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Combined theoretical and spectroscopic Raman study of 3,4-ethylenedioxy and *S,S*-dioxide substituted terthiophenes and their parent polymers

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Abstract

This paper reports on the analysis of the Raman spectra, supported by DFT quantum chemical calculations, of a series of terthiophenes which present the novelty of being selectively functionalized with sulfone groups to increase their photoluminescence properties. The spectra have been carefully assigned on the basis of the theoretical vibrational eigenvectors. They suggest the occurrence of a segmentation of the electronic structure which can become a crucial feature for optimizing linear and non linear optical properties. Sulfonation fixes the two lone electron pairs of the sulfur atom, in particular that involved in the aromatization of the thiophene ring, thus coexisting two different kind of five member (aromatic and non aromatic) units in the same chain. This duality of the structure gives rise to the splitting of the characteristic Raman lines associated to the C=C/C–C stretching modes into components mainly located either on the external rings or on the internal one. The study also focuses on the electrosynthesized polymers obtained upon electropolymerization of the corresponding terthiophenes.

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1. Introduction

Oligothiophenes are presently one of the most intensive field of research in the class of conjugated molecules. They have been used as active organic layers to construct electronic devices such as field-effect transistors and light-emitting diodes [1,2]. Most of conventional aromatic thiophene oligomers generally display very low photoluminescence quantum yields in the solid state. Recently, however, it has been reported that the insertion of one thienyl-*S,S*-dioxide moiety into the aromatic backbone gives rise to an amazing increase of their photoluminescence making these thiophene oligomers useful for LED applications [3–6]. In addition, the introduction of an

‘oxidized thiophene’ among the heteroaromatic rings increases the electron affinity of the whole molecule which favors electron injection. The suitable combination of this good photoluminescence with the improved electron acceptor features makes these new thiophene derivatives very attractive for electroluminescence devices.

In this paper the compounds depicted in Fig. 1 are studied. The relatively small molecular size of these terthiophenes offers the possibility of using accurate quantum chemical calculations to model their structures with a relatively low computational cost. Generally speaking the validity of theoretical calculations is enhanced when are closely compared with experiments. In this sense vibrational spectroscopy is quite well suited for these theory-experiment purposes since the recording of infrared and Raman spectra allows the measure of many bands to compare with a relatively high precision for their wavenumbers and relative

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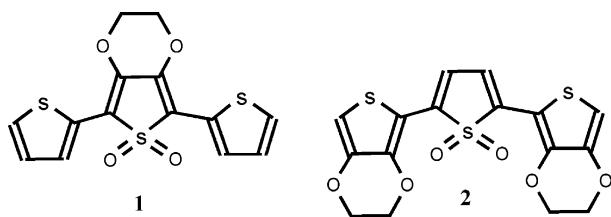


Fig. 1. Chemical structures of **1** and **2**.

intensities. In particular the use of Raman spectra of polyconjugated molecules for assessing information regarding their structural and electronic parameters is nowadays well established in the field of material science [7,8].

This work focuses on the analysis of the vibrational properties in relationship with the structural and electronic features, as deduced by theoretical calculations, of these thienyl-*S,S*-dioxide oligothiophenes. As an additional figure of merit of the work, the samples are also substituted by ethylenedioxy side chains what lowers the oxidation potentials and, regarding their parent polymer systems, strongly reduces the amount of oxidative defects. These structures alternating electron rich moieties (ethylenedioxy) and poor moieties (*S,S*-dioxide) in a same polythiophene chain has already been shown to render polymers with a finite window of conductivity although their electroluminescence and photoluminescence quantum efficiencies are still somewhat low [6]. We propose, by first time, a full assignment of the Raman spectra of the two aforementioned functionalized trimers and then we compare the Raman scattering pattern of one of them with those recorded for the electrochemically synthesized polymers.

2. Experimental and theoretical details

The synthesis of the terthiophenes (whose chemical structures are displayed in Fig. 1) has been reported elsewhere [6]. A FT-Raman spectra were measured using an FT-Raman accessory 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 and the fluorescent background, 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.

Electropolymerizations were carried out in saturated solutions of the terthiophenes in acetonitrile using tetrabutyl ammonium perchlorate as solid electrolyte in a 0.1 M concentration. Either a Pt disk of $1 \times 1\text{ cm}^2$ area or an ITO electrode were used as working electrodes on which the polymers were grown. A Pt disk and an Ag/AgCl electrode were used respectively, as auxiliary and as pseudo-

reference. The polymerization was carried out in cyclic voltammetry conditions between 0 and 1 V at 25 °C. For full electrochemical characterization of the polymers, saturated solutions of the monomer were replaced by freshly prepared solutions of the electrolyte.

Full geometry optimizations were performed in the framework of the Density Functional Theory using the B3LYP functional, with the A.7 revision of the GAUSSIAN 98 program package running on a SGI Origin 2000 computer [9,10]. The 3-21G* basis set was chosen to reduce the high dimension of the problem [11]. In the first step of the procedure, all geometrical parameters (bond distances, bond angles and dihedral angles) were left free to optimize. On the resulting equilibrium geometries vibrational spectra were computed, and no negative eigenvalues were predicted thus assuring that the previously optimized geometries actually represent a stable minimum on the potential energy surface and therefore a reliable conformation for the molecules.

All calculations were carried out in the vacuum considering the molecules as isolated entities. It has already been shown that the B3LYP functional yields similar geometries for medium-sized molecules as MP2 calculations do with the same basis sets. Moreover, and in detriment to many other theoretical approaches, DFT calculations predict wavenumbers and intensities for the vibrational spectra in better agreement with experiments [12]. The calculated harmonic vibrational frequencies were scaled down uniformly by a factor of 0.98 as recommended by Scott and Radom [13].

3. Theoretical geometries

B3LYP/3-21G* optimized geometries and Mülliken atomic charge distribution are shown in Fig. 2. Calculations provide two main messages: (a) the rings are disposed in an all-anti configuration, and (b) the two oxygens of the sulfone group lie almost perpendicular to the plane of the thiophene with its sulfur at the center of a tetrahedron. For compound **1**, one end-thiophene is slightly bent relative to the others, which are nearly coplanar. This feature is not observed for compound **2** in which the three thiophenes are almost coplanar. The driving force for this slight deformation could be the interaction between one oxygen of the sulfone and the closest hydrogen at the β position of adjacent thiophene ring, resulting in a interatomic distance of 2.62 Å. This interaction precludes for a close approximation of the other oxygen and H atoms (atomic distance of 3.28 Å) since it should likely translate into a large deformation of the tetrahedron. Further insights into this intramolecular feature come from the S–O bond distances for both compounds in Fig. 2: for **1** the hydrogen bond makes the two S–O bonds to be non equivalent (lengthening that involved in the interaction) which is not the case for compound **2**.

For both the trimers, the single and double CC bonds of the central ring are larger and shorter, respectively than their

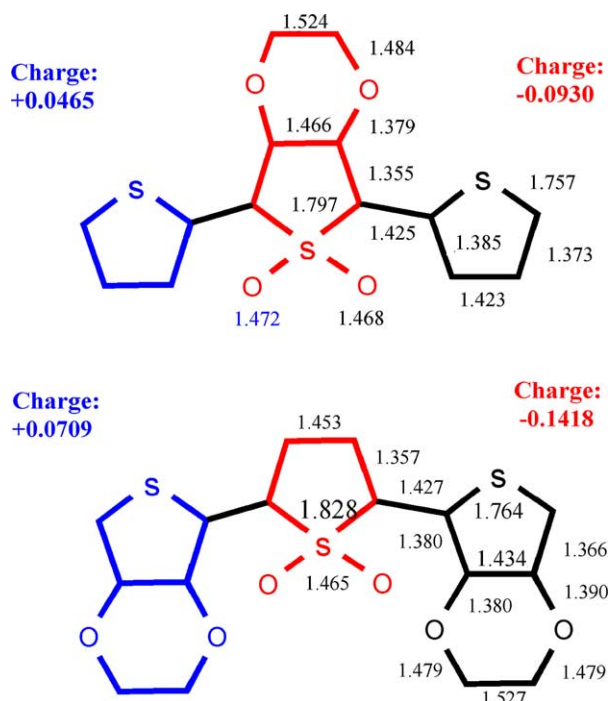


Fig. 2. DFT//B3LYP/3-21G* optimized skeletal bond lengths (in Å) and net Mülliken atomic charges for **1** and **2**.

counterparts in the end thiophene rings. Thus, sulfonation lowers the aromaticity of the central unit, so that this five member ring could be better viewed as two alternating double bonds in a cis configuration. For compound **2**, this effect is clearly observed comparing the C–S distances of the inner ring, 1.828 Å, and the outermost ones, 1.764 Å. For the external rings the thieryl or aromatic character is denoted by the equalization of the C=C/C–C bonds, namely 1.385–1.373/1.423 Å for **1** and 1.380–1.366/1.434 Å for **2**.

The segmentation of the electronic structure upon sulfonation is also present in the effect of the ethylenedioxy groups over the molecular parameters of the rings. Through resonance effect with the rings, the ethylenedioxy oxygens can be termed as electron donors. As a result, the net charge injected by the β groups will be more pronounced for the central ring of **1**, which is somewhat electron deficient upon dioxide introduction, than in the outer rings which indeed are more electron rich due to the aromatization of their sulfur atoms. This is well accounted by the C–O bond distances in **1**, 1.379 Å, versus those in **2**, 1.390 Å. It is relevant to mention the dual role of the oxygen atoms. In the ethylenedioxy groups they act as donor since the non-shared electron pairs occupy an atomic orbital with a suitable symmetry and distance to facially interact with the neighbor π -orbital of the double bonds. In the dioxide groups instead the relevant interaction must take place through the tetrahedral sulfur which already shares its two lone electron pairs, so that electronic coupling of these oxygens is only possible by means of high energy empty sulfur d orbitals

with little or negligible influence in the actual electronic and structural molecular features.

As a consequence of the sum of all these particular electronic effects, the molecules acquire an equilibrium configuration in which the electronic structure becomes polarized, being the central ring always charged negatively while its outermost counterparts balance this distribution remaining charged positively. The overall structures consist in the alternation of positively and negatively charged moieties, more pronounced in the case of **2**.

4. Raman spectra of **1**: theory-experiment comparison

Fig. 3 compares the experimental and B3LYP/3-21G* theoretical Raman spectra of **1**. The agreement between the two spectra regarding both wavenumbers and intensities is quite satisfactory taking in mind the set basis used in the calculations. This finding supports the use of the optimized geometry as a suited model of the real molecular structure and, on the other hand, allows us to use the atomic displacements (normal modes) associated to each theoretical band to assign and interpret the experimental Raman spectrum of **1**. To this end, Fig. 4 depicts the vibrational eigenvectors associated with the most intense Raman bands of the theoretical spectrum.

The weak theoretical band at 1655 cm^{-1} correlates well with the experimental one at 1660 cm^{-1} . This band is due to the antisymmetric stretching vibration of the two double bonds of the central (sulfonated) ring, while its symmetric counterpart, calculated as the most intense band of the spectrum at 1592 cm^{-1} , is also measured as the strongest feature at 1584 cm^{-1} .

The band calculated at 1515 cm^{-1} , which corresponds to the weak experimental feature at 1507 cm^{-1} , is due to the C=C antisymmetric stretching vibration of the two outermost thiophene rings scarcely or negligibly coupled with the vibration of the C=C/C–C of the central ring. The intense

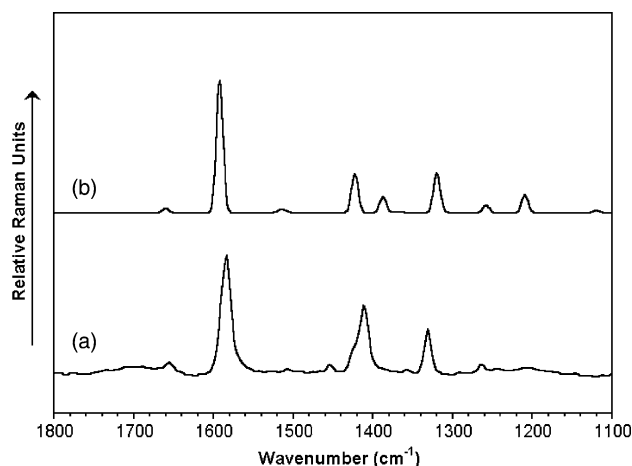


Fig. 3. Experimental (a) and DFT//B3LYP/3-21G* (b) Raman spectra of **1**.

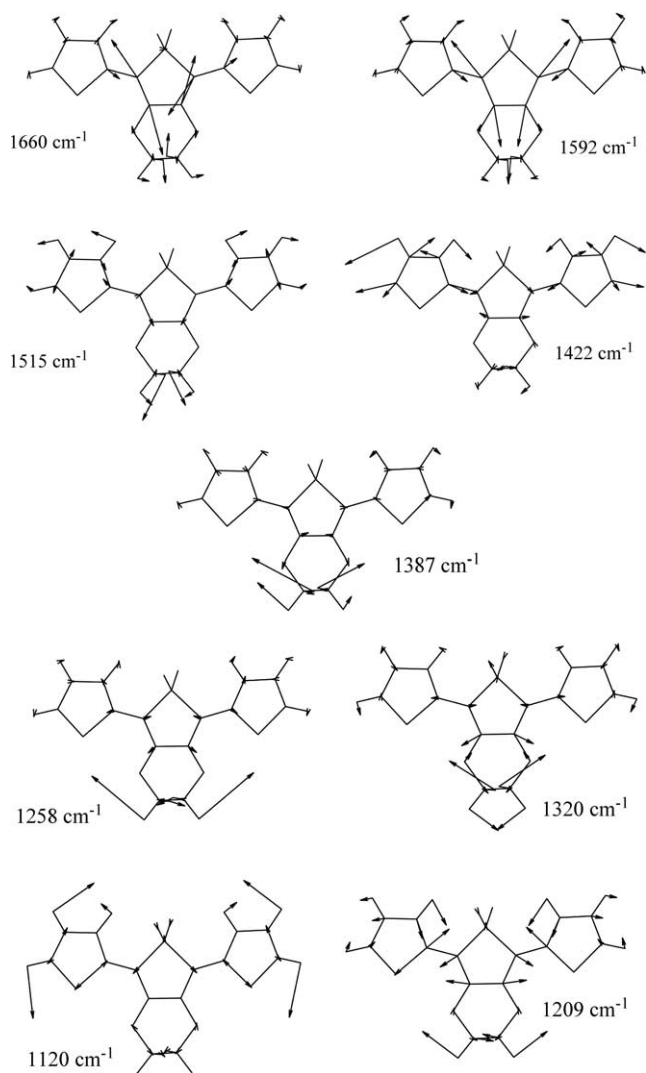


Fig. 4. Schematic B3LYP/3-21G* eigenvectors for the main theoretical Raman bands of **1** (frequencies are given in cm^{-1}).

Raman band measured at 1411 cm^{-1} must be correlated with the theoretical band at 1422 cm^{-1} which is due to a symmetric $\text{C}=\text{C}$ stretching vibration of the two outer thiophene rings slightly coupled with the motion stretching of the inter-ring CC bonds.

At this point of the discussion it is relevant to mention that it has been found two well separated groups of bands arising from two well different parts of the molecule as pointed out by the analysis of the geometries, namely, the inner ring and the outermost thiophenes. This Raman pattern in fact evidences the segmentation of the electronic structure upon sulfonation since two different molecular domains appear now in the thienyl-*S,S*-dioxide terthiophene: the higher energy $\text{C}=\text{C}$ stretchings (around 1600 cm^{-1}) relate with the stronger bonds and shorter $\text{C}=\text{C}$ lengths (1.355 \AA) while the lower energy $\text{C}=\text{C}$ stretchings (around 1400 cm^{-1}) arise from contributions of the weaker bonds and largest $\text{C}=\text{C}$ lengths ($1.373\text{--}1.380\text{ \AA}$).

The medium-weak band calculated at 1387 cm^{-1} correlates with the weak band measured at 1388 cm^{-1} and corresponds to a symmetric deformation vibration of the two methylenes of the ethylendioxy group, $\delta_s(\text{CH}_2)$. The coupling of this mode with the $\text{C}=\text{C}/\text{C}-\text{C}$ stretching vibrations can explain the observation of this local mode in the experimental spectrum. The antisymmetric counterpart, $\delta_a(\text{CH}_2)$, is measured at 1264 cm^{-1} corresponding to the calculated band at 1258 cm^{-1} . The antisymmetric character of this band is referred to the local character of the vibration looking at the methylene group, however, the vibration as a whole obviously corresponds to a symmetric mode in full agreement with the optical selection rules for the Raman experiments considering the C_{2v} punctual group of symmetry.

The medium band recorded at 1331 cm^{-1} is related with the band predicted by calculations at 1320 cm^{-1} which, as can be seen in its associated eigenvector, is due to the $\text{C}-\text{C}$ stretching vibration of the central ring and with three different contributions: (a) it is coupled with the $\delta(\text{CH}_2)$ mode, (b) with the $\text{S}-\text{O}$ stretching vibrations of the SO_2 group and (c) with the $\text{C}-\text{C}$ inter-rings stretching modes. In fact this last vibration, the $\text{C}-\text{C}$ inter-ring stretching, appears associated in the theoretical spectrum with the line at 1209 cm^{-1} and observed in the experiment at 1206 cm^{-1} also with an important contribution from the $\text{C}-\text{C}$ stretching of the central ring. Again the existence of two well separated domains in the molecule is the reason for the splitting of vibrations of the same character, the $\text{C}-\text{C}$ stretching in this case, depending on the physical localization of the atomic motions within a moiety or another. Finally the weak band at 1120 cm^{-1} in the simulated spectrum, which corresponds with a deformation vibration of the aromatic CH bonds, is identified in the experimental spectrum as the weak band at 1147 cm^{-1} .

The Raman spectrum does not provide information about the vibrations of the SO_2 group although it is anticipated their occurrence at around $1350\text{--}1300\text{ cm}^{-1}$ as could be deduced from the analysis of the theoretical Raman line at 1320 cm^{-1} which partially deals with the SO_2 stretching

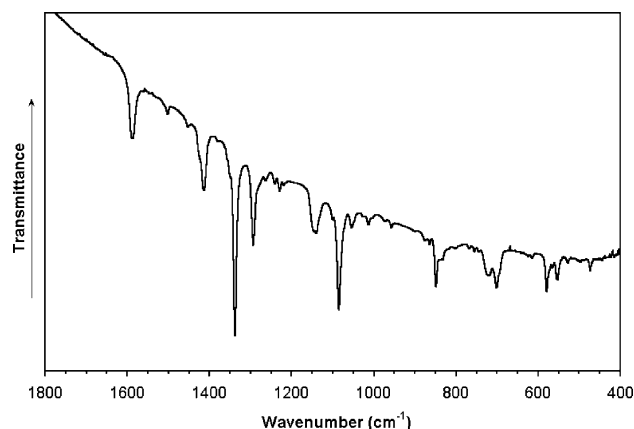


Fig. 5. Solid state FT-Infrared spectrum of **1**.

modes. In the solid state infrared spectrum of **1** (see Fig. 5) it is observed the most intense absorption at 1338 cm^{-1} . As for the largest infrared intensities, they arise from the vibrational displacements involving highly polarized or charged atoms since give rise to the largest flux of charge, namely, high changes of the molecular dipolar moment. In this regard Mülliken atomic charges obtained for **1** at the B3LYP/3-21G* level predict the oxygen atoms of the sulfone group to bear around -0.451 e while the sulfur atom is the most polarized of the whole system since has a net charge of $+1.356\text{ e}$.

5. Raman spectra of **2** and of its electropolymer

The polymer of **2** (poly-**2**) was obtained by electrochemical methods. Fig. 6 shows the continuous electrochemical response in cyclic voltammetry conditions in which the growing of the polymer is evidenced by the continuous increment of the anodic response. After polymerization of the monomer, the polymer film was reduced at -0.5 V for obtaining the neutral form.

Fig. 7 compares the Raman spectra of **2** in solid state with that of its polymer, poly-**2**. For monomer **2**, the most intense Raman band occurring at 1503 cm^{-1} is due to the C=C symmetric stretching vibration of the central ring $\nu_{\text{in}}(\text{C}=\text{C})$, while the medium band at 1426 cm^{-1} is likely due to a mixed C=C/C-C stretching mode located at the terminal thiophene rings. Upon polymerization the most intense line is now measured at 1431 cm^{-1} , related with the scattering in the monomer at 1426 cm^{-1} , while the Raman feature at 1498 cm^{-1} relates with the monomer one at 1503 cm^{-1} . The linear polymerization through the terminal α positions gives rise to the formation of bithiophene moieties between the *S,S*-thienyl rings, what could justify the inversion of the relative intensity pattern on going from **2** to poly-**2**. Finally the frequency downshift, from 1503 to 1498 cm^{-1} , on going from the monomer to the polymer is likely due to the relaxation of the structure or increment of the π -electron

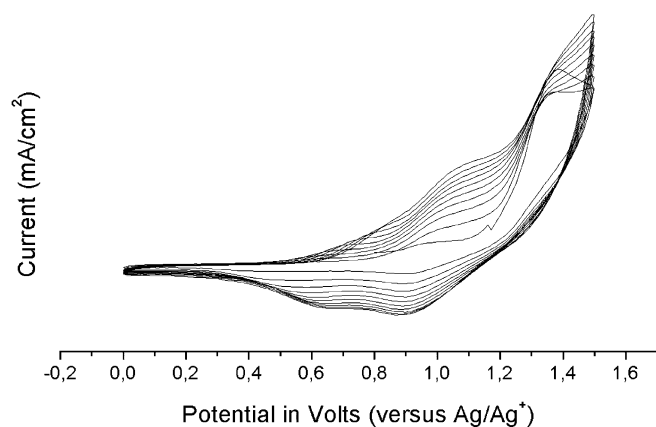


Fig. 6. Successive cyclic voltammograms waves obtained during the electropolymerization of **2**.

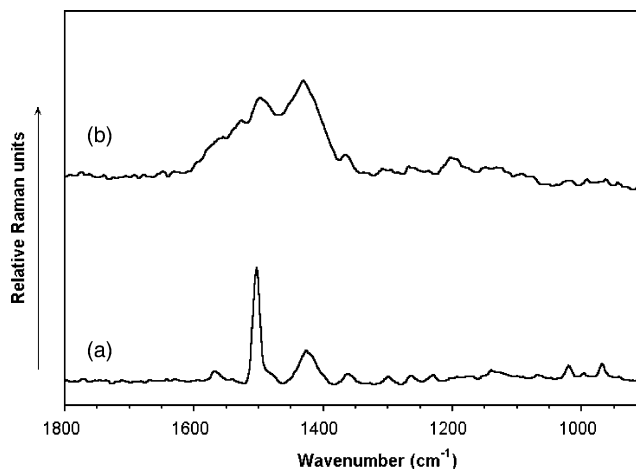


Fig. 7. Solid state Raman spectra of **2** (a) and poly-**2** (b).

delocalization in a bigger system. Despite this straightforward correlation of the monomer-polymer Raman bands, it is not excluded that the structured and intense band at 1426 cm^{-1} could arise from traces of the oxidized or doped forms of the polymer which could be observed due to resonance Raman phenomena.

6. Conclusions

This paper reports on the analysis of the Raman spectra, supported by DFT quantum chemical calculations, of a series of terthiophenes which present the novelty of being selectively oxidized in their central sulfur atom. The spectra have been carefully assigned on the basis of the vibrational eigenvectors as deduced by the theoretical spectra. Opposite to linearly uniform conjugated terthiophenes, this chemical modification gives rise to a segmentation of the electronic structure. This is experimentally observed in the Raman spectrum which shows a splitting of the C=C/C-C stretching bands belonging to either the external or the internal rings. This electronic effect is of great interest in the design of organic molecules with relevant optical properties. The vibrational features of the monomers have been used to qualitatively interpret the Raman spectrum of the electro synthesized polymer and to get some insight into its electronic structure. Much work is now in progress dealing with the study of the electronic absorption and emission spectra and electrochemistry which hopefully will appear in a forthcoming paper.

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