Crown-annelated tetrathiafulvalenes: synthesis of new functionalised derivatives and spectroscopic and electrochemical studies of metal complexation

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Synthetic routes to the first unsymmetrical annelated tetrathiafulvalene–S_2O_4 crowns are reported; the methodology is versatile, affording the parent system 8, functionalised derivatives 6, 7 and 9–12, and amphiphilic derivatives 6 and 13. UV–VIS spectroscopic studies of metal binding (Na^+, Ag^+ and Ba^{2+}) to the crown–TTF systems 8 and 13, and the bis(crown)–TTF 14 have been performed in solution, and stability constants have been calculated. The data establish that for the crown compounds 8 and 13 1:1 complexes are formed, whereas for the bis(crown) compound 14 both 1:1 [14(Na^+)] and 1:2 [14(Na^+)$_2$] complexes are formed. Solution electrochemical studies reveal that metal complexation to the crown unit leads to a small anodic shift in the first oxidation potential of the TTF system. Langmuir–Blodgett films of amphiphilic compound 13 have been assembled on solid substrates by Y-type deposition.

Introduction

Redox-active macrocyclic ligand systems are currently attracting widespread attention, especially when complexation of a guest molecule (or ion) at one site in the molecule induces a change in the electronic properties of the redox centre.[1] In this context, we were attracted to the π-electron donor system tetrathiafulvalene (TTF) **1** as a redox-active unit. TTF undergoes two, reversible, single-electron oxidations, and this molecule and its derivatives have been studied extensively for over 20 years as components of charge-transfer complexes and radical ion salts, many of which are molecular metals and semiconductors.[2] Recent syntheses of functionalised derivatives of TTF have paved the way for the use of the TTF system as a building block within the wider context of supramolecular and materials chemistry:[3] for example, as redox-active components in Langmuir–Blodgett (LB) films,[4] molecular sensors,[5] molecular shuttles,[6] catenanes,[7] multi-stage redox assemblies[8] and dendritic macromolecules.[9] Recent work on the incorporation of TTF into different macrocyclic systems[3,5] has generally concerned symmetrical molecules consisting of a central TTF moiety situated between two macrocycles.[10] Changes in the ^{1}H NMR spectrum of the macrocyclic ligand, and the redox properties of the TTF system, monitored by cyclic voltammetry, have been used to monitor metal binding within the crown rings. Upon addition of metal salts (M = Li, Na, K) to a solution of the TTF–bis(crown) molecule, a shift in the value of $E_1{}^{\frac{1}{2}}$ (which represents the process $TTF^0 \rightarrow TTF^{\bullet +}$) to more anodic (positive) potentials was observed. Although this shift, which signifies that metal complexation has occurred, is relatively small (maximum value of ΔE = 80 mV for Na^+ complexation)[5] compared to some other redox-active crowns,[1f] the scope afforded by the TTF system for structural variation and functionalisation, makes further studies of this system worthwhile.

Herein we report new studies of TTF–crowns, notably (i) the synthesis and electrochemistry of unsymmetrical and functionalised systems, (ii) spectroscopic studies of metal complexation in TTF–crown systems, and (iii) the formation of Langmuir–Blodgett (LB) films of amphiphilic TTF–crowns.

Results and discussion

Synthesis of materials

Three synthetic approaches that have been used previously in TTF chemistry[11] have now been applied successfully to TTF–crowns: namely, (i) cross-coupling reactions to produce functionalised TTF–crown systems, including the amphiphilic TTF–crown **6**, and the diester **7**; (ii) electrophilic substitution of a TTF–crown, *via* a lithiated intermediate, to provide derivative **9**, and (iii) functional group removal and interconversion to give **10**–**12** and again **9**, which are derivatives bearing a reactive 'handle' suitable for further transformations. A few TTF–S_2O_3 crowns have been prepared previously by phosphite-induced cross-coupling of two 1,3-dithiole-2-thione (-one) units, or by base-induced cross-coupling of two dithiolium cations,[10] but, to our knowledge, unsymmetrical TTF–S_2O_4 crowns have not been prepared previously.

Amphiphilic derivative **6**, which was designed for the

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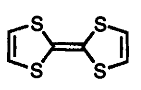

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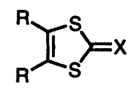
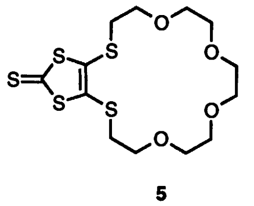


2 R = $SC_{18}H_{37}$; X = S
3 R = H; X = S
4 R = CO_2Me; X = O



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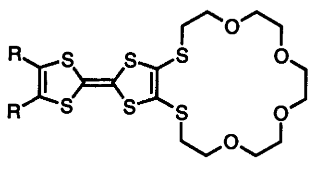
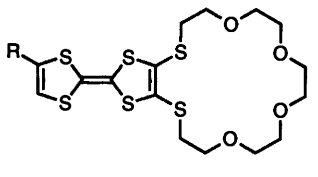
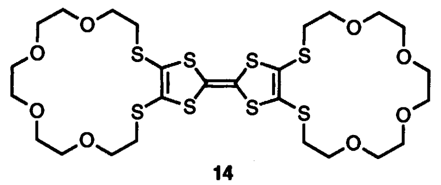


6 R = $SC_{18}H_{37}$
7 R = CO_2CH_3



8 R = H
9 R = CHO
10 R = CO_2Me
11 R = CH_2OH
12 R = CO_2H
13 R = $CH_2OC(O)C_{17}H_{35}$



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formation of LB films, was obtained in 14% yield by cross-coupling of equimolar amounts of 1,3-dithiole-2-thione derivatives **2**[12] and **5**[5] in the presence of freshly distilled trimethyl phosphite (reflux, 3 h).[11a–c] Attempted trimethyl phosphite-mediated cross-coupling of **5** and vinylene trithiocarbonate **3** was unsuccessful: although compound **8** was formed (TLC and NMR evidence) in very low yield it could not be separated from the major product which was the TTF–bis(crown) **14**[5a] resulting from self-coupling of **5**. However, when the cross-coupling was performed in the presence of octacarbonyldicobalt [reagent **5** (1.0 equiv.) reagent **3** (3.0 equiv.) $Co_2(CO)_8$ (2.0 equiv.) toluene, reflux, 12 h] a pure sample of the desired product **8** (albeit in only 9% yield) was obtained, after separation from unreacted **3** and from TTF **1** formed by self-coupling of **3**.

We have demonstrated that **8** can serve as a starting material for novel functionalised TTF–crown ethers. Lithiation of **8** [lithium diisopropylamide (LDA) (1.3 equiv.) in dry THF solution at −78 °C] followed by addition of *N*-methyl-*N*-phenylformamide (2.0 equiv.) afforded aldehyde derivative **9** (31% yield).[13] The latter compound could also be obtained by a different route which, moreover, provides an easy entry into a number of new functionalised TTF–crown derivatives, namely **7** and **10**–**12**. Thus, trimethyl phosphite-mediated cross-coupling of **5** (1.0 equiv.) and 4,5-bis(methoxycarbonyl)-1,3-dithiol-2-one **4**[14] (1.0 equiv.) afforded compound **7** (52% yield) after separation of the corresponding symmetrical byproducts, including bis(crown) **14**. Initial attempts at using triethyl phosphite instead of trimethyl phosphite gave higher yields of compound **7**, but the product could not be isolated in a pure state, so $P(OMe)_3$ is the reagent of choice.

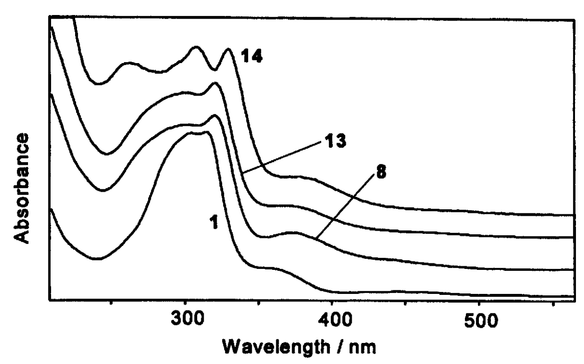

Fig. 1 Absorption spectra of compounds **1**, **8**, **13** and **14** in acetonitrile solution (the spectra are offset on the *y* axis for clarity)

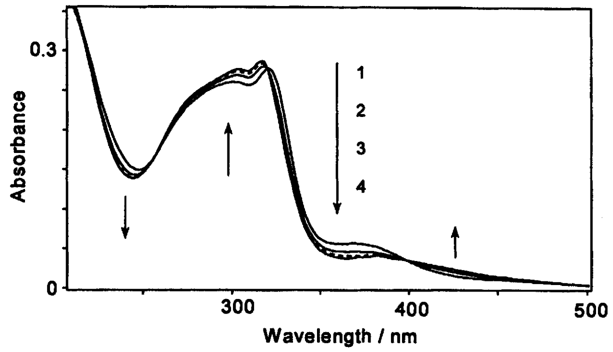

Fig. 2 Absorption spectra of compound **13** in acetonitrile solution (1 cm cell) containing $NaClO_4$ at a concentration of (1) 0; (2) 7.2 × 10^{-3}; (3) 2.8 × 10^{-2} and (4) 0.33 mol dm^{-3}

Monodemethoxycarbonylation[15] of **7** with lithium bromide in hexamethylphosphoramide (HMPA) (80 °C, 2 h) gave ester derivative **10** in 83% yield, which was treated with diisobutylaluminium hydride (5 equiv.) in dichloromethane to afford alcohol **11** (91% yield),[16] or hydrolysed under basic conditions to yield the acid **12** (75% yield). Selenium dioxide oxidation[16b] of **11** in refluxing dioxane gave aldehyde **9** in 43% yield. Moreover, treatment of **11** with stearoyl chloride (1.5 equiv.) in dichloromethane in the presence of triethylamine, afforded the amphiphilic ester **13** in 30% yield. This specific side-chain was chosen because we have recently shown that ethylenedithio-TTF substituted with this side-chain forms high-quality LB films.[4b]

Although the cross-coupling reactions to produce both **6** and **8** proceeded in only low yield, the starting thiones **2**, **3** and **5** are readily available on a multi-gram scale, enabling useful quantities of **6** and **8** to be obtained. It is important to have established that both the cross-coupling and the lithiation/electrophilic substitution methodology, along with functional group manipulation, can be successfully applied to TTF–crown systems.

Spectroscopic studies

Spectroscopic studies of metal binding to crown–TTF systems have not been reported previously. The UV–VIS absorption spectra of TTF **1** and TTF–crown derivatives **8**, **13** and **14** in acetonitrile solution are presented in Fig. 1. The spectra of compounds **8** and **13** are very similar, while those of compounds **1** and **14** are distinctly different. These results indicate that the sulfur atoms within the crown ether group are conjugated into the TTF chromophore, with each additional ring resulting in a specific change in the electronic absorption spectrum.

The absorption spectra of compound **13** in acetonitrile in the presence of sodium perchlorate are shown in Fig. 2; there are clear isosbestic points, indicating that a simple 1 : 1 complexation occurs with Na^+. The dependence of the absorbance at a fixed wavelength on $NaClO_4$ concentration is

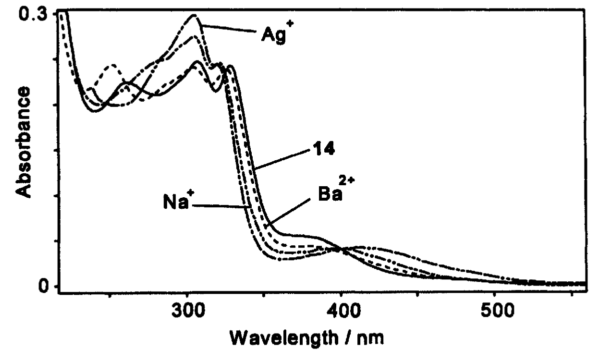

Fig. 3 Absorption spectra of compound **14** (2×10^{-5} mol dm^{-3}) in acetonitrile, and in the presence of $AgClO_4 \cdot H_2O$ (2.1×10^{-2} mol dm^{-3}), $NaClO_4$ (0.29 mol dm^{-3}) and $Ba(ClO_4)_2$ (0.7 mol dm^{-3})

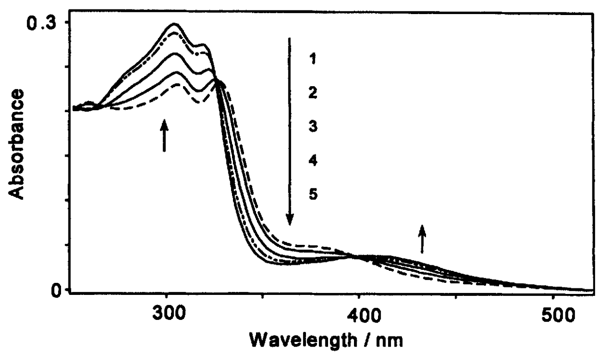

Fig. 4 Absorption spectra of compound **14** (2×10^{-5} mol dm^{-3}) in water–acetonitrile (4:1 v/v; 1 cm cell) containing $AgClO_4$ at concentrations of (1) 0; (2) 2×10^{-4}; (3) 8×10^{-4}; (4) 2.3×10^{-3} and (5) 5.2×10^{-3} mol dm^{-3}

described well by eqn. (1), in accordance with eqn. (2), where A_o

$$(A_o - A)/(A - A_i) = K[Na^+] \qquad (1)$$

$$13 + Na^+ \overset{K}{\rightleftharpoons} 13(Na^+) \qquad (2)$$

and A_i are the absorbances at zero and infinite salt concentrations, respectively. The fitting of eqn. (1) to data taken at two different wavelengths (310 and 374 nm) gave close values for the stability constant, with $\log K = 2.2 \pm 0.1$ for **13**. This experiment was repeated for compound **8**, giving similar results and a value for the stability constant of $\log K = 2.7 \pm 0.1$.

Similar studies on bis(crown) derivative **14** have revealed that complexation occurs with Na^+, Ag^+ and Ba^{2+}. In each case, the complexation results in a specific change in the electronic absorption spectrum, and the spectra of both non-complexed and fully complexed forms are given in Fig. 3. The presence of $NaClO_4$ resulted in clear changes in the absorption spectrum of **14**, with peaks at 403, 322 and 306 nm dominating the spectrum at a $NaClO_4$ concentration of 4.7×10^{-2} mol dm^{-3}. A further increase in the sodium perchlorate concentration resulted in only minor changes in the spectrum. However, two sets of isosbestic points were found to occur for different regions of sodium salt concentration. For example, an isosbestic point at 269 nm was present only at low $NaClO_4$ concentrations (0–6.4×10^{-3} mol dm^{-3}). By contrast, isosbestic points at 326 and 261 nm were valid only at $NaClO_4$ concentrations in the range of 0.025–0.3 mol dm^{-3}. It is clear that Na^+ complexation is occurring and that, in this case, the quantitative analysis has to take into account the possible formation of at least two kinds of complex. The likely forms of these complexes are **14**(Na^+) and **14**$(Na^+)_2$, because two crown ether groups are present in each ionophore molecule [eqns. (3) and (4)].

$$14 + Na^+ \overset{K_1}{\rightleftharpoons} 14(Na^+) \qquad (3)$$

$$14(Na^+) + Na^+ \overset{K_2}{\rightleftharpoons} 14(Na^+)_2 \qquad (4)$$

The changes in the absorption spectra confirm the formation of more than one product, and the occurrence of different isosbestic points in different regions of $NaClO_4$ concentration suggests that the formation of these products proceeds at different salt concentrations. In principle, many other complexes, such as $(\mathbf{14})_2(Na^+)$, $(\mathbf{14})_2(Na^+)_2$ and $(\mathbf{14})_2(Na^+)_3$, may be formed in this system; their formation may be expected at higher concentrations of **14**.

A quantitative analysis of the UV–VIS absorption data is complicated by the fact that the spectra of all of the species (**14** and the different complexes) overlapped in all regions. In addition, the stability constants K_1 and K_2 [eqns. (3) and (4)] may be comparable. As an approximation, the experimental data (absorbance at a fixed wavelength *vs.* metal salt concentration) were fitted to eqn. (5), in agreement with a simplified reaction (6).

$$(A_o - A)/(A - A_i) = K_{obs}[Na^+] \qquad (5)$$

$$14 + Na^+ \overset{K_{obs}}{\rightleftharpoons} \text{complex} \qquad (6)$$

This observed stability constant, K_{obs}, may be wavelength dependent because of the different relative molar decadic absorption coefficients of **14** and its complexes at different wavelengths. Indeed, the fitting of the absorbance data taken at 370, 430 and 306 nm gave estimates for $\log K_{obs}$ of 2.49, 2.44 and 2.10, respectively. In agreement with eqns. (3) and (4), the relationship $\log K_1 \geqslant \log K_{obs}$ may be expected and, as a consequence, $\log K_1 \geqslant 2.5$. This agrees well with the value of the stability constant ($\log K_1 = 2.7$) obtained for compound **8**, and confirms the suggestion that both 1:1 [**14**(Na^+)] and 1:2 [**14**$(Na^+)_2$] complexes are formed. More detailed analysis, based on eqns. (3) and (4), requires the molar decadic absorption coefficient for each of the species present;[17] these coefficients are not available for this system, and hence such an analysis is not feasible.

The absorption spectra of compound **14** did not show perfect isosbestic points on complexation with Ag^+ in acetonitrile solution, using the $AgClO_4 \cdot H_2O$ salt, in any range of salt concentration. Therefore, in order to exclude the possible influence of small amounts of water, the complexation was studied using **14** in acetonitrile containing 1.5 vol% water. The changes in the absorption spectra of **14**, and the observed stability constants ($\log K_{obs} = 2.5$), were similar in both of these cases and indicate that a genuine complex with Ag^+ is formed. Fig. 4 shows the changes in the absorption spectrum of **14** upon complexation with Ag^+ in a mixed water–acetonitrile (4:1 v/v) solvent. The stability constant ($\log K_{obs} = 3.7$) in this case was higher than that found for pure acetonitrile solution. This observation may be explained by the fact that Ag^+ is a 'soft' cation and hence its complexation with a crown ether is expected to be more effective in a 'hard' solvent such as water. The observed stability constant for complexation of **14** with Ag^+ in water–acetonitrile mixture (4:1 v/v) is close to that of $\log K_1 = 3.0$ reported for complexation of 1,4-dithia-18-crown-6-ether with Ag^+ in water[18] for which no evidence of 2:1 ligand:metal cation complexes was found. To the best of our knowledge, the complexation of 1,4-dithia-18-crown-6-ether and its derivatives has not been studied for alkali and alkaline-earth metal cations.

The addition of Ba^{2+} and Mg^{2+} to acetonitrile solutions of **14** resulted in small and very small changes, respectively, in the absorption spectrum. These may occur because Ba^{2+} and Mg^{2+}

Table 1 Cyclic voltammetric data for compounds **6**, **8**, **13** and **14** (ΔE_1^{ox} refers to the anodic shift in the first oxidation potential after saturation of the solution with $NaPF_6$)

Compound and solvent	E_1^{ox}/V[a]	E_2^{ox}/V[a]	ΔE_1^{ox}/mV
6 in CH_2Cl_2–MeCN (2:1 v/v)	0.47	0.72	0
8 in MeCN	0.42	0.66	22–35
13 in MeCN	0.47	0.68	25 (35)[b]
14 in MeCN	0.48	0.64	60–70

[a] Data were recorded *versus* SCE, uncorrected with respect to Fc/Fc$^+$, Pt electrode diameter 0.5 mm, scan rate 100 mV s^{-1}. [b] Data obtained using Bu_4NClO_4 as electrolyte, and $NaClO_4$ instead of $NaPF_6$ as the source of Na^+.

Table 2 Anodic shift in the first oxidation potential for compound **13** in saturated acetonitrile solutions of different metal salts[a]

Metal cation	ΔE_1/mV
Na^+[b]	25 (35)[c]
Ba^{2+}[d]	25
Li^+[b]	0
K^+[b]	0
Ag^+[e]	70–75

[a] Data were obtained using a Pt 1.6 mm diameter electrode, scan rate 50 mV s^{-1}. [b] Electrolyte BuN_4PF_6; MPF_6 as the source of the metal cation. [c] Electrolyte BuN_4ClO_4; $NaClO_4$ as the source of Na^+. [d] $Ba(ClO_4)_2$ as the source of Ba^{2+}. [e] $AgBF_4$ as the source of Ag^+.

are 'hard' cations and will interact preferably with the oxygen atoms in the dithia-18-crown-6-ether, rather than with the sulfur atoms which form part of the conjugated system of the chromophore of **14**. From the results to date, it is not possible to conclude whether these ions complex poorly, or complex effectively but cause only a small change in the UV–VIS spectrum of **14**. In addition, the fact that Mg^{2+} at 0.7 mol dm^{-3} causes only small changes in the UV–VIS absorption spectrum indicates that the effect of ionic strength alone on **14** is small.

Electrochemical studies

We have studied the solution electrochemistry of compounds **6**, **8**, **13** and **14**, in the absence and in the presence of metal cations, by cyclic voltammetry (CV). Hansen *et al.*[5a] reported that sodium ions (250 equiv.) induced the largest shift (80 mV) in the first oxidation potential of bis(crown) compound **14** in acetonitrile solution, while the second oxidation potential was unaffected, and therefore we concentrated on using sodium ions for our studies on metal complexation in solutions and thin films (see below). The data we obtained are collated in Table 1. All the TTF derivatives studied display the usual two, reversible, single-electron redox waves; as expected, the attachment of sulfur atoms to the TTF framework slightly raises the oxidation potential relative to that for unsubstituted TTF.[19] Our results for compound **14** are very similar to those of Hansen *et al.*: we observed a maximum anodic shift of 70 mV in the value of $E_1^{\frac{1}{2}}$ upon addition of a saturated solution of $NaPF_6$ to a solution of **14** in acetonitrile. Under the same conditions mono(crown)–TTF derivatives **8** and **13** both showed an anodic shift of 25–35 mV upon metal complexation. It is notable that these values for **8** and **13** are *ca.* half that for compound **14**: this is consistent with both ionophoric sites in compound **14** being occupied (which Hansen *et al.* concluded was the case from NMR studies) with the two complexed sodium ions exerting an additive effect in raising the oxidation potential of the central TTF unit. The second oxidation potential of the TTF unit of our systems was not affected by the presence of Na^+, in agreement with the data of Hansen *et al.* for compound **14**. The solubility of $NaClO_4$ in acetonitrile is higher than that of $NaPF_6$, so we also used the former salt as a source of Na^+ in the study of compound **13**. However, we observed a similar shift in potentials with both salts (Table 1). Mono(crown) derivative **6** was insoluble in acetonitrile, and solutions in a mixture of dichloromethane and acetonitrile did not show any change in the cyclic voltammograms upon addition of $NaPF_6$, $NaClO_4$ or $NaBPh_4$ as a source of Na^+, probably due to the low solubility of the salts in this mixture of solvents, which meant that a sufficient excess of sodium in solution could not be achieved.

The recognition of cations by compound **13** in acetonitrile solution has been studied in more detail (Table 2). The electrochemical data support the previous observation[5a] that the TTF–S_2O_4 crown system exhibits a low response (in the case of **13** no response) to Li^+ or K^+. The cyclic voltammogram of compound **13** showed a response to the presence of both Ba^{2+} and Ag^+: the latter cation resulted in an anodic shift of 70–75 mV in the first oxidation potential, which is considerably greater than the 25–35 mV shift observed for Na^+ and Ba^{2+}. These data show similar effects to the UV–VIS spectroscopic data, which showed that larger changes were induced in the absorption of the bis(crown) derivative **14** by complexation with Ag^+ than with Na^+ or Ba^{2+} (Fig. 3). Both sets of results are consistent with Ag^+ binding at the sulfur sites, thus inducing large perturbations in the electronic structure of the TTF moiety, while Na^+ and Ba^{2+} bind preferentially at the more remote crown oxygen sites. This differentiation of binding site uncouples these spectroscopic and voltammetric effects from the relative stability constants. However, as with the spectroscopic data, we have used the electrochemical data to estimate the stability constant for the complex of **13** with Ag^+, as follows. The cyclic voltammetric response for different molar ratios of Ag^+: compound **13** was measured [Fig. 5(*a*)]. Similar data were obtained by differential pulse voltammetry. Assuming (i) that the maximum shift of the first oxidation potential in saturated Ag^+ solution corresponds to the state where the equilibrium of complex formation [eqn. (2)] is shifted completely to the right, and (ii) that the concentration of complex is proportional to the shift in the first oxidation potential, if we then assign eqn. (7), then eqn. (8) follows and consequently eqn. (9). Thus, the intercept with the *y* axis for the

$$x = \Delta E_1/\Delta E_1^{max} \qquad (7)$$

$$K = [\mathbf{13}(Ag^+)]/[\mathbf{13}]\,[Ag^+] = x/(1-x)\,[Ag^+] \qquad (8)$$

$$\log\,[x/(1-x)] = \log K + \log\,[Ag^+] \qquad (9)$$

plot of log $[x/(1-x)]$ *versus* log $[Ag^+]$ will represent log K [Fig. 5(*b*)]. The stability constant obtained for $[\mathbf{13}(Ag^+)]$ from these data is log K_{obs} = 2.26, which is similar to the stability constant for $[\mathbf{14}(Ag^+)]$ which we obtained from spectroscopic data.

Langmuir–Blodgett film studies

The LB technique[20] affords unique opportunities for control of supramolecular architecture in thin films.[21] The amphiphilic TTF–crown derivatives **6** and **13** were designed for the assembly of LB films, which could function as thin film sensors for metal ions, with metal binding being monitored by electrochemical or spectroscopic changes to the TTF system. In a similar way, electrodes coated with thin films of crown-substituted and crown-annelated conducting polymers, such as polypyrrole and polythiophene, prepared by electropolymerisation, show an ionochromic response to alkali metal cations.[1d]

Compound **13** formed a stable monolayer at the air–water interface and exhibited an isotherm with a molecular area of *ca.* 0.30 nm^2 at 35 mN m^{-1} (Fig. 6). Multilayers of compound **13** could be built up on solid substrates by Y-type deposition using a dipping pressure of 35 mN m^{-1}. The transfer ratio was 0.8–1.2. The cyclic voltammogram of the LB monolayers recorded in 1 mol dm^{-3} $HClO_4$ electrolyte solution did not show any change in the presence of sodium ions. The reason for this might be that

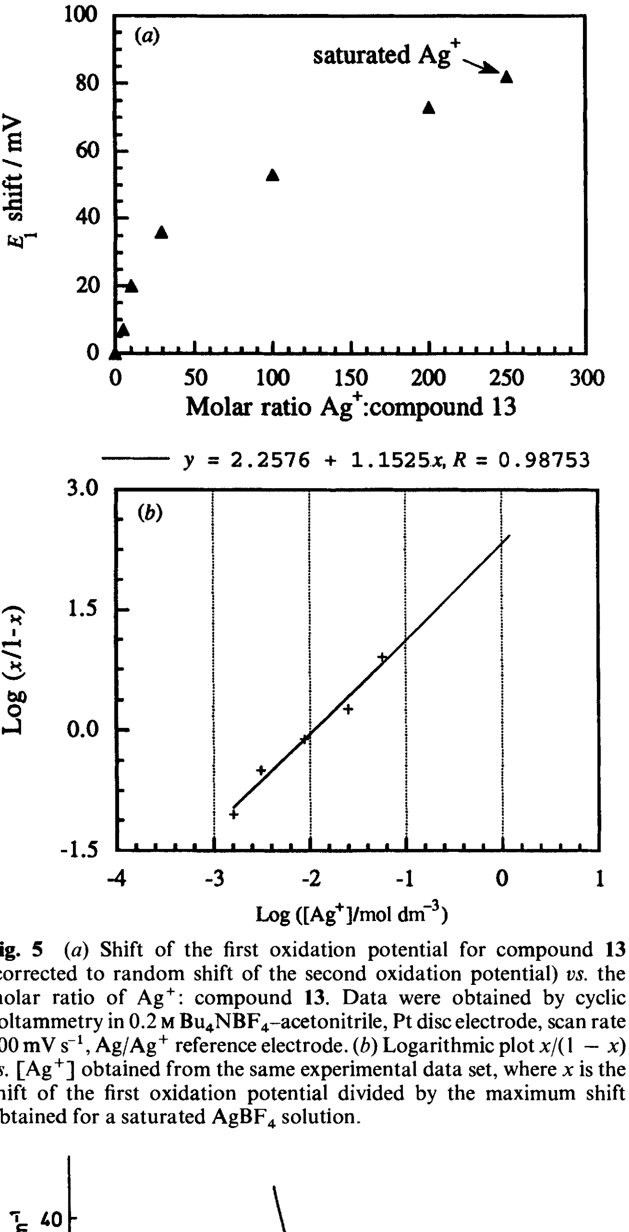

Fig. 5 (*a*) Shift of the first oxidation potential for compound **13** (corrected to random shift of the second oxidation potential) *vs.* the molar ratio of Ag^+: compound **13**. Data were obtained by cyclic voltammetry in 0.2 M Bu_4NBF_4–acetonitrile, Pt disc electrode, scan rate 100 mV s^{-1}, Ag/Ag^+ reference electrode. (*b*) Logarithmic plot $x/(1 - x)$ *vs.* $[Ag^+]$ obtained from the same experimental data set, where x is the shift of the first oxidation potential divided by the maximum shift obtained for a saturated $AgBF_4$ solution.

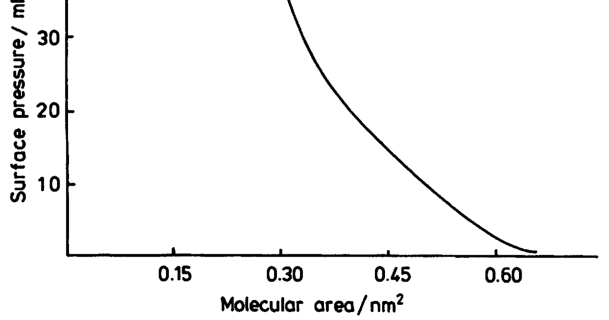

Fig. 6 Surface pressure *vs.* area per molecule isotherm for compound **13**

the small shift of peak potential is difficult to register for a monolayer, as the CV response was not stable in solution. Similarly, the UV–VIS spectrum of LB films of **13** (between 4–18 layers deposited on quartz) was unchanged after treatment of the films with either a 3.0 mol dm^{-3} aqueous $NaClO_4$ solution or a 1.0 mol dm^{-3} aqueous $AgBF_4$ solution for up to 10 h. However, the absorption spectrum for the LB films is usually broader than for the same compound in solution, making it difficult to observe small changes in the peak position.

Compound **6** could also be spread as a monolayer on the surface of an LB trough, with an extrapolated molecular area of 0.5 nm^2. However, monolayer transfer was not uniform, with only the upper edge of the substrate being covered by the film. To improve monolayer transfer, compound **6** was mixed with 40 mol% of stearic acid. An LB monolayer of this mixture was assembled on ITO glass and the CV of the monolayer was recorded in the following electrolyte solutions: $HClO_4$, $LiClO_4$, $NaClO_4$ and $KClO_4$. No significant difference in peak potentials was observed upon comparison of the first voltammetric scans.

We have also prepared electroactive films of non-amphiphilic crown derivatives **8** and **14** by casting from solution onto an ITO electrode. However, the cyclic voltammetric response of these films was unaffected by the presence of Na^+ ions.

These results contrast with those we have recently reported for complexation of LB films of a chromoionophore.[17b,22] In this case, distinct changes in the visible absorption spectrum were noted on complexation with a variety of cations. The different behaviour noted for LB films in this work is probably related to the different molecular organisation in these films. For example, diffusion of Na^+ into the crown binding site of the TTF–crown compounds may be hindered by their compact molecular packing.

Conclusions

In summary, several TTF–crown ether derivatives have been found to show significant changes in their electronic spectra on complexation with Na^+, Ba^{2+} and Ag^+ in solution. The data establish that 1 : 1 complexes are formed for the crown compounds **8** and **13**, whereas for the bis(crown) compound **14** both 1 : 1 [**14**(Na^+)] and 1 : 2 [**14**($Na^+)_2$] complexes are formed. Solution electrochemical studies reveal that metal complexation to the crown unit leads to a small anodic shift in the first oxidation potential of the TTF system. Both sets of results are consistent with Ag^+ binding at the sulfur sites, thus inducing larger perturbations in the electronic spectra and cyclic voltammograms of the TTF chromophore, while Na^+ and Ba^{2+} bind preferentially at the more remote crown oxygen sites.

Experimental

For UV–VIS spectroscopic studies in solution acetonitrile (HPLC grade), sodium perchlorate, silver perchlorate monohydrate, magnesium perchlorate and barium perchlorate (all from Aldrich) were used as received. All measurements were made at room temperature using a Hitachi U-3000 Spectrophotometer. The data were fitted using the SPSS statistical package, which allowed non-linear regression analysis to be performed.

For LB film studies, the troughs were housed in a class 10 000 microelectronics clean room and have been described previously.[23] The TTF derivatives were spread on the surface of ultrapure water (obtained by reverse osmosis, deionisation and ultraviolet sterilisation) from dichloromethane or chloroform solutions (0.5 g dm^{-3}). The surface pressure *versus* molecular area isotherms were measured at 20 ± 2 °C, pH = 5.8 ± 0.2 and compression rate *ca.* 4×10^{-3} nm^2 $molecule^{-1}$ s^{-1}. LB films were deposited onto glass slides, quartz windows, conducting indium tin oxide (ITO, sheet resistance 300 Ω per square, from Balzers) glass slides by conventional vertical dipping techniques. A dipping speed of 10 mm min^{-1} was employed, and the first monolayer was dipped on the upstroke when the slide was dipped in the subphase, before compression of the monolayer. To improve the hydrophilic properties of ITO, the slides were treated with saturated $Na_2Cr_2O_7$–concentrated H_2SO_4 solution for *ca.* 10 s and carefully washed with ultrapure water.[24] Slides with areas of between 20 and 30 cm^2 were used for LB transfer. After LB film deposition, the slides were carefully cut with a diamond tipped stylus to form several electrodes with contact areas between 0.1 and 0.5 cm^2. Cast films were obtained by dropping a solution of the TTF derivative in CH_2Cl_2 onto the conducting side of ITO and allowing the solvent to evaporate. UV–VIS absorption measurements on thin films were performed on a Perkin-Elmer Lambda 19 spectrophotometer for films deposited on glass slides and quartz windows.

Cyclic voltammetry was performed using an EG&G PARC model 273 potentiostat with an Advanced Bryans XY recorder. Pt mesh served as the counter electrode, and an SCE (in aqueous solution) or Ag/Ag^+ (in acetonitrile solution) served as the reference electrode. We checked that the Fc/Fc^+ potential (Fc = ferrocene) was unaffected by the addition of metal ions under these conditions. Cyclic voltammetry in solution was performed in 0.2 mol dm^{-3} Bu_4NPF_6, Bu_4NClO_4 or Bu_4NBF_4–acetonitrile solution on Pt disc [0.5 (home-made) or 1.6 (Bioanalytical System Inc.) mm diameter] working electrodes employing IR compensation. Ions were added to acetonitrile solutions as $LiPF_6$, $NaPF_6$, KPF_6 (Fluka), $Ba(ClO_4)_2$, $NaClO_4$ or $AgBF_4$ (Aldrich), and to aqueous solutions as perchlorate salts (Fluka, microselect). For the preparation of electrolyte solutions, Bu_4NPF_6, Bu_4NClO_4, Bu_4NBF_4 (Fluka, electrochemical grade), $HClO_4$ (Aldrich, ACS reagent), $NaClO_4$, $KClO_4$ (Aldrich), $LiClO_4$ (Fluka, electrochemical grade), dichloromethane and acetonitrile (Aldrich, HPLC grade) and ultrapure water were used. Differential pulse voltammetry (DPV) was performed using a BAS 50W electrochemical analyser with platinum disc (1.6 mm) working electrode at pulse amplitude 50 mV, sample width 20 ms, pulse width 50 ms, pulse period 200 ms, scan rate 20 mV s^{-1}.

Compound 6†

A mixture of thione **2**[12] (700 mg, 1 mmol) and thione **5**[5a] (420 mg, 1 mmol) was heated at 110 °C in freshly distilled trimethyl phosphite (3 cm^3) under nitrogen for 3 h. Upon cooling a solid precipitated, which was removed by filtration. The filtrate, which contained the desired product, **6**, was concentrated *in vacuo* and purified by column chromatography (silica gel, eluent chloroform) to give compound **6** as an orange solid (150 mg, 14%), mp 84–85 °C (Found: C, 60.13; H, 9.25. $C_{52}H_{94}O_4S_8$ requires C, 60.07; H, 9.11%); *m/z* (EI) 1038.5 (M^+); $\delta_H(CDCl_3)$ 3.75 (4 H, t, *J* 6.3), 3.70–3.67 (12 H, m), 3.04 (4 H, t, *J* 6.3), 2.82 (4 H, t, *J* 7.3), 1.6–1.5 (4 H, m), 1.5–1.1 (60 H, m) and 0.89 (6 H, t, *J* 6.5).‡

Compound 7

A solution of thione **5** (900 mg, 2.25 mmol) and oxone **4**[14] (526 mg, 2.25 mmol) in freshly distilled trimethyl phosphite (10 cm^3) was gradually heated from 80 °C to 110 °C under a nitrogen atmosphere for 3 h. The reaction mixture was allowed to reach room temperature and then trimethyl phosphite was removed by vacuum distillation. The resulting crude product was purified by column chromatography [silica gel, eluent CH_2Cl_2–AcOEt (2:1 v/v)]. The first fractions contained tetrakis(methoxycarbonyl)tetrathiafulvalene. The next fractions contained the desired unsymmetrical derivative **7** (674 mg, 52%), followed by bis(crowned) derivative **14**. If desired, compound **7** could be recrystallized from Et_2O–pentane to give a violet solid, mp 74–75 °C (Found: C, 41.12; H, 4.60. $C_{20}H_{26}O_8S_6$ requires C, 40.94; H, 4.47%); *m/z* 586 (M^+); $\delta_H(CDCl_3)$ 3.80 (6 H, s), 3.69 (4 H, t, *J* 5.9), 3.63 (12 H, s) and 2.98 (4 H, t, *J* 5.9).

Compound 8

To a solution of vinylene trithiocarbonate **3** (3.62 g, 27 mmol) and thione **5** (3.6 g, 9 mmol) in dry toluene (100 cm^3) was added octacarbonyldicobalt (6.14 g, 18 mmol) and the mixture was heated at reflux for 5 h. The solvent was evaporated and the residue was chromatographed on a silica column, initially with dichloromethane as eluent to remove tetrathiafulvalene **1** (*ca.* 1.0 g) then unreacted **3** (*ca.* 0.8 g). Changing the eluent to ethyl acetate gave compound **8** (370 mg, 9%) followed by unreacted compound **5** (270 mg). Compound **8**: orange crystals, mp 73 °C (from hexane) (Found: C, 40.75; H, 4.77. $C_{16}H_{22}O_4S_6$ requires C, 40.85; H, 4.68%); *m/z* 470 (M^+); $\delta_H(CDCl_3)$ 6.32 (2 H, s), 3.73 (4 H, t, *J* 6.5), 3.67 (8 H, s), 3.65 (4 H, s) and 3.02 (4 H, t, *J* 6.3).

Compound 9

(*a*) From 11. Selenium dioxide (32 mg, 0.28 mmol) was added to a solution of **11** (140 mg, 0.28 mmol) in dry dioxane (20 cm^3) and the mixture was heated under reflux for 4 h. After cooling to room temperature, the solvent was evaporated under vacuum and the resulting red oil was purified by column chromatography (silica gel, eluent CH_2Cl_2–AcOEt 8:1) affording **9** (60 mg, 43%) as a red solid, mp 92 °C (from hexane) (Found: C, 40.70; H, 4.57. $C_{17}H_{22}O_5S_6$ requires C, 40.96; H, 4.42%); *m/z* 498 (M^+); $\delta_H(CDCl_3)$ 9.49 (1 H, s), 7.45 (1 H, s), 3.74 (4 H, t, *J* 6.3), 3.68–3.66 (12 H, m), 3.04 (2 H, t, *J* 6.3) and 3.03 (2 H, t, *J* 6.3); $\delta_C(CDCl_3)$ 180.15, 139.91, 71.30, 71.26, 71.04, 70.17, 36.20 and 30.19.

(*b*) From Compound 8. To a stirred solution of compound **8** (126 mg, 0.26 mmol) in dry THF (20 cm^3) under nitrogen at −78 °C was added, sequentially, LDA (0.21 cm^3, 0.34 mmol) and *N*-methyl-*N*-phenylformamide (0.08 cm^3, 0.53 mmol) and stirring was continued at −78 °C for 2 h. The mixture was then stirred at room temperature overnight and water (100 cm^3) was added, followed by hydrochloric acid (2 M, 50 cm^3) which turned the mixture deep red. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (5 × 100 cm^3). The combined extracts were washed with water (2 × 100 cm^3), dried ($MgSO_4$) and then evaporated. The residue was chromatographed on a silica column, eluent ethyl acetate, to afford a red oil (65 mg) which was chromatographed a second time [silica column, eluent ethyl acetate–hexane (1:1 v/v)] to give pure compound **9** as a red solid (40 mg, 31% yield), identical with a sample prepared by method (*a*) above.

Compound 10

To a solution of compound **7** (410 mg, 0.7 mmol) in HMPA (20 cm^3), LiBr (0.7 g, 8 mmol) and a drop of water were added. The mixture was heated at 80 °C for 2 h, during which time gas evolution (CH_3Br) was observed. After cooling to room temperature, saturated aqueous sodium chloride was added, and the product was extracted with ethyl acetate. The organic layer was washed with water, dried ($MgSO_4$) and then concentrated under reduced pressure. The resulting reddish oil was purified by column chromatography [silica gel, eluent CH_2Cl_2–AcOEt (4:1 v/v)] giving **10** (309 mg, 83%) as an orange solid, mp 92–93 °C (from dichloromethane–hexane) (Found: C, 40.96; H, 4.42. $C_{18}H_{24}O_6S_6$ requires C, 40.89; H, 4.57%); *m/z* 528 (M^+); $\delta_H(CDCl_3)$ 7.33 (1 H, s), 3.79 (3 H, s), 3.71 (4 H, t, *J* 6.2), 3.67–3.63 (12 H, m), 3.01 (2 H, t, *J* 6.2) and 3.00 (2 H, t, *J* 6.2).

Compound 11

To a solution of **10** (486 mg, 0.92 mmol) in dry dichloromethane (20 cm^3), cooled at −80 °C and under a nitrogen atmosphere, DIBAL-H (1 M in CH_2Cl_2, 4.4 cm^3, 4.4 mmol) was added slowly. After 1.5 h, the mixture was hydrolised at −80 °C with a 1:1 mixture of aqueous HCl–MeOH (10 cm^3) and then was allowed to reach room temperature. Dichloromethane was added and the organic layer was washed with aqueous HCl (1 M, 50 cm^3), then with water, dried (Na_2SO_4), and concentrated under vacuum. The remaining oil was purified by column chromatography [silica gel, initial eluent dichloromethane–

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† IUPAC name for compound **6**: $1^{3',4'}$-bis(octadecylthio)-5,8,11,14-tetraoxa,$1^{2,2',5,5'}$,2,17-hexathia-1(3,4)-(bicyclopent-3-en-1-ylidena)cycloheptadecaphane. Compounds **7**–**13** can be named similarly.

‡ *J* values are given in Hz.

ethyl–acetate (1 : 1) then increasing the AcOEt content until only AcOEt was used] to give **11** (420 mg, 91%) as an orange oil; *m/z* 500 (M$^+$); δ_H(CDCl$_3$) 6.20 (1 H, s), 4.34 (2 H, s), 3.68 (4 H, t, *J* 6.2), 3.64–3.60 (12 H, m) and 2.99 (4 H, t, *J* 6.2).

Compound 12

Compound **10** (520 mg, 1 mmol) was dissolved in dioxane (25 cm^3) and sodium hydroxide (1 M, 5 cm^3) was added. The mixture was stirred at reflux for 2 h. The solvent was removed *in vacuo* and the orange residue was dissolved in water and washed with dichloromethane (2 × 2 cm^3). The aqueous layer was then acidified with HCl (1 M, 20 cm^3) extracted with dichloromethane (with addition of NaCl to assist the extraction). The organic layer was separated, dried (MgSO$_4$), and evaporated to give compound **12** as a red solid (385 mg, 75%), mp 149 °C (from dichloromethane–hexane) (Found: C, 39.6; H, 4.6. $C_{17}H_{22}O_6S_6$ requires C, 39.7; H, 4.3%); *m/z* 514 (M$^+$); δ_H([^{2}H$_6$]DMSO) 7.72 (1 H, s), 3.64 (4 H, t, *J* 6.2), 3.55–3.52 (12 H, m) and 3.04 (4 H, t, *J* 6.2); ν_{max}(KBr)/cm^{-1} 1667 (C=O).

Compound 13

To an ice–water cooled solution of **11** (188 mg, 0.37 mmol) in dry CH$_2$Cl$_2$ (20 cm^3) and under a nitrogen atmosphere, stearoyl chloride (170 mg, 0.56 mmol) and then triethylamine (75.7 mg, 0.75 mmol) were added dropwise. The mixture was stirred at room temperature for 6 h and then the solvent was evaporated under vacuum. The crude product was purified by column chromatography [silica gel, eluent CH$_2$Cl$_2$–AcOEt (4:1 v/v)] giving **13** (85 mg, 30%) as a yellow solid, mp 74 °C (from ethanol) (determined by DSC) (Found C, 54.52; H, 7.84. $C_{35}H_{58}O_6S_6$ requires C, 54.79; H, 7.62%); *m/z* 766 (M$^+$); δ_H(CDCl$_3$) 6.30 (1 H, s), 4.78 (2 H, s), 3.71 (4 H, t, *J* 6.2), 3.66–3.61 (12 H, m), 2.99 (4 H, t, *J* 6.2), 2.31 (2 H, t, *J* 7.4), 1.60 (2 H, t, *J* 7.4), 1.22 (28 H, s) and 0.85 (3 H, t, *J* 6.3).

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