

A Redox-Active Tetrathiafulvalene [2]Pseudorotaxane: Spectroelectrochemical and Cyclic Voltammetric Studies of the Highly-Reversible Complexation/Decomplexation Process

Wayne Devonport, Mark A. Blower, Martin R. Bryce,* and Leonid M. Goldenberg†

Department of Chemistry, University of Durham, Durham DH1 3LE, U.K.

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The complexation of TTF **2** and cyclobis(paraquat-*p*-phenylene) **1**⁴⁺ has been studied by cyclic voltammetry and by spectroelectrochemistry: shifts in the redox potentials for the TTF and the **1**⁴⁺ components of 45 and 30 mV, respectively, occur upon complexation. Decomplexation of **2**·**1**⁴⁺ upon oxidation of the TTF unit to the cation radical species has been monitored by spectroelectrochemistry. The complexation/decomplexation process is highly reversible over at least 10 electrochemical cycles, and this process is accompanied by a color change of the solution from dark green (complexed) to pale brown (uncomplexed) which is clearly visible to the naked eye.

Introduction

The development of strategies for the assembly of large, well-defined molecular arrays,¹ nanostructures, which are endowed with controllable functions, is a fascinating challenge for chemists who are aiming to synthesize materials for applications in nanoscale molecular devices.² Inspiration for this work is provided by the natural world: biological systems are replete with examples of self-assembled nanoscale structures where aggregates are held together by weak noncovalent interactions, *e.g.* π - π stacking, van der Waal's contacts and multiple hydrogen bonds.³ In this context, several recent studies on wholly-synthetic systems have focussed on the assembly and characterization of rotaxanes⁴ and pseudorotaxanes⁵ which are stabilized by virtue of intermolecular π -donor and π -acceptor interactions, typically involving π -rich hydroquinol derivatives, and the π -de-

ficient receptor cyclophane cyclobis(paraquat-*p*-phenylene) **1**⁴⁺.^{4a} Variations on these building blocks have been reported, notably systems which are more easily oxidized than hydroquinols,^{4b,d,e} *e.g.* benzidine derivatives,^{4b} and Mirzozian and Kaifer⁴ⁱ have recently concluded that the best π -electron donors are not necessarily the best substrates for binding to host **1**⁴⁺. The present work was undertaken as part of our studies⁶ on functionalized tetrathiafulvalene (TTF) units as π -electron rich building blocks in supramolecular and materials chemistry,^{7,8} and in the light of the synthesis by Stoddart and co-workers of a rotaxane comprising a bis(2-oxypropylenedithio)TTF derivative,^{4e} and the report that TTF **2** and tetracation **1**⁴⁺ form a 1:1 complex in which TTF is located within the cyclophane.⁹ During the preparation of this manuscript, Becher *et al.* reported the synthesis of related TTF catenanes.¹⁰

† On leave from: Institute of Chemical Physics in Chernogolovka, Russian Academy of Science, 142432 Moscow Region, Russia.

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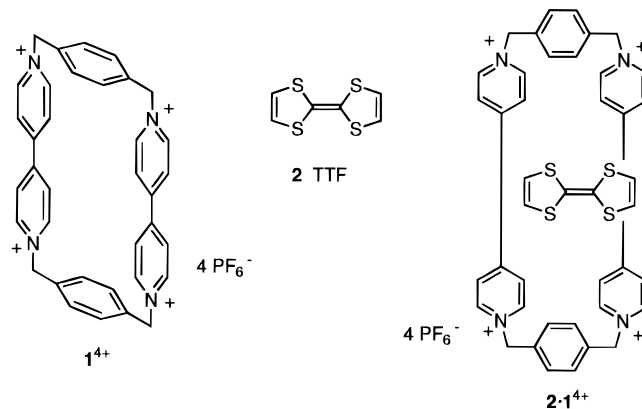
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Herein we report new results on the inclusion complex of TTF **2** and tetracation **1**⁴⁺, which was first synthesized by Stoddart *et al.*⁹ The feature of TTF that is especially attractive for this work is that it is easily oxidized,¹¹ in a wide range of solvents,^{11b} in two, reversible, single-electron processes to form sequentially the cation radical

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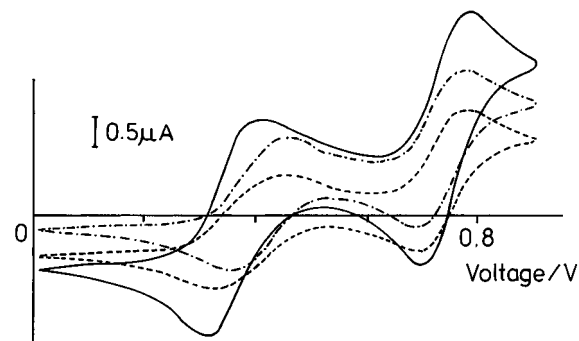


Figure 1. Cyclic voltammetry of TTF **2** (1.1×10^{-2} M) in dry acetonitrile (—) and the same solution after the addition of cyclophane **1**⁴⁺ [0.6 equiv (---) and 1.2 equiv (-·-·)]; electrolyte Bu₄NPF₆ (0.1 M), Pt electrode (diameter 0.127 mm) scan rate 500 mV s⁻¹, versus Ag/AgCl, at 20 °C.

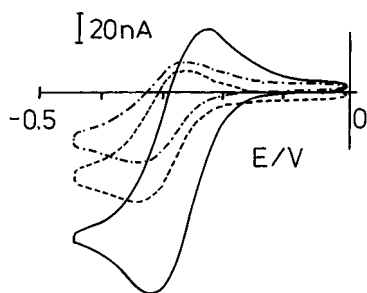


Figure 2. Cyclic voltammetry of cyclophane **1**⁴⁺ (5.8×10^{-4} M) in dry acetonitrile (—) and the same solution after the addition of TTF **2** [1 equiv (---) and 2 equiv (-·-·)]; same conditions as Figure 1.

and dication species, thereby offering the prospect of electrochemical manipulation of the assembly process and the dynamic behavior, perhaps leading to an electrochemically operated nanoscale molecular device.^{4b,h,9}

Results and Discussion

Admixture of equal amounts of TTF **2** and **1**⁴⁺ in acetone at 20 °C resulted in the immediate formation of a dark green solution which is diagnostic of charge-transfer complexation between the two components: an associated broad absorption band appeared at λ_{max} 854 nm in the UV-vis spectrum, as reported previously.⁹ Spectrophotometric dilution analysis¹² was performed on this solution at 854 nm at 21 °C,¹³ which yielded an

(8) Several properties of TTF have been identified which make this system especially attractive as a subunit in supramolecular chemistry.^{6a,7,9} However, while π -donor systems based on TTF have enjoyed extensive use as components of organic metals (Reviews: Bryce, M. R. *Chem. Soc. Rev.* **1991**, 20, 355. Bryce, M. R. *J. Mater. Chem.* **1995**, 5, 1481) they have found very limited use in other areas, because until recently^{6b} efficient routes for the synthesis of multigram batches of functionalized TTF derivatives have not been available.

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(13) Independent experiments conducted in Professor Stoddart's laboratory gave a value of $K = 2680 \text{ M}^{-1}$, for the binding constant of **1**⁴⁺ and **2** in acetone (titration experiments at 25 °C): Stoddart, J. F. personal communication, July 1995.

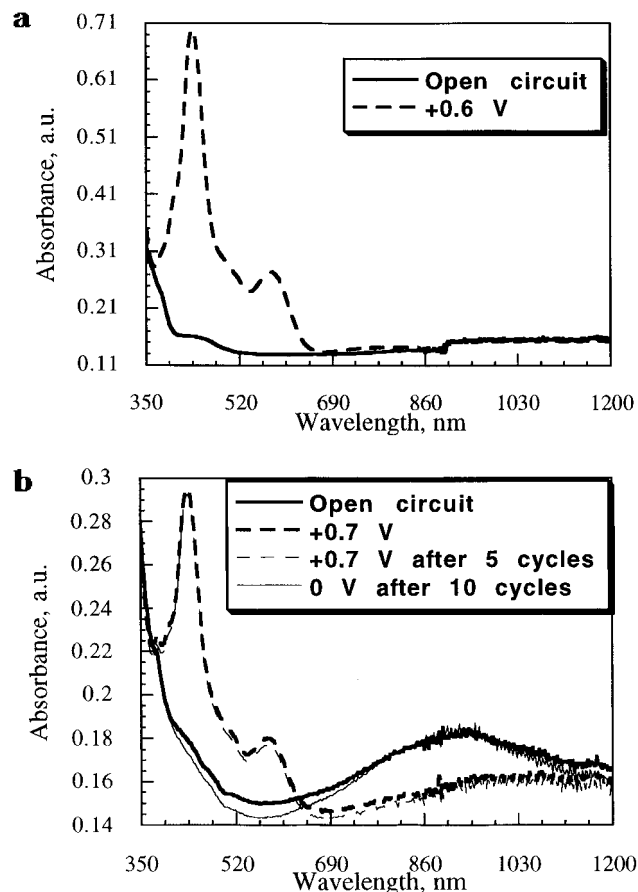


Figure 3. Spectroelectrochemistry: dry acetonitrile; electrolyte Bu₄NPF₆, versus Ag wire pseudo-reference electrode, 20 °C. (a) TTF **2**; (b) an equimolar mixture of **1**⁴⁺ and TTF **2** (ca. 3×10^{-3} M).

association constant $K_a = 2600 \text{ M}^{-1}$, corresponding to a free energy of complexation of 4.6 kcal mol⁻¹.

We have studied for the first time the solution electrochemical and spectroelectrochemical properties of the TTF pseudorotaxane formed by the inclusion of TTF **2** inside host **1**⁴⁺. Figure 1 shows the cyclic voltammogram of TTF **2**, and TTF in the presence of cyclophane **1**⁴⁺ (0.6 and 1.2 equiv). The first oxidation of TTF (*i.e.* TTF⁰ → TTF⁺) occurs at $E_1^{1/2} + 0.370$ V under these conditions, and this value is shifted anodically by 30 mV upon addition of 0.6 equivalents of **1**⁴⁺ and by 45 mV upon addition 1.2 equiv of **1**⁴⁺. Addition of a greater excess of **1**⁴⁺ resulted in no further change in the cyclic voltammogram. It is notable that the potential for the second oxidation of TTF ($E_2^{1/2} + 0.740$ V, corresponding to TTF⁺ → TTF²⁺) remains constant (± 5 mV, which is within experimental error) in these experiments, which demonstrates that the TTF²⁺ species is not being generated within the cavity, but rather by oxidation of free (uncomplexed) TTF⁺. The cyclic voltammogram of host **1**⁴⁺ in the absence and in the presence of TTF **2** is shown in Figure 2. The half-wave redox potential corresponding to the process **1**⁴⁺ → **1**²⁺ shifts cathodically by 30 mV upon addition of either 1 or 2 equiv of TTF **2** to the solution. These potential shifts for system **2**·**1**⁴⁺, induced by complexation, are larger than those reported by Kaifer *et al.* for the inclusion complexes of benzidene and 4,4'-biphenol with host **1**⁴⁺ (maximum observed shift 27 mV)^{4b} which probably reflects the lower thermodynamic stability of these complexes (benzidene·**1**⁴⁺, $K_a = 1044 \text{ M}^{-1}$;

biphenol· 1^{4+} , $K_a = 140 \text{ M}^{-1}$)^{4b} compared to the complex $2 \cdot 1^{4+}$ ($K_a = 2600 \text{ M}^{-1}$, this work).

We have studied the spectroelectrochemistry of the complex $2 \cdot 1^{4+}$. For comparative purposes, Figure 3a shows the UV-vis spectra of TTF **2** and of $\text{TTF}^{+\cdot} \text{PF}_6^-$, generated electrochemically, in the absence of 1^{4+} , in the thin layer cell used for these experiments; the spectrum of $\text{TTF}^{+\cdot}$ shows the expected absorption bands at $\lambda_{\text{max}} = 435$ and 580 nm .¹⁴ Figure 3b shows the spectra of the complex $2 \cdot 1^{4+}$; upon oxidation at $+0.7 \text{ V}$, the absorptions due to $\text{TTF}^{+\cdot}$ appear, accompanied by a marked decrease in the intensity of the broad, low energy charge-transfer band at $>750 \text{ nm}$. It is important to note that *the spectra were unchanged after 5 and 10 redox cycles* (Figure 3b), demonstrating the remarkably clean reversibility of the complexation/decomplexation reaction. This process leads to a distinct color change of the solution in the electrochemical cell from dark green (complexed) to pale brown (uncomplexed, oxidized TTF) which is clearly observable to the naked eye.

Conclusions

In summary, solution electrochemical and spectroelectrochemical studies on the complexation of **2** and 1^{4+} have been performed, and it is clear that electrochemical oxidation of TTF to the radical cation results in decomplexation, which is accompanied by a visible color change to the solution. Moreover, this process is highly revers-

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ible for many redox cycles. The importance of the reversibility of the process cannot be overstated if charge-transfer complexes of this type are to find applications in the development of electrochemically-controlled molecular switches.^{4h}

Experimental Section

UV spectra were recorded on a Unicam UV2 instrument. Cyclic voltammetric data were obtained using a BAS 100 electrochemical analyzer, or a EG&G PARC 273 Potentiostat with an Advanced Bryans XY recorder; working electrode Pt (0.16 mm diameter, BAS; and 0.127 mm diameter, home-made), counter electrode Pt wire; reference electrode Ag/AgCl (3 M NaCl, BAS). Spectroelectrochemistry was undertaken using a Perkin-Elmer Lambda 19 UV-vis-near IR spectrophotometer. The spectroelectrochemical cell was based on a 1 cm thick cuvette; Pt wire was used as the counter electrode, while Ag wire served as a quasi-reference electrode. A thin layer working electrode was constructed from glass and indium tin oxide conducting glass (sheet resistance $30 \Omega/\text{square}$, from Balzers) held together with a PTFE spacer by araldyte.

Complex $2 \cdot 1^{4+} 4\text{PF}_6^-$ was prepared according to the literature route.⁹

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