# Remarkably stable self-assembled monolayers of new crown-ether annelated tetrathiafulvalene derivatives and their cation recognition properties†

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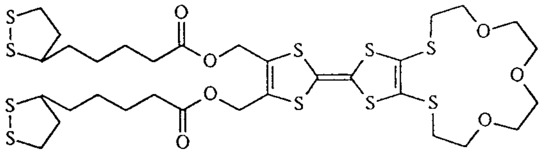
**Bis-thioctic ester derivatives of crown-ether annelated tetrathiafulvalenes (TTFs) form extremely stable self-assembled monolayers (SAMs) on gold electrodes and can recognize alkali metal ions by cyclic voltammetry.**

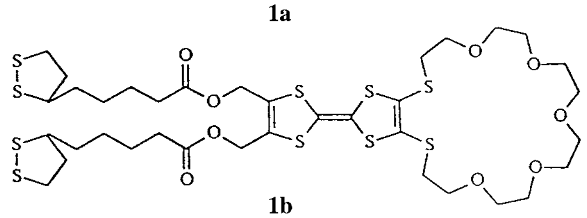
The first TTF-functionalized SAMs, reported by Yip and Ward, were relatively unstable upon electrochemical probing and cycling.[1] Very recently a novel TTF compound containing four thiol groups was reported, which formed very robust SAMs on gold, and these were stable after repeated voltammetric cycling.[2] The use of such multiple anchoring sites provides very strong adherence of the compound to the metal surfaces, especially if the sulfur atoms are present within the same ring structure, in which case they exhibit a chelate effect.[3] For these reasons, the use of thioctic acid derivatives to anchor SAMs on metal surfaces has received considerable recent attention.[4] In addition, thioctic acid (1,2-dithiolane-3-valeric acid) is commercially available and easy to incorporate into a wide variety of structures *via* simple condensation reactions, as reported in the present work.

The incorporation of crown-ether groups into SAMs and their use as potential metal ion sensors were first reported almost simultaneously last year by Moore *et al.*[5] and by Flink *et al.*[6] In one case they prepared simple 12-crown-4 and 15-crown-5 derivatives with appended single chains terminated in a thiol group, and impedance spectroscopy was used to monitor ion binding events on the surface.[6] The other group reported crown-annelated TTF derivatives which also contained single alkyl chains terminated in thiol groups.[5] This work exploited the direct electrochemical response of the surface-confined crown-TTF groups to measure the effect of ion complexation, similar to previously reported work in homogeneous solution by Hansen *et al.*[7] However, these SAMs were apparently not very stable under various conditions and the electrochemical responses observed were very weak and poorly resolved.[5] Here we report the preparation of two bis-thioctic ester derivatives of crown-annelated TTFs, which form remarkably stable SAMs on gold and show very clear and reversible surface-confined electrochemistry and anodic shifts upon binding with alkali metal ions.

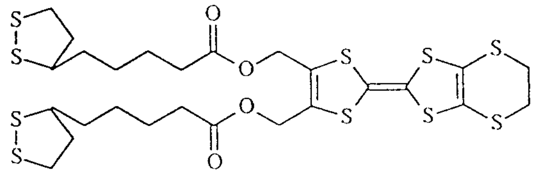
Compounds **1a**–**c** were directly synthesized in high yield by reacting the corresponding bis-alcohols with thioctic acid in $CH_2Cl_2$ in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and 4-pyrrolidinopyridine or 4-(dimethylamino)pyridine (DMAP).[8] The corresponding crown-annelated TTF bis-alcohol precursors were prepared in reasonable yields following literature procedures.[9] The mono-alcohol precursor to prepare **1d** was obtained by reducing one of the ester groups of diester-EDT-TTF.[9b,10] It should be stressed that the synthetic method reported here to prepare crown-ether annelated tetrathiafulvalene derivatives with disulfide groups attached by reacting thioctic acid with derivatives of TTF incorporating hydroxy group(s) is general, straightforward and gives high yields.



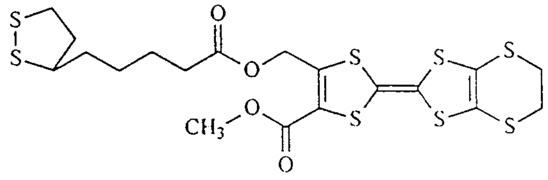
**1a**



**1b**



**1c**



**1d**

Glass-sealed, ultra-clean spherical gold bead electrodes prepared from gold wire (99.9999%, diameter 250 μm) were dipped into 5 mM THF solutions of the corresponding bis-thioctic ester compounds **1a**–**d** for 24 h to form the corresponding SAMs.[11] After washing these with clean THF and allowing them to dry in air, these SAM modified electrodes were placed into 0.1 M $Bu_4NPF_6$–THF (or 0.1 M $Bu_4NPF_6$–$CH_2Cl_2$) and their cyclic voltammograms (CVs) recorded.[12] Fig. 1 shows the

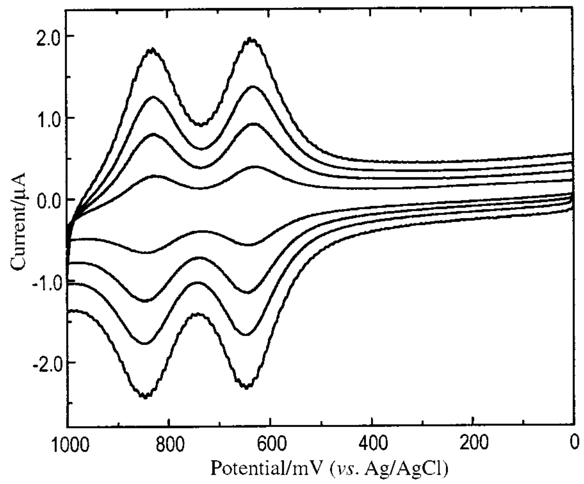


**Fig. 1** Cyclic voltammetric analysis of the SAMs of **1a** in THF solution containing 0.1 M $Bu_4NPF_6$ at different scan rates: 100 (smallest current), 250, 400 and 600 mV $s^{-1}$ (largest current).

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† Data for compounds **1b**–**d** are available from the RSC web site, see http://www.rsc.org/suppdata/cc/1999/1493/

**Table 1** Electrochemical data for the SAMs of the disulfides in THF solution containing 0.1 M $Bu_4NPF_6$ *vs.* an aqueous Ag/AgCl reference electrode

| SAMs of compound | $E_{1/2}{}^1$/V ($\Delta E_p$/mV) | $E_{1/2}{}^2$/V ($\Delta E_p$/mV) | Coverage[a] |
|---|---|---|---|
| **1a** | 0.64 (12) | 0.85 (5) | 1.15 |
| **1b** | 0.62 (20) | 0.80 (15) | 0.33 |
| **1c** | 0.65 (25) | 0.90 (15) | 1.58 |
| **1d** | 0.73 (58) | 0.96 (70) | 2.21 |

[a] In units of $10^{-10}$ mol $cm^{-2}$.

variable scan rate dependence of the CVs for SAMs of **1a** on gold in a THF-electrolyte solution. Both TTF-based oxidations are clearly observed and reversible, and their currents increase linearly with the scan rate, indicative of surface-confined behavior (Fig. 1).

This behavior is also evident from the Gaussian shapes of the peaks and the small potential difference between the anodic and cathodic peaks, 12 mV for the first oxidation at $E_{1/2}$ = +0.64 V (*vs.* an aqueous Ag/AgCl reference electrode and at $v$ = 100 mV $s^{-1}$) and 5 mV for the second oxidation at $E_{1/2}$ = +0.85 V, see Table 1. Essentially identical behavior was observed for **1b**, **1c** and **1d**, but the SAMs of **1d** were much more unstable upon repeated potential cycling, with an 80% decrease in current after four cycles between 0 and +1.1 V. The potentials for the TTF-based oxidations are summarized in Table 1.

The SAMs derived from compounds **1a**, **1b** and **1c** were remarkably stable, exhibiting almost the same current response even after more than 100 potential scan cycles. Perhaps more impressively, these SAMs retained their stability over the course of several days, apparently indefinitely. In our hands, these are the most stable SAMs with which we have ever worked.

The effect of adding alkali metal ions to the THF solutions (typically 5 mM of $MPF_6$, with M = $Li^+$, $Na^+$ or $K^+$) varied for the different compound–$M^+$ combinations. The largest anodic shift was observed for **1b**–$Na^+$, and these cyclic voltammetric results are presented in Fig. 2.

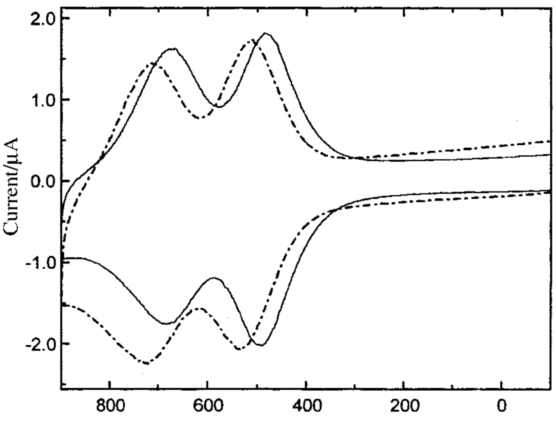

**Fig. 2** Cyclic voltammetry of the SAMs of **1b** in THF solution containing 0.1 M $Bu_4NPF_6$ in the absence (solid line) and in the presence (dotted line) of 5.0 mM $NaPF_6$ at a scan rate of 400 mV $s^{-1}$. A non-aqueous Ag/AgCl containing 0.1 M $Bu_4NPF_6$ in THF was used as a reference electrode. Thus the potential axis is different from that in Fig. 1.

The first oxidation process was anodically shifted by 60 mV in this case, while the second oxidation was also shifted anodically, by 55 mV. This behavior is somewhat in contrast to that previously reported for crown-annelated TTF compounds in homogeneous solution, for which the first oxidation is shifted anodically, but the second remains unchanged, presumably due to electrostatically-induced decomplexation of $M^+$ following the first oxidation to form $TTF^+$–crown.[7] Either surface aggregation or cooperativity effects between neighboring crown rings on the SAMs could account for the different behavior observed here. The effects of the alkali metal ions tested on the CVs of **1a** and **1b** are summarized in Table 2.

**Table 2** Shifts (mV) of redox potentials of the SAMs of **1a** and **1b** upon addition of alkali metal ion salts

| Metal ion salt (5.0 mM) | SAMs of **1a** $E_{1/2}{}^1$ | SAMs of **1a** $E_{1/2}{}^2$ | SAMs of **1b** $E_{1/2}{}^1$ | SAMs of **1b** $E_{1/2}{}^2$ |
|---|---|---|---|---|
| $LiPF_6$ | 0 | 0 | 0 | 0 |
| $NaPF_6$ | +10 | 0 | +60 | +55 |
| $KPF_6$ | 0 | 0 | +20 | +30 |

Note that $Li^+$ showed no effect on either of the crown compounds, while $Na^+$ showed the largest effect with both SAMs. $K^+$ induced a smaller anodic shift than $Na^+$, and only with **1b**. As expected, **1c** did not exhibit any cation-induced effects, since there is no crown ether ring present in the structure. All of these results indicate that the cation-induced shifts result from complexation between the crown rings and the metal ions.

In summary, electrochemically active SAMs have been prepared which are almost indefinitely stable and show promise as potential thin-film sensors for electrochemically inactive metal ions. Further work is underway to improve the selectivity properties of these SAMs.

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## Notes and references

1 C. M. Yip and M. D. Ward, *Langmuir*, 1994, **10**, 549.

2 I. Fujihara, H. Nakai, M. Yoshihara and T. Maeshima, *Chem. Commun.*, 1999, 737.

3 Y.-S. Shon and T. R. Lee, *Langmuir*, 1999, **15**, 1136.

4 (*a*) Q. Cheng and A. Brajter-Toth, *Anal. Chem.*, 1992, **64**, 1998; (*b*) Y. Wang and A. E. Kaifer, *J. Phys. Chem. B*, 1998, 9922; (*c*) R. Blonder, I. Willner and A. F. Buckmann, *J. Am. Chem. Soc.*, 1998, **120**, 9335.

5 A. J. Moore, L. Goldenberg, M. R. Bryce, M. C. Petty, A. P. Monkman and S. N. Port, *Adv. Mater.*, 1998, **10**, 395.

6 S. Flink, B. A. Boukamp, A. v. d. Berg, F. C. J. M. van Veggel and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1998, **120**, 4652.

7 T. K. Hansen, T. Jorgensen, P. C. Stein and J. Becher, *J. Org. Chem.*, 1992, **57**, 6403.

8 All new compounds were fully characterized by spectroscopic techniques. *Selected data* for **1a**: isolated as a red–orange solid in 87% yield, $\nu$ (KBr)/$cm^{-1}$ 2932 (s), 1710 (vs), 1630 (vs), 1542 (s), 1163 (s); $\delta_H$($CDCl_3$/TMS) 4.91 (4H, s), 3.91 (4H, t, *J* 5.34), 3.74–3.67 (12H, m), 3.58 (4H, t, *J* 5.40), 3.19–3.14 (4H, m), 2.99 (2H, t, *J* 5.90), 2.45–2.37 (4H, m), 1.94–1.85 (2H, m), 1.79–1.63 (8H, m), 1.49–1.46 (4H, m); $\delta_C$($CDCl_3$) 173.70, 173.17, 154.47, 142.04, 129.92, 128.82, 111.84, 108.38, 71.98, 71.51, 70.38, 60.38, 58.37, 56.36, 40.62, 38.95, 37.05, 36.19, 34.17, 26.72, 25.07; $\lambda_{max}$($CHCl_3$)/nm 327.5, 304.0; $FAB^+$-MS: *m/z* 862 ($M^+$, 60%), 864 ($M^+$ + 2, 100%); HRMS ($FAB^+$): *m/z* found 862.0453, calc. for $C_{32}H_{46}O_7S_{10}$: 862.0453. For data for **1b**–**d**, see footnote †.

9 (*a*) Detailed synthesis will be published elsehwere; (*b*) S. G. Liu, M. Cariou and A. Gorgues, *Tetrahedron Lett.*, 1998, **39**, 8663.

10 P. Blanchard, M. Sallé, G. Duguay, M. Jubault and A. Gorgues, *Tetrahedron Lett.*, 1992, **33**, 2685.

11 F. Arias, L. A. Godínez, A. E. Kaifer and L. Echegoyen, *J. Am. Chem. Soc.*, 1996, **118**, 6086.

12 All electrochemical experiments were performed using a BAS-100W system. Electrolyte solutions were prepared from recrystallized materials using spectroscopic grade solvents and purged with argon prior to use. A three-electrode configuration was used with a Ag/AgCl reference electrode and a platinum wire as the counter electrode. The geometric areas of the gold electrodes were calculated from the slopes of the linear plots of cathodic peak current *vs.* the square root of the scan rate obtained for the diffusion-controlled reduction of $Ru(NH_3)_6{}^{3+}$ [ref. 4(*b*)]. We employed a diffusion coefficient of $7.5 \times 10^{-6}$ $cm^2$ $s^{-1}$ (at 25 °C in 0.1 M NaCl). Typical values for the geometric area of the electrodes varied from 0.01 to 0.02 $cm^2$. Surface coverages of the SAMs of TTF derivatives were calculated by integration of the current during the first scan.

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