Electrochemistry and time dependent DFT study of a (vinylenedithio)-TTF derivative in different oxidation states

Yvonne Halpin, Martin Schulz, Andrew C. Brooks, Wesley R. Browne, John D. Wallis, Leticia González, Peter Day, Johannes G. Vos

A R T I C L E   I N F O
Article history:
Received 22 January 2013
Received in revised form 16 March 2013
Accepted 16 March 2013
Available online xxx

Keywords:
Tetrathiafulvalene
Pyridine
Monolayer
Density functional theory

A B S T R A C T
The electrochemical and spectroelectrochemical properties of a bis-pyrid-4-yl functionalised vinylenedithio-TTF derivative, 1, in solution are reported. The compound was immobilised on a Pt electrode and the resulting layers formed were investigated using electrochemical techniques. Two oxidation processes were observed for 1, typical of TTF derivatives. A solvent dependence study revealed that the stabilisation of the radical cation intermediate, 1+, towards further oxidation is achieved in solvents with a low Gutmann donor number such as dichloromethane. Analysis of 1+ in solution under aerobic and anaerobic conditions reveal that its stability is compromised in the presence of oxygen and therefore the stability of monolayers of 1 is greatly enhanced under anaerobic conditions. Time dependent DFT calculations of the compound in several oxidation states are discussed to obtain information on the location of the various redox processes.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

In the latter half of the 20th century the discovery of metal-like behaviour in the organic compound, tetrathiafulvalene (TTF) [1] has led to considerable interest in TTF derivatives. Extensive studies have been performed on properties such as metal-like conductivity and superconductivity of organic salts and charge transfer complexes incorporating the TTF core [2–4]. The strong π-electron donor properties of the TTF unit have attracted significant attention in the development of donor-acceptor systems exhibiting both intermolecular (TTF-TCNQ [5]) and intramolecular charge transfer properties [6–8]. Adding to this, TTF complexes are also useful building blocks for supramolecular systems [9–13]. There are several advantages associated with using the redox active TTF core as a building block for more advanced materials: upon oxidation of the TTF ring system, a thermodynamically stable cation radical is formed and further oxidation results in formation of the dication; both of these processes are electrochemically quasi-reversible and occur within a readily accessible potential window. By adding electron donating/withdrawing groups to the TTF core, the oxidation potentials can be tuned [2]. The non-aromatic 14 π-electron system undergoes aromatisation when going from the neutral species to the dithiolium form in the singly and doubly oxidised states. TTF and its derivatives have featured in a wide variety of applications from crown-ether anelated electrochemical sensors [13–16], to molecular electronics [17–21] including organic field-effect transistors [22] and other advanced molecular assemblies [23–25].

An important feature in the development of such nanostructures is the immobilisation of the associated molecules on a surface creating mono/multilayers and providing a route to organisation within the assembly. This proposed organisation within the monolayer is not only a function of the behaviour of, and interaction between the molecules themselves, but also the interaction between the molecules and the surface [26]. Stable redox chemistry in self-assembled monolayers of TTF derivatives have been reported by several groups including those of Bryce, Ward, Cooke, Sallé, Echegoyen and Stoddart, where the core TTF moiety is anchored to the surface using a surface active functional group such as an alkyl chain with a thiol end group on Au [13,14,27–30], thioctic acid disulfide linkers on Au [31–33] and oxide-free
hydrogen-terminated Si(1 0 0) surfaces [34]. Non-covalent binding of TTF derivatives on graphite has also been reported where the molecule's core TTF unit has a strong interaction with the π-system of the graphite surface; this allows the molecule to orientate parallel to the graphite surface through π–π interactions [35,36]. However, the addition of amide groups on the TTF core results in this unit orientating orthogonally to the graphite surface as opposed to in plane [35].

The presence of long alkyl chains as the surface linkers in a monolayer can be unfavourable when the redox active species is intended for use in highly conducting layers designed for the fabrication of electronic devices [37]. The work presented herein is focused on a bis(pyrid-4-yl) functionalised 4,5-ethylenedithio-4′,5′-vinylendithiobis(tetrathiafulvalene) derivative (EVT-TTF) 1 (Fig. 1), in which the substituted carbons are connected by a double bond (the synthesis and characterisation of which has been reported previously) [38]. The nitrogen atom of the pyridine ring has been reported to have a strong affinity for Pt resulting in the formation of stable monolayers [39–41] and in systems which are potentially suitable for use in molecular electronic devices [42–45]. The absence of long alkyl chain linker groups in 1 may be favourable for forming conductive layers on the surface. The electrochemical properties of 1 are presented for both the solution phase and as monolayers formed on platinum. The electronic and electrochemical properties of the compound in different oxidation states are investigated using time-dependent DFT techniques. The results obtained herein are compared with those of bis(ethylenedithio)tetrathiafulvalene, 2 and the unsymmetrical TTF derivative, 4,5-ethylenedithio-4′,5′-vinylendithiobis(tetrathiafulvalene), 3 [46] (Fig. 1).

2. Experimental

2.1. Electrochemistry

Prior to analysis, the surface of the platinum working electrode was prepared by polishing sequentially using 1.0, 0.3 and 0.05 μm alumina slurry (CH Instruments, Inc.) followed by sonication in deionised water for 5 min after each successive polishing with the alumina slurry. The Pt electrode was then electrochemically cleaned by cycling in 0.5 M H2SO4 followed by sonication in the appropriate solvent. Electrochemical experiments were carried out using a CH instruments version 8.15 software controlled electrochemical bipotentiostat (CH750C). Typical concentrations of 1 mM were used for solution phase electrochemical measurements throughout. A Pt wire was used as the counter electrode with either a Ag/AgCl (3 M KCl solution) or a Hg/HgSO4 (saturated K2SO4) as the reference electrode. All potentials are referenced against the saturated calomel electrode (SCE) using ferrocene as an internal standard. Cyclic voltammograms were recorded using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6, Fluka electrochemical grade ≥99.0%) in dichloromethane (CH2Cl2, Aldrich anhydrous, 99.8%) as the electrolyte. Where anaerobic environments were required, prior to experiments, the solutions were deoxygenated with argon and a blanket of argon was maintained during analysis. The solvent dependence was investigated using TBAPF6 as electrolyte in dimethylformamide (DMF, Aldrich spectrophotometric grade, 99.8%), acetone (Aldrich, spectrophotometric grade, ≥99.5%) and tetrahydrofuran (THF, Aldrich, HPLC grade 99.9%). As well as TBAPF6, both tetrabutylammonium perchlorate (TBAClO4, Fluka electrochemical grade, ≥99.0%) and potassium hexafluorophosphate (KPF6, Aldrich, 99.99%) were used with CH2Cl2 and acetone to investigate the influence of the electrolyte on the redox properties.

2.2. Monolayer formation

Monolayers of 1 were formed on a Pt substrate using a solution phase deposition method. The Pt electrode was first pre-treated using the polishing and electrochemical cleaning method described above. The clean metal electrode was then immersed in a 500 μM solution of 1 in CH2Cl2 for 24 h. Prior to the experiment the electrode was removed from the deposition solution and rinsed with acetonitrile (Aldrich anhydrous, 99.8%) to ensure the removal of any unbound material. Either 0.1 M tetrabutylammonium tetrafluoroborate (TBABF4, Fluka electrochemical grade ≥99.0%) or TBAClO4 in acetonitrile were used as electrolyte.

2.3. Oxidative spectroelectrochemistry

JASCO 630 UV–vis and 570 UV–vis–NIR spectrophotometers were used to record the UV–vis–NIR absorption data. The potentials were controlled using bulk electrolysis on a model CH760C bipotentiotstat (CH Instruments, Inc.). Analyte concentrations were typically 0.5–1.0 mM. CH2Cl2 and TBAPF6 were used as solvent and electrolyte with a Ag wire as reference electrode. A Pt wire and Pt gauze was used as the counter and working electrodes respectively. Preparation of the Pt gauze electrode comprised of electrochemical cycling in 0.5 M H2SO4. A custom made 2 mm path length quartz cuvette (volume: 1.2 mL) was employed for all oxidative spectroelectrochemical measurements. The absorbance maxima are ±1 nm.

2.4. Modelling of electronic properties

Geometry was optimised with the GAUSSIAN 03 programme [47] in the gas phase at the B3PW91/6-31+G(d) [48–52] level of theory without constraints to symmetry. The default Berny optimisation algorithm and the default threshold values for the maximum force and displacement were used for 1 and 2 and Gaussian to optimise 1+ and 1+ [53–55]. Stationary points were confirmed as local minima by a frequency calculation (absence of imaginary frequencies). The charged species were calculated with unrestricted wave functions. Single point energy calculations and time-dependent DFT (TD-DFT) [56–58] were performed with the Gaussian 03 programme at the B3PW91/6-31+G(d) level and the Gaussian 09 programme [59] at the BMK [60]/6-31+G(d), M06HF [61]/6-31+G(d) and B3LYP2-TZVPP+R [62,63] level of theory employing the CPCM [64,65] solvent model and dichloromethane as the solvent [66]. Full convergence of the SCF procedure was requested with the SCF=tight keyword. Atomic radii were calculated by the Universal Force Field (UFF) method, which is the default in Gaussian 09. Percent contributions and density of states (DOS) of selected groups were analysed with the GaussSum programme.
As a result of the additional electron withdrawing properties of the pyridine rings in 1, a further increase in the oxidation potential of the first anodic process relative to the un-substituted 3 may be expected. These values are similar to those observed for other related pyridine substituted TTF compounds [70].

Reductive solution phase cyclic voltammetry of 1 (within a potential window of 0 to −2.0 V) reveals two irreversible processes ($E_{pc} = −1.41$ and −1.80 V, vs. SCE). TTF compounds have an electron rich core and exhibit strong π-donor properties. There are relatively few reports of reduction potentials of the TTF component in such systems. Reduction potentials have been reported by Shen and co-workers [71] for perylene substituted TTF derivatives and by Martín and co-workers [72] for benzoquinone substituted TTF dyads. In both cases reduction of the compound was assigned to being based on the perylene and benzoquinone moieties and not the TTF core itself. As outlined below, DFT studies carried out for 1 reveal a LUMO that is comprised of collective contributions of over 50% from the pyridine rings whereas the TTF core itself contributes 4%, vide infra. It is, therefore, reasonable to suggest that the cathodic processes observed for 1 are taking place at the pyridine rings and not the central TTF moiety [73].

3. Results and discussion

3.1. Electrochemistry

The oxidative electrochemistry of 1 is shown in Fig. 2. The resulting electrochemical parameters obtained in a range of solvents are shown in Table 1.

The two reversible redox waves observed in the cyclic voltammogram (CV) for 1 are characteristic of the oxidative electrochemistry of TTF and its derivatives [2–4]. The first process corresponds to the oxidation of the neutral species forming the monocation radical, $1^{\ddagger}$ at +0.62 V, vs. SCE, with a peak-to-peak separation, $\Delta E_p$, of 70 mV (see Fig. 2). At higher potentials the formation of the dication $1^{2\ddagger}$ is observed (+0.95 V, vs. SCE, $\Delta E_p = 100$ mV). DFT calculations discussed below confirm that the oxidation are centred on the TTF core and not on the pyridyl rings. Comparison of the oxidative electrochemistry, recorded for compounds 1, 2 [68] and 3 [46] with that reported for TTF [69] further confirms this assignment and indicates that the oxidation potentials and therefore HOMO levels, are sensitive to the electron donating/withdrawing properties of substituents on the dithiophene rings, this is confirmed by the DFT calculations shown below.

The electron withdrawing ethynylidithio groups of 2 stabilise the HOMO levels and increase the oxidation potentials (in CH2Cl2) by 200 mV compared to TTF. In compound 3, the first redox process occurs (in THF) at a potential that is 60 mV more positive than observed in 2 as a result of the addition of a double bond in the dithienyl ring [46]. A similar increase in the oxidation potential of the first redox process in 1 compared to 2 is observed (Table 1).

### Table 1

Electrochemical data for 1 in various solvents under anaerobic conditions, recorded at a Pt macro working electrode. All potentials are quoted vs. the SCE. AN and DN are the Gutmann acceptor and donor numbers, respectively. Electrochemical data for TTF and reference compounds 2 and 3 included below.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_{pa}$ (V) ($\Delta E_p$ (mV))</th>
<th>$E_{pa}$ (V) ($\Delta E_p$ (mV))</th>
<th>$\Delta E$ (mV)</th>
<th>AN</th>
<th>DN</th>
<th>Polarity index</th>
<th>Dielectric constant ($\varepsilon$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH2Cl2</td>
<td>+0.62 (70)</td>
<td>+0.95 (100)</td>
<td>330</td>
<td>20.4</td>
<td>0</td>
<td>3.1</td>
<td>8.9</td>
</tr>
<tr>
<td>Acetone</td>
<td>+0.64 (70)</td>
<td>+0.81 (75)</td>
<td>170</td>
<td>12.5</td>
<td>17</td>
<td>5.1</td>
<td>21.0</td>
</tr>
<tr>
<td>THF</td>
<td>+0.73 (90)</td>
<td>+0.83 (65)</td>
<td>100</td>
<td>8</td>
<td>20</td>
<td>4.0</td>
<td>7.5</td>
</tr>
<tr>
<td>DMF</td>
<td>+0.66 (60)</td>
<td>+0.73 (50)</td>
<td>90</td>
<td>16</td>
<td>26.6</td>
<td>6.4</td>
<td>38.3</td>
</tr>
</tbody>
</table>

TTF: $E_{pa} = +0.30$, +0.67 V (CH2Cl2, vs. SCE) [34]; 2: $E_{pa} = +0.52$, +0.94 V (CH2Cl2, vs. SCE) [33,68]; +0.69 V (THF, vs. SCE) [46]; 3: $E_{pa} = +0.75$ V (THF, vs. SCE) [46].

3.2. Solvent dependence

The influence of the solvent and electrolyte on the oxidative electrochemical properties of 1 was investigated and the effects of solvent parameters such as Lewis basicity/acidity (Gutmann donor/acceptor numbers [74]), polarity [75] and dielectric constant [76] were considered. Table 1 shows that the potential of the first redox process is largely solvent independent, however, the separation $\Delta E$ (mV) between the first and second redox waves is sensitive to changes in the solvent-electrolyte medium. As Table 1 indicates, the most important solvent parameter in this case is the donor number (DN). Importantly, upon an increase of this parameter from CH2Cl2 to DMF, the separation between the two waves decreases, i.e. they are inversely proportional to one another ($R^2 = 0.98$).

This observation indicates that for the radical monocation intermediate $1^{\ddagger}$, the positive charge of the radical cation is stabilised by solvation by a nucleophilic solvent. As a result, oxidation of the monocation radical $1^{\ddagger}$ to $1^{2\ddagger}$ becomes thermodynamically easier [77]. For this reason the spectroelectrochemical experiments carried out in this study were carried out in CH2Cl2, the solvent that presents the largest separation between the two redox processes.

3.3. Influence of supporting electrolyte

The effect of electrolyte on the redox properties of species in solution through ion-pairing has been reported for other organic and inorganic systems [78–80]. The influence of anion-pairing on the redox chemistry of 1 was examined through the use of TBAPF6 and TBAClO4 as electrolyte (Table 2).

From the $\Delta E$ values recorded for both electrolytes in CH2Cl2 it is clear that the degree of separation between the first and second redox wave is heavily dependent on the nature of the anion component of the electrolyte. With ClO4− the value of $\Delta E$ is 240 mV
and the parent TTF compound [82–84]. Four absorbance bands are observed in the spectrum of 1 prior to oxidation. Comparing these values with those reported for 2 and 3 it is noted that there are two common features in the spectra of all three compounds. The two lower energy transitions reported for 2 are in good agreement with those reported for TTF with the bands at 466 and 349 nm. The DFT results indicate that these represent the transitions from the HOMO (π*) to the LUMO (σ*) and from the HOMO to LUMO + 1 π → π* respectively. Andreu et al. [81] proposed that the absorbance band at 324 nm is composed of three energetically similar bands. The absorbance bands of 1 at 316, 346 and ~450 nm are close in energy to those observed in the absorbance spectrum of 2 (324, 349 and 466 nm) and 3 (318 and 344 nm). Considering this, it may be proposed that these bands represent similar transitions in 1. This issue is further addressed in the DFT section below.

For 1•+ a decrease in the absorbance bands at 316 and 346 nm is observed with the appearance and concomitant increase in new absorbance bands at 424, 457, 479, 561 and 924 nm (see Fig. 3). There are similarities between the energies of the absorbance bands of 1•+ and those of 2•+ (Table 3) with the lowest energy absorbance band at 922 nm assigned by DFT as the transition of charge from the HOMO (highest doubly occupied molecular orbital) to the SOMO created upon oxidation to 2•+ [81].

An isosbestic point is observed in the absorption spectra at 376 nm (Fig. 3) indicating that conversion from 1 to 1•+ is a direct reaction with no intermediates or side products formed. The electrochemical ΔE_p value of 70 mV indicates that this process is reversible. The resulting absorption spectrum from reduction of 1•+ back to 1 supports this with almost complete reversibility observed on the timescale of the experiment and shows that the monocation radical species is stable in air.

With continuous cycling between 0 and +1.2 V (vs. Ag/AgCl) in aerobic conditions, the dication shows limited stability with the observed current response diminishing with time. This limited stability has also been observed by Bryce and co-workers for similar compounds [14,16]. The importance of traces of moisture for the stability of the second redox process has been outlined by Khodorkovsky and co-workers [85]. However, the dication exhibits increased stability under argon. As such, it is probable that the instability involves reaction of 1•+ and molecular oxygen, but moisture may also play a role [86–89]. As a result the spectroscopic features obtained for this species may be affected.

The electronic features of 1•+ are shown in Fig. 4. Applying a potential of 1.1 V (vs. Ag wire) results in the formation of the dication. This is indicated in Fig. 4 (dashed line) by a further decrease in the absorbance bands at 280, 290, 316 and 346 nm. The absorbance bands at 424, 457, 479, 561 and 924 nm, observed for 1•+ also appear with much weaker intensity in the spectrum of 1•+. There is an absence of an isosbestic point in the spectra upon reduction back to 1 indicating that full reversibility is not observed (Fig. 4). This suggests that the dication has limited stability under the conditions and timescale (~75 min) of the experiment even when under an argon atmosphere.

3.5. Surface immobilisation of 1

Cyclic voltammetry of 1 immobilised on an electrode surface in aerated solution shows two oxidation waves (not shown). A linear relationship between the peak current, i_p, and the scan rate, v, is observed under aerobic conditions, which is characteristic of a surface confined process. The ΔE_p values observed for a monolayer of 1 are greater than zero with the anodic and cathodic current maxima separated by a minimum of 40 mV (v = 7 V/s) and a maximum of 90 mV (v = 30 V/s). The FWHM, calculated for the redox waves in the CV, ranges from 120–160 mV. As the scan rate increases, ΔE_p compared to 330 mV with PF_6−. This suggests that ClO_4− provides for tighter ion pairing with oxidation to 1•+ at less positive potentials than that observed with PF_6− [78]. The influence of the cationic component of the electrolyte indicates that the observed effect on ΔE is confined to anions as the ΔE values obtained for TBA PF_6 and KPF_6 in acetone are the same, as shown in Table 2.

Table 2
Electrochemical data for 1 detailing the changes observed with different electrolytes. All potentials are quoted vs. the SCE reference electrode.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>E0 (V)</th>
<th>ΔE_p (mV)</th>
<th>ΔE (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBA PF_6 in CH_2Cl_2</td>
<td>+0.62 (70)</td>
<td>+0.95 (100)</td>
<td>330</td>
</tr>
<tr>
<td>TBA PF_6 in CH_3Cl</td>
<td>+0.66 (70)</td>
<td>+0.90 (100)</td>
<td>240</td>
</tr>
<tr>
<td>TBA PF_6 in acetone</td>
<td>+0.64 (60)</td>
<td>+0.81 (65)</td>
<td>170</td>
</tr>
<tr>
<td>KPF_6 in acetone</td>
<td>+0.55 (90)</td>
<td>+0.72 (75)</td>
<td>170</td>
</tr>
</tbody>
</table>

Table 3
UV–vis absorption spectroscopic data for compounds 1 (in dichloromethane), 2 and 3 and their different oxidation states and the parent TTF.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption λ_{max}/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>252, 316, 346, 450 (weak)</td>
</tr>
<tr>
<td>1•+</td>
<td>424, 457, 479, 561, 924</td>
</tr>
<tr>
<td>2•+</td>
<td>280, 290, 342, 453, 477, 560, 909</td>
</tr>
<tr>
<td>3•+</td>
<td>324, 349, 466 [81]</td>
</tr>
<tr>
<td>2•+</td>
<td>458, 486, 599, 992 [81]</td>
</tr>
<tr>
<td>3•+</td>
<td>318, 344 [46]</td>
</tr>
<tr>
<td>TTF</td>
<td>303, 317, 368, 450 [82]</td>
</tr>
<tr>
<td>TTF•+</td>
<td>400, 433, 492, 580 [83]</td>
</tr>
<tr>
<td>TTF•+•+</td>
<td>273, 353 [84]</td>
</tr>
</tbody>
</table>

4 Recorded in 1,1,2-trichloroethane.
5 Recorded in tetrahydrofuran.
6 Recorded in cyclohexane.
7 Recorded in acetonitrile [83].

3.4. Oxidative spectrotoclectrochemistry

Spectroelectrochemical studies were carried out to obtain information about the electronic properties of the radical monocation, 1•+. As outlined below, measurements were carried out in CH_2Cl_2 to investigate the stability of this species. Fig. 3 shows the changes in the UV–vis-NIR absorption spectrum upon oxidation of 1 to 1•+ via bulk electrolysis at +0.7 V (vs. Ag wire). Table 3 lists the UV–vis absorption spectroscopic data for 1 and its oxidised forms and these values are compared with those reported for 2 [81], 3 [46] and the parent TTF compound [82–84]. Four absorbance bands are observed in the spectrum of 1 prior to oxidation. Comparing these values with those reported for 2 and 3 it is noted that there are two common features in the spectra of all three compounds. The two lower energy transitions reported for 2 are in good agreement with those reported for TTF with the bands at 466 and 349 nm. The DFT results indicate that these represent the transitions from the HOMO (π*) to the LUMO (σ*) and from the HOMO to LUMO + 1 π → π* respectively. Andreu et al. [81] proposed that the absorbance band at 324 nm is composed of three energetically similar bands. The absorbance bands of 1 at 316, 346 and ~450 nm are close in energy to those observed in the absorbance spectrum of 2 (324, 349 and 466 nm) and 3 (318 and 344 nm). Considering this, it may be proposed that these bands represent similar transitions in 1. This issue is further addressed in the DFT section below.

For 1•+ a decrease in the absorbance bands at 316 and 346 nm is observed with the appearance and concomitant increase in new absorbance bands at 424, 457, 479, 561 and 924 nm (see Fig. 3). There are similarities between the energies of the absorbance bands of 1•+ and those of 2•+ (Table 3) with the lowest energy absorbance band at 922 nm assigned by DFT as the transition of charge from the HOMO (highest doubly occupied molecular orbital) to the SOMO created upon oxidation to 2•+ [81].

An isosbestic point is observed in the absorption spectra at 376 nm (Fig. 3) indicating that conversion from 1 to 1•+ is a direct reaction with no intermediates or side products formed. The electrochemical ΔE_p value of 70 mV indicates that this process is reversible. The resulting absorption spectrum from reduction of 1•+ back to 1 supports this with almost complete reversibility observed on the timescale of the experiment and shows that the monocation radical species is stable in air.

With continuous cycling between 0 and +1.2 V (vs. Ag/AgCl) in aerobic conditions, the dication shows limited stability with the observed current response diminishing with time. This limited stability has also been observed by Bryce and co-workers for similar compounds [14,16]. The importance of traces of moisture for the stability of the second redox process has been outlined by Khodorkovsky and co-workers [85]. However, the dication exhibits increased stability under argon. As such, it is probable that the instability involves reaction of 1•+ and molecular oxygen, but moisture may also play a role [86–89]. As a result the spectroscopic features obtained for this species may be affected.

The electronic features of 1•+ are shown in Fig. 4. Applying a potential of 1.1 V (vs. Ag wire) results in the formation of the dication. This is indicated in Fig. 4 (dashed line) by a further decrease in the absorbance bands at 280, 290, 316 and 346 nm. The absorbance bands at 424, 457, 479, 561 and 924 nm, observed for 1•+ also appear with much weaker intensity in the spectrum of 1•+. There is an absence of an isosbestic point in the spectra upon reduction back to 1 indicating that full reversibility is not observed (Fig. 4). This suggests that the dication has limited stability under the conditions and timescale (~75 min) of the experiment even when under an argon atmosphere.

![Fig. 3. Spectral changes for 1 (solid black line) with controlled electrochemical oxidation (E = +0.7 V, vs. Ag wire) to 1•+ as a function of time (dashed black lines). Recorded in CH_2Cl_2 (0.1 M TBA PF_6) in air at a Pt gauze working electrode.](image-url)
Fig. 4. Spectral variations of 1 (solid grey line) under controlled electrochemical oxidation ($E = +1.1\,\text{V}, \text{Ag wire}$) to 1$^{2+}$ (dashed black line) and reduction back to 1 (dotted black line). The spectra were recorded in CH$_2$Cl$_2$ (0.1 M TBAPF$_6$) under argon using a Pt gauze working electrode.

Table 4

<table>
<thead>
<tr>
<th>Scan rate</th>
<th>$\Delta E_p$ (mV)</th>
<th>Surface coverage, $\Gamma$ (mol cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic conditions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 V/s</td>
<td>40 (a)</td>
<td>5 × 10$^{-12}$ (a)</td>
</tr>
<tr>
<td>35 (b)</td>
<td>45 (b)</td>
<td>3 × 10$^{-12}$ (b)</td>
</tr>
<tr>
<td>Anaerobic conditions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 V/s</td>
<td>60 (a)</td>
<td>1 × 10$^{-11}$ (a)</td>
</tr>
<tr>
<td>60 (b)</td>
<td>80 (a)</td>
<td>1 × 10$^{-11}$ (b)</td>
</tr>
</tbody>
</table>

The final scan was recorded after cycling with scan rates up to 50 V/s (approximately 5 min). a = initial scan, b = final scan.

also increases possibly suggesting that slow charge transfer kinetics are associated with the observed response [39].

The CVs of 1 under these conditions on Pt, show the surface coverage of the monolayer, is in the order of 10$^{-12}$ mol cm$^{-2}$ (Table 4). For a dense monolayer, a surface coverage in the range of 10$^{-10}$ mol cm$^{-2}$ is expected [90]. The value calculated for the monolayer analysed in air is almost two orders of magnitude lower than this optimum value which suggests that under aerobics conditions a dense monolayer is not recorded on Pt. Further analysis of the surface coverage in air, shows a decrease by approximately 40% after the potential is applied over the range of scan rates.

Oxidation of 1 to 1$^{2+}$ under air indicates a lack of stability of the assembly on a surface as has been reported previously [14,16,91]. However, restricting the potential to the formation of the monocation redox intermediate resulted in more stable responses.

The behaviour of the monolayers under argon is shown in Fig. 5. As shown for the monolayer in air, the $\Delta E_p$ values observed are greater than zero and the anodic and cathodic current maxima are separated by a minimum of 60 mV ($\nu = 10\,\text{V/s}$) and a maximum of 80 mV ($\nu = 50\,\text{V/s}$). The FWHM, calculated for the redox waves in the CV, ranges from 110 to 140 mV. Increasing the scan rate from 10 to 50 V/s results in minimal changes in the peak potential ($E_p$). A value of approximately 1 × 10$^{-11}$ mol cm$^{-2}$ was estimated for the surface coverage at the initial scan rate of 10 V/s with a projected area per molecule of 1640 Å$^2$. When the monolayer was subsequently scanned at up to 50 V/s before final scanning at 10 V/s the surface coverage had not significantly changed, even when the scan included the oxidation to the dication as shown in Fig. 5.

So 1$^{2+}$ is unstable in air both under solution-phase diffusion controlled conditions and when immobilised on the surface which is likely due to its exposure to oxygen in the surrounding environment. Under argon a considerable improvement of the stability of the monolayer is observed.

3.6. Modelling of electronic properties

The parent tetrathiafulvalene (TTF) and bis(ethylenedithio) tetrathiafulvalene (BEDT-TTF, 2) were modelled by Andreu et al. [81] Their comparison of different functionals and basis sets showed that the hybrid functionals B3P86 and B3PW91 are superior over the common B3LYP for geometry optimisations. Furthermore, they pointed out that the different basis sets (6-31G(d), 6-31+G(d), 6-311+G(d,p), cc-pVDZ, aug-cc-pVDZ) used with these functionals had little influence on the results of single point TD-DFT calculations. We also found B3PW91/6-31+G(d) to give good accuracy for geometry optimisation of 1, 1$^{+}$, the singlet dication 1$^{2+}$ and 2. Application of CH$_2$Cl$_2$ as solvent for the SCRF calculations is appropriate since the Gutmann donor number is 0 (vide supra) and thus orbital interactions can be neglected. One should therefore be able to model the influence of this solvent by an SCRF procedure.

3.7. DFT modelling of electronic and electrochemical properties

Density functional theory was employed in order to shine light on the localisation of the frontier orbitals of 1, 1$^{+}$ and 1$^{2+}$, as well as on the localisation of the low energy transitions observed by spectroelectrochemistry. In agreement with X-ray diffraction results, the compounds 1, 1$^{+}$, 1$^{2+}$ and 2 were optimised in boat conformations (Fig. 6) and are in excellent agreement with experimental data [38,92]. The calculated structural changes introduced by oxidising 1 to 1$^{+}$ are in good agreement with the changes observed by Almeida and co-workers in the solid state.
[38]. Furthermore, the experimental observations indicate that the unpaired electron and hence the positive charge is located on the TTF moiety, which is in agreement with the calculated spin density shown in Fig. 6.

Contributions from atoms or groups to the frontier orbitals in the ground state were investigated. The results were compared with the data obtained for 2 to examine the extent of contributions of the pendant pyridyl groups. In 1, these substituents have no orbital contributions to the HOMO. In both compounds 1 and 2, the HOMO is localised on the TTF moiety. The pyridyl rings mainly contribute to the LUMO of 1 as well as to lower lying occupied states. In accord with the interpretation of the electrochemical data, oxidation of 1 removes an electron from the TTF core (HOMO), while reduction furnishes a radical anion with a significant probability on the pyridyl substituents. Oxidation of 1 to 1•+ yields a singly occupied orbital (SOMO), which is also located on the TTF moiety (cf. spin density in Fig. 6) and is the location for the second oxidation from 1•+ to 12•+ yielding a TTF core based LUMO of 12•+. Although fully delocalised orbitals are found among the frontier orbitals (e.g. L + 3 of 1) the pyridyl substituents leave the electronic properties of EVT-TTF nearly unaffected.

Information about the nature of the near-IR transitions observed by spectroelectrochemistry was further investigated by time-dependent DFT (TD-DFT) calculations (Fig. 7). Theoretical investigations were performed with 1, 1•+ and 12•+ using the B3PW91, M06HF and BMK functionals with the 6-31+G(d) basis as well as on the larger BMK/def2-TZVPP+R level. The B3PW91 functional satisfactorily modelled electron excitation of the uncharged compound 1. Satisfactory results were obtained also for the lowest energy transition of 1•+ and 12•+, although at slightly lower energies. Modelling of the high energy transitions furnished unsatisfactory results at the B3PW91/6-31+G(d) level. They were therefore compared to BMK functional of Boese and Martin [60] as well as to the M06HF functional of Zhao and Truhlar [61]. M06HF gave unsatisfactory results for both the charged and uncharged species. The BMK functional was able to model the low energy transitions of the charged species. But the higher energy transitions could not still be satisfactorily modelled. Additionally, the large def2-TZVPP+R basis was applied where 1s1p1d diffuse Gaussian Rydberg functions are added to sulphur [62,63]. This basis turned out to be superior over TZVP and TZVPP for vertical excitation energies of thiophene [62] but did not give satisfactory results for the high energy transition of 1•+ and 12•+.

The low energy bands of the experimental spectra of 1 and 2 are similar in energy. The lowest energy band in 2 can be
assigned to a HOMO $\pi \rightarrow$ LUMO $\sigma^*$ transition and is a TTF core based transition. For 1 the lowest energy transition occurs as a flat shoulder in the experimental spectrum and could only satisfactorily be modelled on the B3PW91/6-31+G(d) level. This feature is assigned to a HOMO-1 — LUMO transition with charge transfer from the TTF-core to the pyridyl substituents. The B3LYP/6-31+G(d) and B3LYP/TZVPP-R model chemistries also predict a small shoulder which is blue shifted and assigned to a HOMO — LUMO+1 transition. In accordance with the B3PW91 results significant charge transfer to the pyridyl substituents is found. All three model chemistries predict an intensive low energy HOMO — LUMO+3 transition but with a significant blue shift for the B3LYP calculations. Thereby an electron is transferred from the TTF-core to the fully delocalized LUMO + 3. The low energy near infrared absorptions of $1^{1+}$ and $1^{2+}$ are known features of this type of cation. The employed model chemistries were only able to predict the low energy band but failed for the higher energy absorptions. Although slightly different in the predicted energies (0.01–0.14 eV), all three models predict a transition from the highest doubly occupied molecular orbital (HDOMO) to the SOMO of $1^{1+}$. Electron transfer occurs from an orbital delocalised on the vinylenedithio-TTF moiety of $1^{1+}$ to the TTF core based SOMO. The same charge transfer is predicted for the lowest energy band of $1^{2+}$ representing a HOMO — LUMO transition.

4. Conclusions

In the present contribution, the redox and spectroscopic properties, together with molecular modelling of a vinylenedithio-TTF derivative, 1, have been examined. Two redox waves are observed for 1, the $\Delta E$ values of which are solvent dependent. Stabilisation of the monocation intermediate ($1^{1+}$) towards further oxidation is achieved in solvents with a low Gutmann donor number. Successful formation of a monolayer of 1 has been achieved on platinum, a less common substrate for monolayers of TTF type compounds, without the use of long alkylic chain linker groups which can be disadvantageous in the fabrication of molecular electronic devices [37]. This monolayer is stable in deaerated solvents but in the presence of oxygen the dication formed is decomposed. Normally, the presence of oxygen is not a problem when carrying out electrochemical oxidations at these potentials. In this case however, the dication formed is most likely involved in a chemical reaction which leads to its decomposition. As a result of the decomposition process the spectroelectrochemical data observed for the dication needs to be treated with care. The compound can be immobilised on Pt surfaces but surface coverage values suggest that sparse monolayers are formed. From these data alone it is not possible to determine if the monolayer is formed on Pt via the nitrogen atom of the pyridine ring, monolayers of which have been reported by Forster et al. [39], or whether the molecules stack parallel to the surface for example through $\pi$-stacking, as has been shown for graphene and graphite surfaces [35]. TD-DFT calculations reveal a HOMO that is predominantly located on the TTF core and that the addition of pyridine rings does not affect the attractive oxidative properties of the TTF unit. In addition, the modelling of vertical excitations with TD-DFT and the applied model chemistries gives acceptable results for the low energy transitions but is less satisfactory for high energy transitions.

Acknowledgement

The authors thank COST D35 for financial support. JW thanks EPSRC for support. YH and JGV thank Science Foundation Ireland (grant number: 06/RFP/029) for supporting this work.

References


