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Diferrocenyl oligothiophene wires: Raman and quantum chemical study of valence-trapped cations

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A combination of Raman spectroscopy and density functional theory calculations is used to describe the structural and spectroscopic properties of the different isomeric cations of diferrocenyl quaterthiophenes. Isomerisation of the thienyl \( \beta \)-positions provides site selective oxidation, which gives rise to species that can interconvert by moving the charge over the bridge. The spectroscopic study allows us to describe a sequence of stationary trapped cationic, either ferrocenyl or thienyl, states which constitutes an energy cascade of accessible sites through which the charge transfer can proceed. © 2011 American Institute of Physics. [doi:10.1063/1.3669653]

I. INTRODUCTION

Molecular wire design based on \( \pi \)-conjugated bridges promises the largest miniaturization in electronics since it uses single molecules as the conducting elements in the miniaturized highly dense device.1–4 In either of the two mechanisms (tunnelling or hopping) controlling conductance (charge transfer) in molecular wires, translation of the injected charge through the different positions of the wire is required. The estimation of the sequence and relative energies of wire sites accessible by the charge in its displacement between the termini groups, together with their dependence with the chemical structure of the \( \pi \)-conjugated moiety, are mandatory for a comprehensive knowledge of the charge motion within the wire.5–11

Molecular wires linking two redox centers with different oxidation states can give rise to mixed-valence (MV) compounds.12, 13 Among MV compounds, those referred to as class II or localized valence-trapped MV systems, according to Robin-Day classification,14 show the charge excess placed in one redox center. The potential energy surface (PES) of the ground electronic state of these class II MV systems is featured by two minima separated by an energy barrier as displayed in Scheme 1 (top-left). The displacement of the charge from one redox center to the other implies surmounting the energy barrier for the charge transfer process (Scheme 1, middle). The molecular wire participates by providing intermediate electronic/conformational states in the charge transfer.5–11 The bridge can therefore be “designed” by judicious chemical synthesis to provide the best conditions to assist the charge jump. Class III MV systems have the charge fully delocalized between the external sites and the bridge, and are characterized by a unique minimum in the PES (Scheme 1, top-right).14

Raman spectroscopy is widely used in the field of functional \( \pi \)electron organic molecules to investigate the structure of the conjugated platform (degree of \( \pi \)electron delocalization) either as neutral entities or in their oxidized states (charge bearing situation). For instance, the delocalization lengths of radical cations and dications in oligothiophenes have been successfully evaluated using Raman spectroscopy.15–21 The aromatic-to-quinoid structural evolution with oxidation and the alteration of the carbon-carbon bond length alternation pattern on which the most active Raman modes reside are the basis for the application of this technique. Moreover, Raman spectroscopy in the mode of resonance allows the recording of the spectra of species occurring at the level of traces or species in complicated chemical equilibria (mixtures) simply by exciting the absorption bands of the target species with the laser energy of the Raman experiment.

In this contribution, we investigate two structural isomers of a diferrocenyl quaterthiophene (1 and 2 in Scheme 1), in which the isomeric pattern of the thienyl bridge is changed to induce different electronic environments.22 The ferrocenyl groups act as redox centers, whereas the conjugated oligomer acts as the molecular wire.23–25 The paper deals with the study of the structural properties of isomers 1 and 2 in their radical cation states.22 Raman spectroscopy is used as a probe of the evolution of the ground electronic state of these mixed-valence systems. Emphasis is made on the tuning of the structural and energetic properties of the oxidized species depending on the chemical pattern used in the molecular wire. \( \alpha,\alpha' \)-Dimethylquaterthiophene (3) is studied as reference compound.26, 27 Density functional theory (DFT) calculations are performed to gain insight into the experimental results.
II. EXPERIMENTS AND CALCULATIONS

A. Synthesis

The synthesis of compound 2 has been carried out following a synthetic protocol analogous to that already described for compound 1. The synthetic procedure is presented in Scheme 2 and the characterization of compound 2 and its precursors is provided in the supplementary material. Chemical oxidation of compounds 1–3 was carried out in dried dichloromethane by stepwise addition of FeCl₃ to the solution.

B. Spectroscopic details

In a FT-Raman accessory kit (FRA/106–S) of a Bruker Equinox 55 FT-IR interferometer, 1064 nm FT-Raman spectra were obtained. A continuous-wave Nd-YAG 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 back-scattering configuration with a standard spectral resolution of 4 cm⁻¹. For each spectrum, 1000–3000 scans were averaged. The 785 nm Raman spectra were obtained by using the 1 × 1 camera of a Bruker Senterra.

C. Theoretical details

DFT calculations were carried out by means of the GAUSSIAN 03 program. All the calculations including geometry optimizations and vibrational spectra were performed using the Becke’s three-parameter B3LYP exchange-functional. The 6-31G** basis set was chosen as a compromise between accuracy and applicability to large molecules. Radical cations were treated as open-shell systems and computed within the spin-unrestricted DFT (UDFT) approach as doublets. The localized (lrc-l and lrc-r) and delocalized (drc) molecular structures for radical cations 1⁺⁺ and 2⁺⁺ were optimized by approaching the Cl⁻ counteranion to different molecular environments (Figure S1 in the supplementary material). For all radical-cation structures, the oligothiophene backbone converged to almost planar...
conformations. The deviations from a fully planar all-trans conformation (inter-ring rotation angles of 180°) were very small and always lower than 3°. Cl\textsuperscript{−} was selected as the counteranion instead of the Cl\textsuperscript{−} anion present in solution because previous theoretical studies have shown that it leads to realistic localized and delocalized radical cation structures and does not form covalent bonds with oligothiophenes even in the gas phase\textsuperscript{32, 33}. Solvent effects were considered within the SCRF (self-consistent reaction field) theory using the polarized continuum model (PCM) approach to model the interaction with the solvent\textsuperscript{34, 35}.

### III. RESULTS AND DISCUSSION

#### A. Dependence of the Raman displacements with the substitution pattern

Figure 1 displays the off-resonance (neutral species) and on-resonance (radical cation) Raman spectra recorded for compounds 1–3. For the MV inactive reference compound 3, the off-resonance Raman spectrum in its neutral state is dominated by an intense band at 1487 cm\textsuperscript{−1} and by two weak bands at 1535 and 1450 cm\textsuperscript{−1}, respectively\textsuperscript{26, 27}. These Raman bands are associated with symmetric C\textsubscript{–}C/C\textsubscript{=}C stretching vibrations that spread over the whole \pi-conjugated backbone as previously reported\textsuperscript{26, 27}. Upon oxidation, the on-resonance Raman spectrum shows two enhanced bands at 1498 and 1463 cm\textsuperscript{−1}, respectively, which are correlated with the neutral features at 1535 and 1487 cm\textsuperscript{−1}. The significant displacement of the main Raman bands with oxidation (37 and 24 cm\textsuperscript{−1}) arises from the quinoidization of the conjugated skeleton since the positive charge defect is placed at the middle of the thiynyl chain.

The changes observed in the Raman spectra of 3 upon oxidation contrast with those found for compounds 1 and 2, for which the Raman bands associated to the conjugated oligothiophene bridge remain quite unaltered (Figure 1). For instance, for isomer 2, the most intense Raman band at 1455 cm\textsuperscript{−1} scarcely moves with oxidation whereas the band at 1500 cm\textsuperscript{−1} experiments a downward shift of 7 cm\textsuperscript{−1}. Similar shifts are recorded for compound 1. The Raman spectra therefore suggest that the extraction of an electron upon oxidation takes place mainly around the ferrocene units and affects in a low degree the quaterthiophene bridge. These findings are supported by the cyclic voltammetry results reported by Sato et al.\textsuperscript{22}, which indicate that the first oxidation peak for compound 1 corresponds to the extraction of an electron from one of the ferrocene units. Therefore, the radical cations of 1 and 2 in dichloromethane solution can be interpreted as class II MV systems in which the PES presents two minima separated by an energy barrier that impedes a full charge delocalization from one ferrocene to the other.

#### B. Dependence of the localized-delocalized energy profile with the substitution pattern

In an attempt to understand the properties of these molecules in the context of the mixed-valence theory, we have explored the electronic and molecular structures of the radical cations 1\textsuperscript{•+} and 2\textsuperscript{•+} by performing DFT calculations at the B3LYP/6-31G** level.

To simulate the experimental conditions, calculations have been carried out in the presence of the solvent (CH\textsubscript{2}Cl\textsubscript{2}), treated as a continuous medium, and the counteranions (see computational details and the supplementary material). Figure 2 gives the relative energies calculated for localized and delocalized radical cations (denoted as lrc and drc, respectively) of isomers 1 and 2. lrc structures imply the extraction of an electron either from the ferrocene on the left-side of the molecule (lrc-l) or from that on the right-side (lrc-r), as depicted in Scheme 1 (middle). The lrc-l and

![FIG. 1. Off-resonance Raman spectra of the solid state neutral species (bottom) and 785 nm on-resonance Raman spectra of the radical cation species (top) for compounds 1 (left), 2 (middle), and 3 (right) in dichloromethane at room temperature. The band of the solvent is dashed for clarity.](http://jcp.aip.org/about(rights_and_permissions)
**lrc-r** structures are not equivalent owing to the asymmetry of the quaterthiophene bridge. In contrast, the charge in the **drc** structure is extracted from the quaterthiophene spine. The localized and delocalized nature of these radicals is illustrated by the unpaired-electron spin density calculated for the respective cations (see Figure S2 in the supplementary material). While the unpaired electron is mainly located on one of the Fe atoms in the **lrc** structures, it spreads over the oligothiophene backbone in the **drc** form.

The **lrc-l** structure is the most stable both for **1**$^+$ and **2**$^+$. For **1**$^+$, the **lrc-l** and **lrc-r** states differ by 1.09 kcal mol$^{-1}$ due to the different substitution pattern of the thiophene rings linked to the ferrocene units. The energy difference between the localized states is obviously less in **2**$^+$ (0.37 kcal mol$^{-1}$) since both terminal thiophene rings bear a methoxy group. However, the relative energy of the **lrc** structures is still sensitive to the molecular asymmetry remaining in **2**$^+$ caused by the presence of the hexyl substituent attached to only one of the central thiophene rings (see Scheme S1 in the supplementary material). Calculations reveal that the delocalized **drc** structure is not a real transition state but it corresponds to a local minimum in the pathway between the two localized structures. Interestingly, the energy difference between **lrc-l** and **drc** significantly decreases from 0.8 kcal mol$^{-1}$ in **1**$^+$ to 0.38 kcal mol$^{-1}$ in **2**$^+$.

### C. Structural-energetic-spectroscopic relationships: The case of the solid state

Table I compares the carbon-carbon C=C/C=C bond length alternation (BLA) values calculated for neutral and cation structures of compounds 1–3. The BLA parameter is calculated for each thiophene ring as the difference between the length of the C$_β$–C$_β$ single bond and the averaged length of the two C$_β$–C$_γ$ double bonds. Oxidation to the radical cations causes the quaterthiophene chain and both localized and delocalized cations undergo a decrease of the BLA values compared to the neutral compounds. The carbon skeleton of **3**$^+$ is largely quinoidized with negative BLA values for the inner thiophene rings and small positive BLA values for the outer rings (Table I). Similar changes are predicted for the delocalized **drc** cations of **1**$^+$ and **2**$^+$. These structural changes are responsible for the large downward shifts observed in the Raman spectra of **3** upon oxidation (Figure 1). In cations **1**$^+$ and **2**$^+$ the most stable **lrc-l** structure presents a slight quinoidization of the π-conjugated backbone, which is more accentuated for the thiophene rings closer to the charged ferrocene. For instance, the BLA value calculated for the terminal methoxy-substituted thiophene ring (T$_1$) decreases from 0.042 (1 and 2) to 0.021 (1$^+$ and 0.019 Å (2$^+$), whereas it remains mainly unaffected for the thiophene ring T$_4$ linked to the non-oxidized ferrocene (0.040 Å for both 1$^+$ and 2$^+$). Calculations therefore show that there is a significant tuning of the aromatic/quinoidal character along the oligothiophene chain depending on the localized or delocalized nature of the radical cation. The structural changes predicted for the localized cations are significantly smaller and justify the small shifts observed in the Raman spectra of **1** and **2** upon oxidation.

This localized/delocalized description of the radical cations in terms of their energies and molecular structures can address some of the Raman changes observed for **1** and **2** upon oxidation. First, the relative energies calculated and the comparison of the Raman data agree with a localized class II state for the radical cations at room temperature with most of the charge located on the ferrocene units. Second, the smaller barrier calculated for **2**$^+$ suggests that the charge defect can more easily affect the central part of the bridge getting more delocalized. This explains the larger frequency changes observed for **2**, for which the 1519 and 1500 cm$^{-1}$ bands move by $-13$ and $-7$ cm$^{-1}$, respectively, compared with **1**, for which the 1494 cm$^{-1}$ band shifts down by 4 cm$^{-1}$.

The Raman spectrum of **1**$^+$ in solid state was obtained by oxidation with I$_2$ vapours and is compared with the spectrum in solution in Figure 3. An overall downshift of the strongest Raman band is observed on going from solution to the solid state. This shift indicates a charge defect more delocalized on the thienyl bridge which should become more quinoidized (large reduction of the BLA). The solid-state environment would force the molecule to get more planar due to intermolecular packing forces, and this would favour the delocalization of the charge from the ferrocenes towards the central bridge. To support our interpretation, the Raman spectra of the **lrc-l** and **drc** structures of **1**$^+$ were calculated at the

![FIG. 3. Raman spectra of the radical cation of **1** in dichloromethane solution (bottom: oxidized with FeCl$_3$) and in solid state (top: oxidized with I$_2$).](image-url)
IV. CONCLUSIONS

In summary, the structural shape and the stationary point energy sequence of the ferrocenium and/or bridge cation states of two asymmetrically substituted structural isomers of a diferrocenyl quaterthiophene are described. Structure-property relationships are deduced by addressing the phenomenon by means of isomerization of thienyl β-positions of the tetrathiophene wire. It turns out that this subtle isomerization effectively controls site selective oxidation. The behaviour of the experimental Raman spectra is related with the structural alteration of the conjugated path upon oxidation in terms of quinoidal-benzenoid structures and BLA data. This structure-spectroscopy connection allows us to propose a sequence of stationary charged states (absolute and local minima trapped ferrocenium and thienyl states) which might assist cation motion through the bridge between the external ferrocenes. The spectroscopic and theoretical exploration of this cascade of states is central to understand charge mobility, to elucidate the mechanisms of wire charge transport, and to design new molecular wire candidates for single-molecule electronics.

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UB3LYP/6-31G** level as representative cases of localized and delocalized states (see Figure S3 in the supplementary material). The theoretical spectra show that the delocalized structure gives rise to a Raman signature with the main drc positions, which supports the interpretation of the solution/solid Raman changes (Figure 3) in terms of an evolution from ferrocenyl-localized to thienyl-delocalized radical cation species.