▌ Organic Electronics

[All]-*S,S*-dioxide Oligo-Thienylenevinylenes: Synthesis and Structural/Electronic Shapes from Their Molecular Force Fields

Cheryl Aharon,[a] Fernando G. Guijarro,[b] Samara Medina Rivero,[c] Francisco J. Ramírez,[c] Rubén Caballero,[b] Juan Casado,*[c] Fernando Langa,*[b] and Shlomo Rozen*[a]

Abstract: Oligo-*S,S*-dioxothienylenevinylenes have been prepared by transferring oxygen atoms to the sulfur atoms using the HOF·CH$_3$CN complex. Their photophysical properties are presented in comparison with their thiophenevinylene congeners. Together with their vibrational properties and molecular force fields, this study allows for the interpretation of the alteration of aromaticity and inter-ring exocyclic π-conjugation in this series.

In the last decades, technology involving devices based on organic semiconductors have stimulated research in π-conjugated systems.[1,2] In particular, π-conjugated oligomers based on thiophene or oligothiophenes (OTs) have become key platforms for the construction of molecular devices as their properties can be easily tuned by chemical functionalization.[3–10] A theoretical prediction, suggested already in the '80s, concluded that the corresponding *S,S*-dioxides of oligothiophenes would be better compounds for electronic semiconductors, as their HOMO–LUMO gap should be significantly reduced.[11] At that time, this prediction could not be verified since none of the orthodox oxidizing agents were able to convert all sulfur atoms in the oligothiophenes to the corresponding sulfones.[12] From a materials point of view, the common non-oxidized oligothiophenes mostly behave as p-type semiconductors in electrical devices,[13–15] whereas their electron-deficient *S,S*-dioxides derivatives would complement this behavior acting as n-type substrates.[16,17] Compared with OTs, the presence of double bonds in oligo-thienylenevinylenes (OTVs) yields a higher π-electron delocalization.[18–23] OTVs, however, have never been successfully oxidized to sulfones. Obviously, such compounds would be highly interesting.

[a] C. Aharon, Prof. S. Rozen
School of Chemistry, Tel Aviv University, 69978 Tel Aviv (Israel)
E-mail: rozens@tauex.tau.ac.il

[b] F. G. Guijarro, Dr. R. Caballero, Prof. F. Langa
INAMOL, Universidad de Castilla-la Mancha, Toledo (Spain)
E-mail: fernando.langa@uclm.es

[c] S. Medina Rivero, Prof. F. J. Ramírez, Prof. J. Casado
Department of Physical Chemistry
Universidad de Málaga, 29071 Málaga (Spain)
E-mail: casado@uma.es

📄 Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/chem.201805245.

We are using elemental fluorine for this purpose.[24] Among the offspring of F$_2$, one can mention acetyl hypofluorite (AcOF),[25] methyl hypofluorite (MeOF),[26,27] bromine trifluoride (BrF$_3$)[28] and, especially, the acetonitrile complex of the hypofluorous acid (HOF·CH$_3$CN), readily made by passing dilute F$_2$ through aqueous acetonitrile.[29] Currently, the last reagent is considered to be one of the best oxygen transfer agent chemistry has to offer.[30–32] Among other unprecedented transformations the electrophilic oxygen of the reagent has been successfully used in preparation of several [all]-*S,S*-dioxooligothiophenes,[33] including certain relevant nanoparticles.[34] Even more, one of the advantages of this reagent is that its source of electrophilic oxygen is water.

In this work, a series of *S,S*-dioxothienylenevinylenes oligomers, carrying hexyl chains at the 3 and 4 positions of the thiophene heterocycles for solubility reasons, are prepared by selective oxidation of the S atoms (Scheme 1). The main synthet-
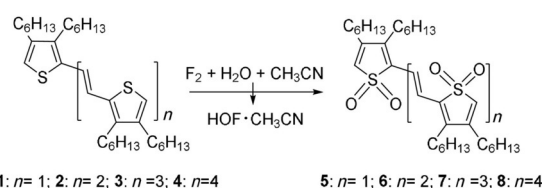
Scheme 1. Synthesis of oligo-*S,S*-dioxothienylenevinylenes **5**–**8**.

ic obstacle, of course, is the fact that HOF·CH$_3$CN is known to epoxidize most double bonds[35,36] Our first challenge was therefore to transfer oxygen atoms to all sulfur atoms in the chain of the oligo-thiophenevinylenes but leaving the exocyclic double bonds unaffected. Although the sulfur atom is generally a somewhat better Lewis acid than a double bond, the thiophene electrons are part of the aromatic sextet which makes the prediction of which of the two will react faster with HOF·CH$_3$CN somewhat difficult. Fortunately, it turned out that the sulfur atoms in OTVs are indeed somewhat more susceptible to be attacked by the electrophilic oxygen and if the temperature is kept low, and if of about 95% mole-equivalent of HOF·CH$_3$CN is used, the reaction proceeds very satisfactorily.

This reaction has been used to transform a series of thiophene-vinylene oligomers (**1**–**4** in Scheme 1) in all S,S-dioxides (**5**–**8** in Scheme 1) and their electronic and molecular structures have been studied by photophysics and vibrational dynamic calculations (i.e., molecular force field). In particular we will address: i) competition between aromaticity and one-di-

mensional π-conjugation, and ii) the shape of the newly formed π-bonds.

All starting materials used in this work have been prepared as previously described. Thus, 1,2-bis(3,4-dihexylthiophen-2-yl)ethene (2TV) (**1**)[37,38] was dissolved in CH$_2$Cl$_2$, and cooled to 0 °C. The solution was then treated with the acetonitrile complex of hypofluorous acid. The corresponding, previously unknown, 2,2′-(ethene-1,2-diyl)-bis(3,4-dihexylthiophene-1,1-dioxide) (2TVSSDO) (**5**) was obtained in about 5 seconds in >85 % yield (Scheme 1). Its ^{1}H NMR spectrum clearly shows that the exocyclic double bond has not been affected: $\delta = 6.96$ ppm (2 vinyl H) while the two hydrogen atoms of the end thiophene rings were found at 6.35 ppm. The HRMS also unequivocally supports the structure: m/z found for $M+$: 592.3624 (calcd for C$_{34}$H$_{56}$O$_4$S$_2$ = 592.3620). See the Supporting Information for more characterizations as well as for the synthetic details of the preparation of the other compounds.

Figure 1 shows the electronic absorption, excitation, and emission spectra of compound **5** together with those of its non-oxidized **1**. The spectrum of **5** is dominated by the lowest energy absorption band that corresponds to a HOMO–LUMO
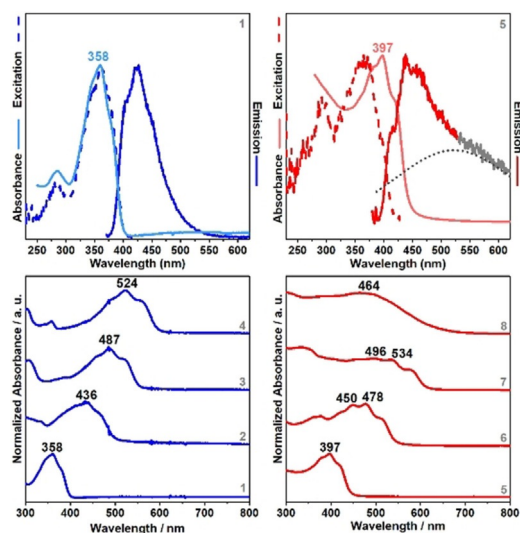

Figure 1. Top: Absorption, excitation and emission spectra of **1** (left), and of **5** (right) in CH$_2$Cl$_2$. Bottom: UV/Vis absorption spectra in CH$_2$Cl$_2$ of **1–4** (left) and of the *S,S*-dioxothienylenevinylenes, **5–8** (right).

one-electron transition (see Figure S1) or π–π* type band. This absorption feature is bathochromically shifted relative to that of **1** (358→397 nm for the wavelength maxima of the strongest peaks) revealing the decrease of the HOMO–LUMO gap upon oxidation. The absorption/excitation spectra of **1** mirrored its emission spectrum, which is indicative of an optically active excited state (i.e., S$_2$, or bright excited state).[39,40] In addition to this main component band, the emission spectrum of **5** has another long wavelength signal which might be related to the previously reported emission in the parent bithiophene dioxide (i.e., without vinylene central bond) (see Scheme S1 and Figure S2) owing to the presence of a "dark" lowest-energy lying singlet (i.e., S$_1$), which produces a weak emission

that cohabitates with the main band from the "bright" S$_2$ excited state.[10] The nature of this "dark" excited state is reminiscent of oligoenes and polyenes[41–45] and is stabilized by action of the increasing electronic correlation in the *S,S*-dioxothienylenevinylenes. This state is non-allowed by one-photon absorption selection rules and gets slightly active due to the vibrational mixing. In the new oxidized oligomers, **5–7**, an initial red-shift of the main absorption band is observed on **5–7** as 3.123→2.594→2.322 eV (i.e., $\Delta E = 0.801$ eV) that is overall smaller than in **1–3** (3.463→2.844→2.546 eV, i.e., $\Delta E = 0.917$ eV), which is, again, the outcome of the already smaller/larger HOMO–LUMO gap/π-conjugation in the dioxide compounds in comparison to the non-oxidized homologues.[46] From another perspective, this smaller ΔE in **5–7** compared to **1–3** reveals the saturation of the π-electron delocalization in π-conjugated oligomers,[47] in the case of the dioxides, with the same number of π-electrons, a larger π-conjugation is attained [TD-DFT calculations on these compounds have been carried out to support the experimental results (Figure S3 and Table S1)].

A study of the vibrational dynamics and the molecular force fields of **1/5** has been carried out. **1/5** belong to the C_{2h} symmetry point group, by which upon definition of the respective internal coordinates (i.e., bond stretching, angle deformation, etc. in Table S2), these can be easily transformed into the C_{2h} symmetry-adapted internal vibrational coordinates (Table S2). Furthermore, of all A$_g$ in-plane vibrations, the A$_g$ in-plane stretching modes (Q_i in Figure S4 with i even and Q_5) carry out the electron-vibrational coupling and, consequently, are very sensitive to changes in the π-electronic and molecular structures.[48,49] An example of this methodology from the initial definition of an internal C=C stretching mode up to the selection of the relevant symmetry adapted in-plane A$_g$ stretching modes for **1/5** is in Figure S4. Now, a detailed discussion of the force constants associated to the A$_g$ in-plane CC and CS stretching vibrational coordinates is presented (referred hereafter as to "bond" force constants).

Based on the dynamic vibrational analysis, the experimental Raman spectra of **1** and **5** (experimental and B3LYP/6-31G** spectra in Figure 2) can be assigned in terms of the symmetry adapted A$_g$ C–C stretching coordinates. Table 1 summarizes these assignments. The comparison of **1** and **5** is indicative of the changes in the structure upon oxidation. **1** has the main Raman band at 1612 cm^{-1} (theoretically at 1637 cm^{-1}), which is described as a mode exclusively of the central C=C moiety (i.e., see Table 1). Significantly, no relevant contributions from the stretches of the C=C of the thiophenes are predicted. Passing to **5**, the highest frequency band is at 1613 cm^{-1} (theoretically at 1624 cm^{-1}) and is due to a stretching mode of the C=C of the oxidized rings with a minor contribution from the central C=C stretching mode, a description which is totally different from that in **1**. This indicates the profound change in the electronic structure on **1**→**5** in terms of the fact that the aromaticity of the thiophene produced the segmentation of the vibrational structure of **1** whereas thiophene dearomatization upon oxidation oppositely provokes strong vibrational coupling alongside the whole C=C–C path including the (oxidized)
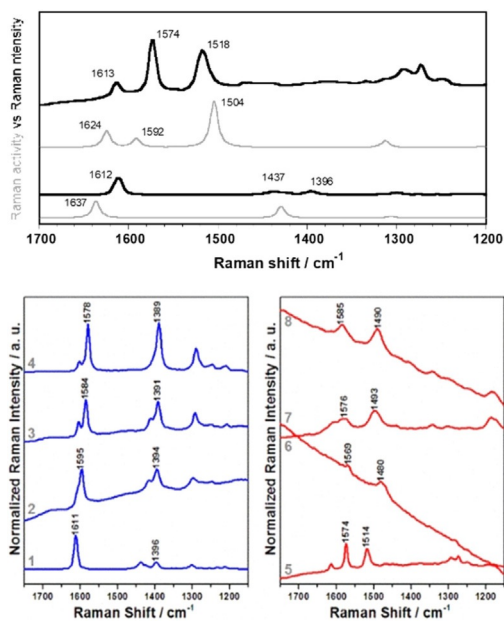
Figure 2. Top: Experimental FT-Raman spectra (black lines) of **1** (bottom) and **5** (top) in solid state at room temperature compared with their theoretical DFT/B3LYP/6–311G** Raman spectra (grey lines) calculated as isolated entities in the vacuum. Bottom: Experimental Raman spectra of **1**–**4** (left) and of **5**–**8** (right) in solid state at room temperature.

thiophenes and the vinylene. The 1574 cm^{-1} band in **5** (theoretically at 1592 cm^{-1}) is described as an equally contributed C=C stretching of the oxidized rings and of the central vinylene, whereas the Raman feature at 1518 cm^{-1} (theoretically at 1504 cm^{-1}) already corresponds to the C=C stretching of the oxidized rings (Table 1 also summarizes the assignments of other Raman bands).

The Raman spectra of the nTV oxidized compounds in Figure 2 display several tendencies: i) a downshift from 1574/1514 cm^{-1} in **5** to 1569/1480 cm^{-1} in **6**, which is in line with the increasing oligoene-like character of **6** compared to **5**, due to the enlargement of the size of the chain and is consistent with the further delocalization of these modes along the C=C/C—C conjugated path; and ii) from **6** to **7**/**8**, upward shifts of the frequencies of these bands are observed. This behavior contrasts with that of the non-oxidized **1**–**4** where the Raman

bands always downshift in frequency. This differing behavior of **1**–**4** and **5**–**8** might reveal the placement of the dioxide derivatives in the vicinity of the chain-length saturation of the electronic properties wherein spectroscopic changes with the oligomer size are smaller and even reversed.[50]

Figure 3 shows the force constants associated with the C=C bonds of **1**, **3**, **5**, **7**, **2T** and **2TSO**. The force constant of the central vinylene of **1** is 8.64 mdyn Å^{-1} and decreases to 8.36 mdyn Å^{-1} upon oxidation in **5** meaning that this bond is weakened upon oxidation. Note that this could not be concluded from the simple inspection of the frequencies of the highest frequency band (1613 and 1612 cm^{-1}) given that they do not correspond to the same vibrational normal mode. For the C=C bonds of the thiophenes, contrary to the case of the vinylenes, their force constants increase with oxidation (9.28/8.78 mdyn Å^{-1} in **1** and 10.01/9.39 mdyn Å^{-1} in **5**) indicating that these get stronger, an effect that is accompanied, on the one hand, by the decrease of the force constant of the C—C bond of the thiophene (6.11 mdyn Å^{-1} in **1** and 4.94 mdyn Å^{-1} in **5**) and, on the other, with the decrease of the force constants associated with the stretching modes of the C—S bonds (3.91/3.62 mdyn Å^{-1} in **1** and 3.04/2.77 mdyn Å^{-1} in
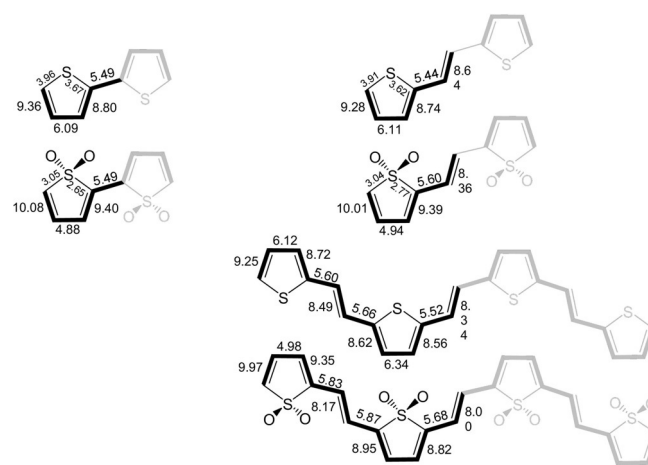
Figure 3. "Bond" force constants (in mdyn Å^{-1}) which refer to the force constant associated to the symmetry adapted Ag in plane stretching vibrational coordinates defined as Q_i (Figure S4 in the Supporting Information) calculated at the DFT/B3LYP/6–311G** level of theory for **1**, **3**, **5**, **7**, **2T** and **2TSO**.

Table 1. Experimental and calculated (DFT/B3LYP/6–311G**) vibrational wavenumbers (in cm^{-1}) for **5**. Only vibrations belonging to the A$_g$ symmetry species of the C$_{2h}$ punctual group are shown. ν = stretching; δ = bending (Table S2 for mathematical definitions).

5			1		
Exp.	calcd (by 0.98)	Potential Energy Distribution (greater than 10%)	Exp.	calcd (by 0.98)	Potential Energy Distribution (greater than 10%)
1613	1623	59ν(tioph) 22ν(C=C) 22δ(C—H)$_v$ 16ν(C—C) 14δ(tioph)	1612	1636	67ν(C=C) 44δ(C—H)$_v$ 23ν(C—C)
1574	1590	42ν(C=C) 35δ(C—H)$_v$ 32ν(tioph) 11δ(C=C)	1437	1519	86ν(tioph) 28δ(C—H)$_t$
1518	1503	114ν(tioph)	1396	1429	110ν(tioph)
1283	1315	51δ(C—H)$_v$ 44δ(C=C) 29δ(C—H)$_t$ 11ν(C=C)	1302	1343	49δ(C—H)$_t$ 34ν(tioph)
1273	1312	52δ(C—H)$_t$ 34δ(C—H)$_v$ 15ν(C=C) 15δ(C=C)	1276	1305	92δ(C—H)$_v$ 18ν(C=C)
1248	1248	52δ(C—H)$_t$ 11δ(C=C) 10ν(C—C)	1233	1225	50δ(C—H)$_t$ 20ν(tioph) 12ν(C—S)
1192	1205	32ν(C—C) 31δ(C—H)$_t$	1213	1192	37ν(C—C) 20δ(C—H)$_t$ 15ν(tioph)
1112	1098	57ν(S=O) 34δ(C—H)$_t$	1103	1082	80δ(C—H)$_t$ 17ν(tioph)
1063	1052	46δ(C—H)$_t$ 37ν(S=O)	932	1046	43δ(C—H)$_t$ 43ν(tioph)
1021	986	64ν(tioph) 20δ(C—H)$_t$	823	851	39δ(tioph) 29ν(C—S)

5). Noticeably, the largest change of the stretching force constants on oxidation in **1**→**5** is calculated for the stretching modes of the C−S bonds which decrease by nearly 30%, followed by ≈20% of that of C−C of the rings and 10% for that of the C=C of the rings. This indicates that the C=C−C=C *cis*-diene of the rings is largely involved in the thiophene aromaticity in **1**, and in **5**, they prefer to π-conjugate with the vicinal vinylenes. Actually, this *cis*-diene→vinylene conjugation causes the reversal change of the force constant of the vinylene (they decrease upon oxidation contrarily to the increase of those to the thiophenic C=C's and it is at the origin of the oligoene-like character of the oligothiophene vinylene dioxides described in previous sections. In line with this, finally, the molecular force field of **3** and **7** have been also obtained that show that there are two different force constants for the vinylene stretching modes of **3**, which is in line with the appearance of two different Raman bands in the spectra of the non-oxidized compounds at 1560–1590 cm^{-1}. In addition, these two "vinylene" force constants of **3** are reduced and get more similar in **7** and are smaller compared to that of **5** (Figure S5 shows the B3LYP/6-31G** optimized distances associated to the bonds to which their force constants have been discussed in the text).

In summary, we show that conjugated oligo-vinyl thiophenes could be effectively oxygenated to the corresponding *S,S*-dioxides using the HOF·CH$_3$CN complex with good yields and under mild conditions. No other oxygen transfer agent can achieve this goal of removing multiple or all thiophene rings from their aromaticity, leaving intact the vinyl double bonds. This reaction protocol has been used in constructing long chains of conjugated polyenes. These, to a large extent, are amorphous solids so the analysis in detail of their structures must be carried out by using spectroscopic methods. In this paper, we adopt an approach based on the classical dynamical vibrational analysis and by obtaining the full set of relevant molecular force constants that we discuss in the framework of the oligomer approach (size-dependent properties in oligomeric series). The main conclusion is that the oligothiophene vinylene dioxides represent more conjugated compounds due to the lack of aromaticity of the thiophene that promotes oligoene-like exocyclic π-conjugation. With these new dioxides, for the same number of conjugating π-electrons, their conjugation extension is closer to the saturation limit compared to oligothiophenes and oligothiophene vinylenes. The phenomenon of dearomatization and exocyclic π-conjugation enhancement is reported in terms of changes "bond" force constants.

The unique approach to the preparation of thiophene dioxides in oligothiophene vinylenes together with the study of their photophysics in comparison with the existing homologues and the approach to the nature of their π-bonds in the context of their molecular force fields has produced, in our opinion, an original research which could potentially attract the attention of a large community of chemists, materials scientists, and spectroscopists, etc.

Conflict of interest

The authors declare no conflict of interest.

Keywords: electronic/structural features · force fields · oligothienylene vinylene · Raman spectroscopy · sulfur dioxides

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