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The Frontiers of Quinoidal Stability in Long Oligothiophenes: Raman Spectra of Dicationic Polaron Pairs

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 Supporting Information

ABSTRACT: The transformation of bipolarons into polaron pairs in long oligothiophene dications has been reported by Raman spectroscopy. These polaron-pair dicationic species possess singlet open-shell biradicaloid ground electronic states. The formation of biradical polaron pairs marks the end of the quinoidal stability promoted by the intrinsic proaromatic character. The quinoidal stability in TCNQ oligothiophenes in comparison with dicationic oligothiophenes has been addressed.

Whether the charge carriers in heavily doped electrically conducting polythiophenes are spinless bipolarons (i.e., dications localized over one limited polymer section) or spin-carrying polaron pairs (i.e., dications formed by two interacting cation radicals localized on different polymer sections) is one of the interesting questions that still needs to be clarified, despite considerable experimental and theoretical efforts.^{1–4} In general, oligothiophenes make the elucidation of polymer properties possible by means of the oligomeric approach.⁵ Because of their extended conjugational properties, long oligothiophenes constitute ideal polythiophene models. On their own way, oligothiophenes have been successfully used as semiconductor elements in organic electronic devices as a result of their well-defined molecular and electronic structures.⁶

In the bipolaron versus polaron pair context, many electron EPR and UV–vis–NIR spectra^{1,2} and elaborate theoretical calculations^{3,4} for long oligothiophene dications have recently been reported. Our contribution here deals with a new set of spectroscopic characteristics of long polymer-like oligothiophene dications, namely, their vibrational Raman spectra. Our purpose is twofold: (i) to account for these spectra in terms of their variation with the oligomer size and the oxidation level and (ii) to draw conclusions about the transformation of bipolarons into polaron pairs. The intrinsic biradicaloid nature of the polaron pair species, resulting from the competition of quinoidal and aromatic stabilities, will also be discussed. The paper closes with a generalization of the intrinsic stability of thiophene quinoidal arrangements, a topic of great relevance for a comprehensive understanding of π -electron systems.

Recently we have proved by Raman spectroscopy that tetracyanoquinodimethane (TCNQ) oligothiophenes^{7,8} (Q_n in Scheme 1) are characterized by a ground electronic state that transforms from a closed-shell *quinoidal* structure for the shortest elements into an open-shell *aromatic* biradical structure for the largest members (the Q_n series varies from a tetracyanobithiophene to a

hexathiophene).⁹ The Raman spectral fingerprint of the *quinoidal* (closed-shell) \rightarrow *aromatic* (open-shell) transition (Scheme 1) concerns the turning-point behavior of the strongest Raman band, which moves down in frequency with increasing extension of the quinoidal segment in the shorter members (i.e., from Q_2 to Q_4) and is upshifted in Q_4 – Q_6 [see the Supporting Information (SI)].^{7,10} We were able to ascribe this frequency turning point effect of the main Raman band in terms of aromatization of the thienyl core and biradical formation in the longer members at the expense of the quinoidal path, which is stable only in the first quinoidal oligomers (Scheme 1). Consequently, we propose to study a series of three polymer-like oligothiophene dications with six (D_6), eight (D_8), and twelve (D_{12}) thiophene rings (Scheme 1).¹¹ Our hypothesis is similar for these dications: *dication formation provokes the quinoidization of the thienyl core, but this quinoidal structure is not indefinitely stable and there is an oligomer length at which it experiences instability, turning into an aromatic-like structure with a biradicaloid nature.* It turns out that the clarification of the *quinoidal* \rightarrow *aromatic* transformation is the elucidation of the evolution from a bipolaron structure (full quinoidal pattern in Scheme 1) to a polaron-pair structure (pseudoaromatized pattern in Scheme 1). The methodology involves studying the three dications D_6 , D_8 , and D_{12} by normal, resonance, and variable-temperature Raman spectroscopies. The experimental data are supported by theoretical electronic structure calculations.

A particularity of our oligothiophenes is that they are conceived to possess a fully planar π -electron system.¹¹ Their massive bulky group functionalization in all lateral thienyl β -positions induces steric congestion that blocks inter-ring rotation and forces backbone planarization. This is a key feature regarding previously studied long oligothiophene dications, in which partial β -substitution is not a guarantee of a distortion-free conjugated path.¹² Planarization is a requirement for a fine balance between bipolarons and polaron pairs. Inter-ring rotation, in contrast, favors the conversion of bipolarons directly into independent polarons.

Oxidation of the neutral samples was carried out by stepwise addition of FeCl_3 to a dried oxygen-free solution of the samples in dichloromethane. The oxidation reaction up to the dication was followed by UV–vis–NIR spectroscopy (see the SI). The Raman spectra of the neutral, radical cation, and dication of the three oligothiophenes are shown in Figure 1. The spectrum of the neutral hexamer is characterized by the main Raman band at 1506 cm^{-1} due to a collective $\text{C}=\text{C}/\text{C}-\text{C}$ stretching vibration, $\nu(\text{C}=\text{C}/\text{C}-\text{C})$, spreading over the whole thienyl path.¹³ After

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Scheme 1. (top) Representation of the Bipolaron and Polaron-Pair Structures in Polythiophene; (bottom) Chemical Structures of the TCNQ Oligothiophenes Q_n ($n = 2-6$) and the Oligothiophene Dications D_{n+2} ($n = 4, 6, 10$)

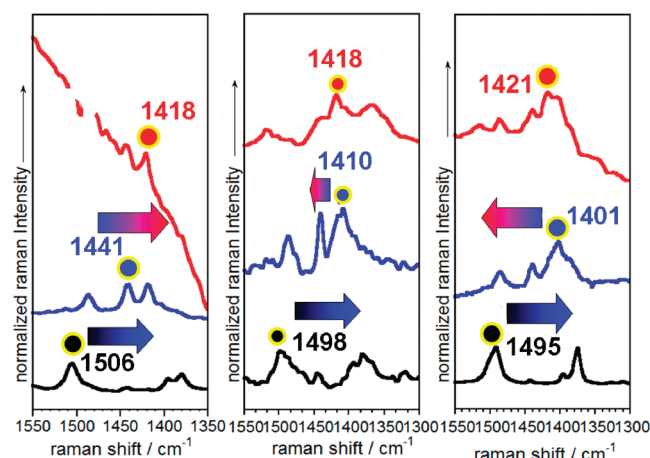
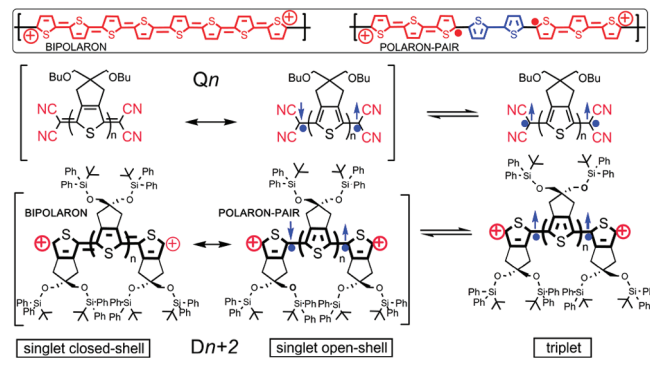


Figure 1. Raman spectra of neutral (black), radical cation (blue), and dication (red) of 6T (left), 8T (middle), and 12T (right). The arrows mark the tendency of the most intense band frequencies with oxidation.

one-electron oxidation and generation of the radical cation, the strongest Raman band is displaced to 1441 cm^{-1} , in consonance with the attainment of a quinoidal structure located in the center of the molecule and extending toward the ends. One-electron oxidation of the radical cation yields the dication species D6, which is characterized by an additional displacement of the main Raman band to a lower frequency of 1418 cm^{-1} , in line with a full quinoidization of the thienyl backbone as a result of the strong electrostatic repulsion between the positive charges confined in a relatively small molecular platform. These results are fully consistent with previous reports on Raman spectroscopy of several hexathiophene dications.¹⁴ If the length of the hexamer is duplicated, the Raman spectrum of the neutral 12T has its $\nu(\text{C}=\text{C}/\text{C}-\text{C})$ Raman band at 1495 cm^{-1} and downshifts by 94 cm^{-1} in the singly oxidized species, which indicates that the radical cation delocalizes on a very large quinoidal segment. Subsequent oxidation to the dication gives rise to a Raman spectrum with the strongest Raman feature upshifted by 20 cm^{-1} to 1421 cm^{-1} . This is the opposite behavior in comparison with the continuous frequency downshift found in $6\text{T} \rightarrow 6\text{T}^{+\bullet} \rightarrow \text{D6}$ interpreted according to a progressive quinoidization of the skeletal thiophene backbone with oxidation.

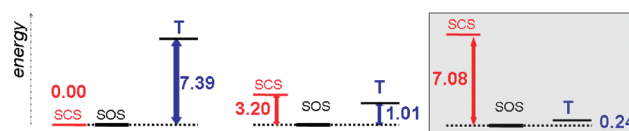


Figure 2. DFT/(U)B3LYP/6-31G** relative energies (kcal/mol) of the singlet closed-shell (SCS), singlet open-shell (SOS), and lowest-energy triplet (T) states for D6 (left) and D12 (right). In the box are shown the same data for D12 considering the effect of the counteranions.

Figure 2 represents the relative energies of the dicationic singlet states considering a singlet closed-shell (SCS) configuration and a singlet open-shell (SOS) configuration of the dications, which would eventually consider the contribution of a biradicaloid form. It is noticeable that in D12, the SOS configuration is by far the most stable and represents the ground electronic state. The SOS molecular structure features the aromatization of the central thiophene rings, while the quinoidal arrangements are confined to the terminal moieties. For D6, however, calculations predict the SCS configuration to be the most stable situation which is characterized by a complete quinoidization of the molecular backbone. This theoretical description nicely justifies the evolution of the Raman spectra in going from D6 to D12: the aromatization of the central thiophenes in the largest member causes the Raman band frequency to be upshifted, as in the case of the quinoidal tetracyano oligothiophenes. In addition, the behavior of D8 turns out to be in between the cases of D6 and D12, where the slight aromatization in the central backbone in the SOS configuration provokes a slight inversion of the Raman band frequency. See the SI for a complete discussion of the molecular structures.

The aromatization of the central part of the D12 system in the SOS state is an indication of its biradical properties.¹⁵ An additional property of singlet biradical states is the presence, very close in energy, of a triplet state, with the energy difference between the open-shell singlet and triplet states (the exchange energy) being an indication of the strength of the spin coupling in the biradical state.¹⁶ Consequently, calculations anticipate the presence of the triplet state at $\sim 1\text{ kcal/mol}$ above the singlet, which allows us to explore it spectroscopically by variable-temperature Raman measurements (i.e., this triplet state should be populated at the expense of the SOS state by heat-activated singlet-to-triplet intersystem crossing).¹⁷

To check this property of the biradicals, we obtained D12 in the solid state in order to carry out the heating process. The spectra along the heating/cooling process are shown in Figure 3. The spectrum at room temperature equally shows the most prominent band at 1420 cm^{-1} , which at $50\text{ }^{\circ}\text{C}$ quickly evolves into a stronger band at 1379 cm^{-1} and a band at a higher frequency of 1482 cm^{-1} . These two bands continuously increase their intensity with increasing temperature. The 1482 cm^{-1} band is typical of aromatic oligothiophenes¹³ with chain lengths of 4–5 rings, while that at 1379 cm^{-1} is typical of fully quinoidal oligothiophenes with three thiophenes (see the SI for a detailed comparison).¹⁸ These are spectroscopic properties that reveal the accentuation of the aromatic pattern in the center and of the quinoidization at the outermost parts, which is in consonance with the molecular structure of the triplet state as deduced by the DFT/UB3LYP/6-31G** calculations on D12.

Another entry to study the biradicaloid properties of the D12 sample is to exploit the dependence of the Raman spectrum on the stabilizing counteranion. In Figure 3 we also show the Raman

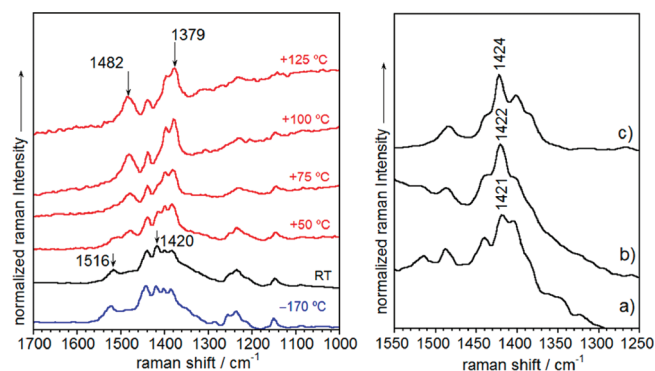


Figure 3. FT-Raman spectra of D12 at 1064 nm: (left) as a function of the temperature in the solid state and (right) with different counteranions: (a) D12(Cl[−])₂, (b) D12(PF₆[−])₂, and (c) D12(SbCl₅[−])₂.

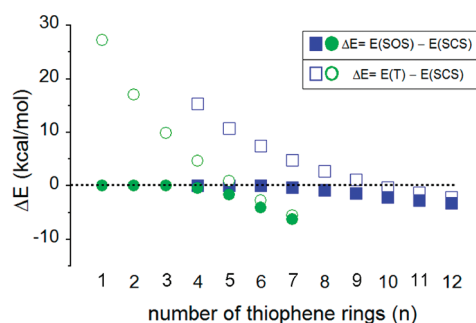


Figure 4. DFT/(U)B3LYP/6-31G** relative ΔE energies (kcal/mol) between the singlet closed-shell (SCS) state and the singlet open-shell (SOS) and triplet (T) states for the dicationic series (D_{n+2}, squares) and TCNQ oligothiophene series (Q_n, circles).

spectra of D12 obtained in the presence of three different counteranions. There are changes in the frequency of the most intense Raman band, which moves +3 cm^{−1} in going from D12(Cl[−])₂ to D12(SbCl₅[−])₂. It seems that a bigger anion better stabilizes the biradical species of the dication because the aromatic part associated with the biradical structure of the molecular core slightly extends toward the molecular ends. This is corroborated by calculations indicating the large stabilizing effect of the counteranions (0.77 kcal/mol in D12 at the DFT/UB3LYP/6-31G** level).

Figure 4 presents the theoretical energy differences, ΔE , between the SCS state and the SOS and triplet states in the TCNQ oligothiophenes (Q_n) and the dication series (D_{n+2}). In both series, $\Delta E = 0$ kcal/mol marks the end of the quinoidal pattern stability and the dominance of the aromatic biradical structure. In the TCNQ series, the quinoidal stability ends between the tetramer ($n = 4$) and the pentamer ($n = 5$). However, the limit in the dicationic series is found at twice number of thiophenes, between 9 and 10 thiophene rings. This lack of stability of the quinoidal arrangement in the tetracyano series versus the dicationic one is due to the double biradical stabilization effect in the Q_n compounds. On one hand, the strong electron-accepting or -withdrawing effect of the dicyano groups that strongly reduces the bond-length alternation pattern followed by Peierls distortion,¹⁹ and on the other, energy is gained by cooperative aromatization of the proaromatic quinoidal thiophenes. It turns out that these two forces are sufficient to eventually break a double bond and form a biradical even in the compounds with a

small number of thiophenes. In the case of the dications, the unique cause for the biradical formation is the thiophene aromatization, and the quinoidal stability appears in compounds with many more thiophene units. This energetic discussion is nicely supported by the Raman data, where the quinoidal → aromatic transition as deduced by the Raman turning point behavior is found in longer oligomers in the dication (~D8), while in the Q_n series we previously reported that the tetracyano tetramer Q4 is the last quinoidal closed-shell unit.

This provides an argument to evaluate the intrinsic stability of quinoidal structures, which turn out to be inherently unstable for a given oligothiophene length at which a double bond of the C=C/C–C conjugated sequence is sacrificed, generating an aromatic biradical segment. Quinoidization of oligothiophene skeletons is one of the most important strategies for obtaining low-band-gap systems,²⁰ which are of tremendous interest for organic electronic applications.⁶ Here we show that the concept has the limitation of the oligothiophene dimension, since there is a length at which the quinoidal structure gives way to aromatic biradicals. These effects have been similarly described in polyacetylene chains, in which Peierls distortion generates solitonic structures.²¹ Soliton species and biradical species share a common origin that is highlighted by the oligoene (oligoacetylene) character of quinoidal thiophene arrangements.

In conclusion, we have explored the spectroscopic properties of dications of long planar oligothiophenes. Their radical cations are stabilized by largely delocalized quinoidal forms that continuously increase in length with the molecular size. The long dications, in turn, display shorter quinoidal sequences because of the formation of aromatic biradical species. These dication biradicals are elusive to characterize by EPR spectroscopy (see the SI), but Raman spectroscopy appears to be instrumental. In relationship with the dication structures, there is a given length at which the energy gained by thiophene aromatization overcomes the energy required to break a double bond, giving way to biradical species; this point marks the end of the quinoidal stability. These biradical species turn out to represent a polaron-pair structure. The polaron-pair biradicals therefore represent the end of the bipolaron regime and the inflection point of the quinoidal stability. We consider that these items are not only appealing from the point of view of basic chemistry but also motivating from the perspective of material science, i.e., for the design of low-band-gap molecules (quinoidal dyes) and the elucidation of the mechanisms of electrical conductivity (bipolarons/polaron pairs) and magnetism (biradicals) in organic compounds (semiconductors).

■ ASSOCIATED CONTENT

S Supporting Information. Spectroscopic characterization of the oxidized species and theoretical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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