(DA-3T)\textsubscript{2} and C(DA-3T)\textsubscript{4}, thus lying in linear dispositions.\textsuperscript{10} For C(DA-3T)\textsubscript{2}, the ν(C≡C/C−C) at 2120 cm\textsuperscript{-1} indicates that the DA moiety would be folded and their carbon atoms partially rehybridized due to the cyclic shape.

Continuing with this comparison, the vertices of the molecular polygons should be occupied by the terthiophenyl moieties, and as a result, their geometries accordingly distort depending on the macrocycle shape. The extent of this distortion can be given by the total angle α=360°/n, where n is the number of polygon edges. Therefore, each terthiophene undergoes a total α distortion that can be referred to a per-CC-bond dividing by 11 (i.e., each terthiophene has 11 peripheral CC bonds). For C(DA-3T)\textsubscript{2} with a cyclic geometry, the calculus of the degree of per-CC-bond distortion is 360°/32, where 32 is the number of total peripheral CC bonds including diacetylenes and terthiophenes. This geometric approach yields a per-CC-bond distortion angle of 11.25° in C(DA-3T)\textsubscript{2}, 10.91° in C(DA-3T)\textsubscript{3}, 8.18° in C(DA-3T)\textsubscript{4}, and 6.54° in C(DA-3T)\textsubscript{5}. On the other hand, the most intense Raman bands (collective C=C/C−C stretches) associated with the 3T moiety behave or decrease as the per-CC-bond distortion angle in the polygonal macrocycles, namely, 1474 cm\textsuperscript{-1} in C(DA-3T)\textsubscript{4}, 1467 cm\textsuperscript{-1} in C(DA-3T)\textsubscript{3}, and 1459 cm\textsuperscript{-1} in C(DA-3T)\textsubscript{2}. For the cyclic and triangle-shaped C(DA-3T)\textsubscript{2} and C(DA-3T)\textsubscript{3}, the per-CC-bond angles are similar, 11.25° and 10.91°, respectively, in line with the resemblance of their line B wave number peaks, 1471 cm\textsuperscript{-1} in C(DA-3T)\textsubscript{2} and 1474 cm\textsuperscript{-1} in C(DA-3T)\textsubscript{3}. As a consequence, it is found that geometrical and spectroscopic properties seemingly share a common origin (i.e., lower line B wave number relates to increased π-electron delocalization, while increased per-CC-bond terthiophenyl distortion is detrimental for it).\textsuperscript{10}

D. Raman spectra: Pt functionalization

Figure 5 also compares the Raman spectra of C(DA-3T)\textsubscript{2} and C(Pt-DA-3T)\textsubscript{2}. The Raman ν(C=C/C−C) scattering is now measured at 2105 cm\textsuperscript{-1} in C(Pt-DA-3T)\textsubscript{2}. As for the peak position of this line, a mass effect due to the Pt atoms is expected to be negligible because of the delocalized character of this mode. Another point concerns the mechanical decoupling expected for stretches in the 2100–2200 cm\textsuperscript{-1} energy interval and carbon/metal vibrations usually appearing in the far-IR region. As a result, the wave number of this ν(C≡C/C−C) line in C(Pt-DA-3T)\textsubscript{2} is mainly determined by structural/electronic effects (i.e., conjugation or π-electron delocalization, etc.) and the 2120→2105 cm\textsuperscript{-1} downshift on C(DA-3T)\textsubscript{2}→C(Pt-DA-3T)\textsubscript{2} might reveal the involvement of the metallic atoms in the structure of the spacer.

As for line B in C(Pt-DA-3T)\textsubscript{2}, this appears at 1462 cm\textsuperscript{-1} between 1471 cm\textsuperscript{-1} of the circle-shaped C(DA-3T)\textsubscript{2} and 1459 cm\textsuperscript{-1} of the pentagon-shaped C(DA-3T)\textsubscript{5}. This spectroscopic finding can be interpreted in two ways. First, as due to the breaking of the circular shape of C(DA-3T)\textsubscript{2} upon insertion of the Pt atoms, being the metallic centers placed at the “breaking” points. Second, the
downshift of line $B$ by 12 cm$^{-1}$ on going from C(DA-3T)$_2$ to C(Pt-DA-3T)$_2$ might be due to a softening of ring strain in a noncircular system.

IV. SPECTROSCOPIC-STRUCTURE RELATIONSHIPS IN CHARGED SPECIES

Figure 6 shows the cyclic voltammograms of C(DA-3T)$_2$ in CH$_2$Cl$_2$ and C(Pt-DA-3T)$_2$ in benzonitrile. For C(DA-3T)$_2$, two well resolved and reversible peaks at 0.36 and 0.56 V versus Fc/Fc$^+$ are observed. These two electrochemical waves are due to the consecutive generation of the radical cation followed by the formation of the dicationic species. The cyclic voltammetry of C(Pt-DA-3T)$_2$ is more complicated. At very low potentials, the irreversible oxidation of Pt(II) to Pt(III), or presumably to Pt(IV), occurs ($E_{pc}$ =0.06 V versus Fc/Fc$^+$). Furthermore, it is well illustrated that oxidation of the metallocmacrocycles is followed by the elimination of the Pt centers and the formation of new C–C bonds.$^5$ Therefore the two oxidation processes at $E_{pc}$=0.44 and 0.57 V can be attributed to the oxidation of the C(DA-3T)$_2$ follow-up product. The small current density wave at $E_{pc}$=0.72 V corresponds to the oxidation of the phosphine ligand.

Raman spectrochemistry (using iodine vapors and the samples in the form of thin solid films) was carried out for C(DA-3T)$_2$ and C(DA-3T)$_3$ in order to characterize the single oxidized species and to elucidate the structural evolution of the neutral macrocycles upon charge injection. No Raman data for the oxidized C(Pt-DA-3T)$_2$ are discussed due to the elimination reaction upon oxidative treatment. DFT//UBP86/cc-pVDZ theoretical calculations of the radical cation of the model C(DA-3T)$_2$ (i.e., lacking in butyl chains) have been obtained to support the spectroscopic measurements. Figure 7 compares the experimental Raman spectrum of iodine obtained [C(DA-3T)$_2$]$^+$ and the UBP86/cc-pVDZ theoretical Raman spectrum of the radical cation of its model. On the other hand, Fig. 8 summarizes the calculated optimized CC bond lengths of the skeletal backbone for the neutral and cationic forms.

The generation of radical cations gives rise to the disappearance of the Raman scatterings of the neutral forms. The main $\nu$(C=C) Raman lines upon oxidation appear shifted to lower frequency values (i.e., compared to the neutral case) and the following neutral/oxidized Raman band correlation (Fig. 9) can be established: 1546/1452–45 cm$^{-1}$ (i.e., $\nu$=−99 cm$^{-1}$), 1471/1414 cm$^{-1}$ (i.e., $\nu$=−57 cm$^{-1}$), and 1391/1395 cm$^{-1}$ (i.e., $\nu$=+4 cm$^{-1}$). As for the optimized geometries (Fig. 8), the most significant effect upon electron extraction is the C(DA-3T)$_2$ $\rightarrow$ C(DA-3T)$_2$ $^+$ relaxation (i.e., quinoidization in the thiophene units and bond length equalization in the DA spacers) of the skeletal C=C/C=C path, which can result in the observed shifting to lower wave numbers of the main Raman features. More precise bond length C=C/C=C−changes upon oxidation are −0.01/ +0.01 Å for the terthienyl moieties and −0.01/ +0.005/ +0.04 Å for the C$_{thiophene}$−C=C=C=C−C=C bond distances of the acetylene spacers. These results indicate that the structural relaxation affects the whole system. In this sense, the C=S bond lengths are minimally affected, meaning that the S atoms play the same role (electron donation towards the C=C=C=C path) in both neutral and oxidized states.

FIG. 7. (a) Experimental FT-Raman spectrum of iodine obtained [C(DA-3T)$_2$]$^+$ and (b) DFT//UBP86/cc-pVDZ theoretical one of its model molecule.

FIG. 8. DFT//UBP86/cc-pVDZ (radical cation) neutral optimized bond lengths of CC skeletal backbone of the model C(DA-3T)$_2$.
On the other hand, the theoretical Raman spectrum of the model [C(DA-3T)2]+ reproduces the appearance of the four important experimental bands in the 1600–1350 cm−1 interval. The following experimental/theoretical band pairs can be established: 1452/1487, 1445/1460, 1414/1404, and 1395/1368 cm−1. The line at 1414 cm−1 in [C(DA-3T)2]+ arises from a thienyl CC stretching vibration coupled with the CC stretches of the acetylene spacer (see Fig. 7 for its eigenvector). In contrast, in the [C(DA-3T)2]+ line at 1395 cm−1 (theoretically at 1368 cm−1) the CC thienyl stretching modes are not coupled to the spacer vibrations.

Figure 10 displays the Raman spectra of the iodine oxidized C(DA-3T)2 and C(DA-3T)3. Both samples show relatively similar spectra, with the most intense line in [C(DA-3T)2]+ being downshifted by 21 cm−1 (i.e., 1393 cm−1) relative to the strongest scattering in [C(DA-3T)3]+ (i.e., 1414 cm−1).

In order to account for this wave number difference, one can invoke the mitigation of ring strain in C(DA-3T)3, which likely deactivates the diacetylene/terthiophene CC stretching vibration occurring for the 1414 cm−1 line of [C(DA-3T)2]+. This decoupling pushes down the strongest Raman line in [C(DA-3T)3]+ at 1393 cm−1, in analogy to the 1395 cm−1 band in [C(DA-3T)2]+ (i.e., this band is not affected by such a coupling).

FIG. 9. Solid state FT-Raman spectra of (a) neutral C(DA-3T)2 and (b) radical cation of [C(DA-3T)2]+ obtained upon treatment with iodine.

FIG. 10. Solid state FT-Raman spectra of iodine treated (a) C(DA-3T)3 and (b) C(DA-3T)2.

V. CONCLUSIONS

This paper presents a combined experimental spectroscopic (Raman and electron absorption/emission) and density functional theory (DFT) study of a series of cyclo(diacetylenes-oligothiophenes) with different shapes and dimensions. The case of a macrocycle fragmented by the insertion of Pt metallic atoms is illustrated as well. The study covers the neutral and oxidized samples. The spectral features have been assigned with the help of BP86/cc-pVDZ calculations. Relevant relationships between ring shape and strain, bond length alternation values, and Raman wave numbers have been proposed. Metallic insertion within the acetylene spacer mostly affects the molecular structure by softening the ring strain through the breaking of the circular shape. For the oxidized species, the changes of the Raman spectra seem to outline the occurrence of a relaxation (i.e., quinoidization within the thienyl moieties and CC bond length equalization in the diacetylene moiety) of the CC conjugated perimeter. Macrocyle ring shapes are seemingly conserved upon oxidation.

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