Electrochimica Acta 100 (2013) 188–196

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

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

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ARTICLE INFO

Article history:
Received 22 January 2013
Received in revised form 16 March 2013
Accepted 16 March 2013
Available online 29 March 2013

Keywords:
Tetrathiafulvalene
Pyridine
Monolayer
Density functional theory

ABSTRACT

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, $\mathbf{1}^{\bullet+}$, towards further oxidation is achieved in solvents with a low Gutmann donor number such as dichloromethane. Analysis of $\mathbf{1}^{2+}$ 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.

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 annelated 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

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http://dx.doi.org/10.1016/j.electacta.2013.03.114

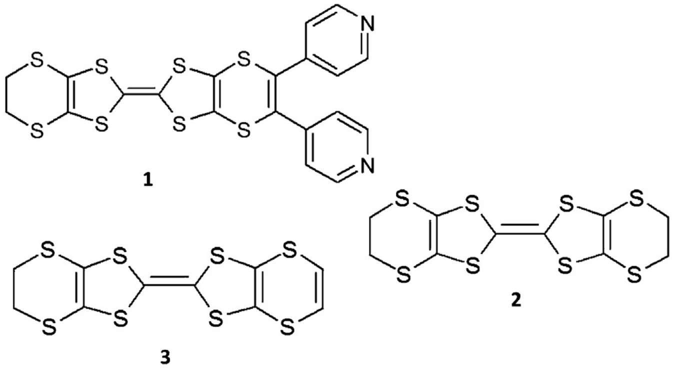

Fig. 1. Molecular structures of TTF derivatives **1**, **2** and **3**.

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′-vinylenedithiotetrathiafulvalene 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′-vinylenedithiotetrathiafulvalene, **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 H_2SO_4 followed by sonication in the appropriate solvent. Electrochemical experiments were carried out using a CH Instruments Version 8.15 software controlled electrochemical bipotentiostat (CHI750C). 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/HgSO$_4$ (saturated K_2SO_4) 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 (TBAPF$_6$, Fluka electrochemical grade ≥99.0%) in dichloromethane (CH_2Cl_2, 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 TBAPF$_6$ 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 TBAPF$_6$, both tetrabutylammonium perchlorate (TBAClO$_4$, Fluka electrochemical grade, ≥99.0%) and potassium hexafluorophosphate (KPF$_6$, Aldrich, 99.99%) were used with CH_2Cl_2 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 CH_2Cl_2 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 (TBABF$_4$, Fluka electrochemical grade ≥99.0%) or TBAClO$_4$ 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 CHI760C bipotentiostat (CH Instruments, Inc.). Analyte concentrations were typically 0.5–1.0 mM. CH_2Cl_2 and TBAPF$_6$ were used as solvent and electrolyte with a Ag wire as reference electrode. A Pt wire and Pt gauze were used as the counter and working electrodes respectively. Preparation of the Pt gauze electrode comprised of electrochemical cycling in 0.5 M H_2SO_4. 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 GDIIS to optimise $\mathbf{1}^{\bullet+}$ and $^{1}\mathbf{1}^{2+}$ [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 BMK/def2-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