PERKIN 2 COMMUNICATION

A tetrathiafulvalene derivative with an acyclic S_4 domain as a voltammetric silver sensor

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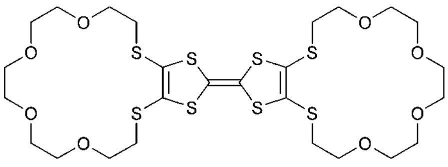
TTF derivative 5 bearing an acyclic S_4 ligating domain has been synthesised and shown to function as a redox-responsive ligand in the selective voltammetric recognition of Ag^+.

The design of redox-responsive ligand systems for the electrochemically-controlled uptake and release of guest metal cations is a topic of continuing interest in sensor technology.[1] In this context, typical molecular[2] redox transducers are derivatives of ferrocene,[3] metal-coordinated dithiolate[4] and diimine,[5] and tetrathiafulvalene (TTF),[6] all of which possess reversible redox waves within a convenient potential window. Typically, macrocyclic crown-ether or -thioether ligands act as the antenna, and cation binding within the crown cavity induces a positive shift of the potential of the oxidation process E_1^{ox}. TTF derivatives have been widely studied since the pioneering work in Becher's laboratory on ionophoric bis(crown) systems such as **1**.[6a] Compound **1** undergoes a maximum shift of E_1^{ox} of 80 mV in the presence of Na^+ in acetonitrile solution (*cf.* 10 mV for Li^+ and K^+) although a very large excess (250 equivalents) of cation was required to saturate the response. An additional attractive feature of TTF is that while E_1^{ox} is responsive, the second oxidation process (E_2^{ox}, *i.e.* cation radical→dication) is usually unaffected. Subsequent studies have addressed mono- and bis(crown) TTFs and a dioxopyrimido-TTF in solution,[6b–d,g] and crown TTFs as self-assembled monolayers.[6e,f] For example, compound (*Z*)-**2** [the (*Z*) and (*E*) isomers could not be separated] forms a 1 : 1 complex with Ag^+ in solution.[6d]



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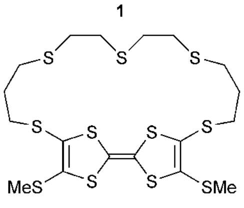
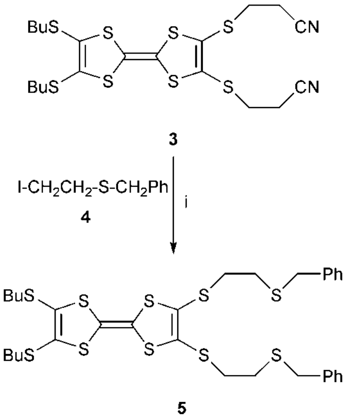


(*Z*)-**2**

We now report that efficient sensing of Ag^+ using TTF as the transducer can be achieved with appended *acyclic* thioether domains. The significance of this is that it circumvents the synthetic problems and insolubility which can be encountered with the macrocyclic systems (especially with thiacrowns)[6b] and allows a greater diversity in the structure of the ligand, without a loss of selectivity or efficiency, *e.g.* compared to compound **2**.[6d] Conformational flexibility in the acyclic ligating chains can allow the sulfur atoms to achieve the optimum geometry for metal coordination. Compound **5** has been synthesised and metal complexation has been monitored voltammetrically and spectroscopically.

Deprotection of compound **3**[7] using the methodology of Becher *et al.*[8] and alkylation of the resultant transient dithiolate species with two equivalents of benzyl 2-iodoethyl sulfide **4**[9] gave compound **5** in 67% yield.‡ Cyclic voltammetry§ established that compound **5** showed two reversible redox waves typical of the TTF system. [Reversibility was established by a linear plot of the square root of the scan rate (25 to 500 mV s^{-1}) *vs.* the diffusion current, in accordance with the Randles-Sevëick equation.]



Scheme 1 *Reagents and conditions*: i, NaH, THF, MeOH, 20 °C.

Titration of compound **5** with Li^+, Na^+, Ba^{2+}, K^+, Cr^{3+} or Ni^{2+} salts (0–20 equivalents) resulted in no significant change in the cyclic voltammogram (±5 mV) whereas titration with $AgClO_4$ or $AgNO_3$ showed a significant positive shift in the value of E_1^{ox}. The maximum observed shift for E_1^{ox} was 40 mV, saturating after the addition of *ca.* 6 equivalents of Ag^+, while E_2^{ox} shifted (positively) by only 5–10 mV. The square wave voltammograms are shown in Fig. 1, and the shift in potential, ΔE_1^{ox}, with added equivalents of $AgNO_3$ is shown in Fig. 2.

A spectrophotometric titration for compound **5** in acetonitrile with added equivalents of $AgNO_3$ is shown in Fig. 3. Three isosbestic points are observed at 270, 348 and 412 nm. The data, which were corrected for dilution and nonlinearly fitted (with the Microcal Origin 4.1 program, and using procedures reported previously)[6c] are consistent with the formation of a 1 : 1 complex with a stability constant $\log K = 3.0$ (this is the average value for three determinations at five different wavelengths, *viz.* 245, 290, 320, 380 and 436 nm). This is a suitable value for an ionophore to be applicable in practical sensor applications, as a binding constant that is too high results in irreversible binding.

We can dismiss the possibility that the observed effect is due to silver binding to the TTF framework,[10] as the same titration experiments using tetrakis(methylsulfanyl)TTF **6**,[11] instead of compound **5**, resulted in no response in the voltammogram, the ^1H NMR spectrum and the UV–vis spectra. Downfield shifts were observed for the S–CH_2–CH_2–S protons of **5** (and, to a lesser extent for the CH_2Ph protons) upon addition of Ag^+: the chemical shifts of the other protons were unaffected.

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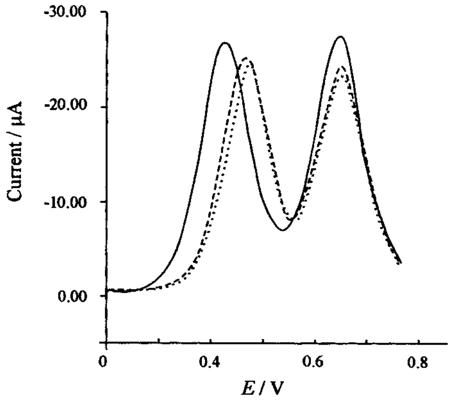


Fig. 1 Square wave voltammograms of compound **5** (——) in acetonitrile (5×10^{-4} M) with addition of 3.0 equiv. (– – – –) and 9.0 equiv. (· · · · ·) of $AgNO_3$, *vs.* Ag/AgCl.

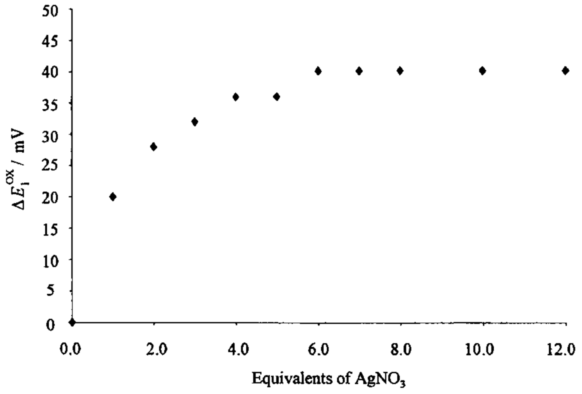


Fig. 2 Plot of the shift of the potential E_1^{ox} in the square wave voltammogram of compound **5** with added equivalents of $AgNO_3$.

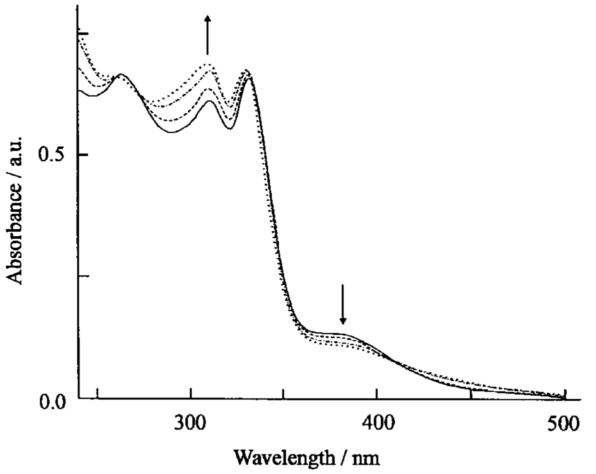
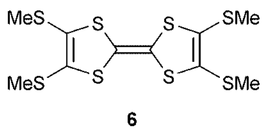


Fig. 3 Absorption spectra of compound **5** (5×10^{-5} M) in the presence of 0, 5, 10 and 40 equivalents of $AgNO_3$.



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In summary, using prototype TTF derivative **5** with an acyclic S_4 metal ligating site, we have established selective recognition of Ag^+ which can be monitored voltammetrically and spectrophotometrically. These studies suggest there is considerable scope, hitherto unrecognised, for the use of *acyclic* substituents as antennae on the TTF framework (and possibly other transducer units) in redox-controlled molecular recognition processes in solution. An extension of this to derivatives suitable for the formation of self-assembled films should also be possible.

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Notes and references

‡ *Synthesis of compound* **5**. To a solution of compound **3** (250 mg, 0.40 mmol) in tetrahydrofuran–methanol (100 cm^3, 1 : 1 v/v) was added sodium hydride (60% suspension in oil) (310 mg, 1.36 mmol) at 20 °C and the mixture was stirred for 1 h. Compound **4** (380 mg, 1.36 mmol) dissolved in tetrahydrofuran (10 cm^3) was then added and the mixture was stirred at 20 °C for 12 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography [silica gel, eluent chloroform–hexane (1 : 1 v/v)] to give compound **5** as an orange oil (180 mg, 67%). HRMS found 744.0337, $C_{32}H_{40}S_{10}$ requires 744.0340; δ_H (200 MHz, $CDCl_3$) 7.35–7.24 (10H, m), 3.70 (4H, s), 2.92–2.78 (8H, m), 2.63–2.50 (4H, m), 1.66–1.50 (4H, m), 1.50–1.25 (4H, m) and 0.88 (6H, t, *J* 8 Hz); δ_C ($CDCl_3$) 137.90, 128.85, 128.59, 128.08, 127.83, 127.12, 112.21, 109.17, 36.05, 36.02, 35.75, 31.69, 30.84, 21.59 and 13.56.

§ Voltammetric analysis was carried out using a Bioanalytical Systems CV-50W instrument. The reference was a non-aqueous (acetonitrile) silver/silver ion electrode; the counter electrode was platinum and the working electrode was glassy carbon. The solvent was acetonitrile (Aldrich, HPLC grade) and the supporting electrolyte was Bu_4NClO_4 (Fluka, puriss grade). Metal ClO_4 and metal NO_3 salts were Aldrich, puriss grade. Titrations were performed using 10 cm^3 of a 5×10^{-4} M solution of **5** to which the Ag^+ solution (0.04 M) was added using a micropipette. All silver solutions were stored in the dark. CV was performed with a scan rate of 100 mV s^{-1}. Square wave voltammetry was performed at potential step 4 mV, pulse amplitude 25 mV and frequency 15 Hz. Data were referenced to decamethylferrocene.

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