Pergamon

Tetrahedron Letters 41 (2000) 8163–8166

TETRAHEDRON
LETTERS

The reversible complexation of a tetrathiafulavene functionalised self-assembled monolayer by cyclobis(paraquat-*p*-phenylene)

Graeme Cooke,[a,]* Florence M. A. Duclairoir,[a] Vincent M. Rotello[b] and J. Fraser Stoddart[c]

[a]*Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, UK*
[b]*Department of Chemistry, University of Massachusetts at Amherst, Amherst, MA 01002, USA*
[c]*Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, CA 90095, USA*

Received 10 July 2000; revised 16 August 2000; accepted 23 August 2000

Abstract

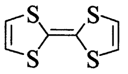
The first example of redox controlled host–guest complexation of a tetrathiafulvalene functionalised self-assembled monolayer with the electron deficient tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene) is reported. © 2000 Elsevier Science Ltd. All rights reserved.

The study of electro-active self-assembled monolayers (SAM's) which have the propensity of both controlling and signalling the specific molecular recognition of a guest is a burgeoning field of study.[1] In particular, the development of systems utilising the tetrathiafulvalene (TTF, **1**) unit are especially promising due to the ability of this system to exist[2] in three stable oxidation states (TTF^0, $TTF^{+\bullet}$ and TTF^{2+}). However, all of the systems reported to date have involved the use of crown ether functionalised derivatives and the study of their subsequent metal cation recognition properties. Remarkably, the recognition properties of immobilised TTF units for charged and neutral organic molecules have not been reported. In recent solution-phase studies, it was shown that the TTF^0 redox state has the ability to form charge-transfer complexes with the electron deficient tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene) **2**.[3] Furthermore, upon electrochemical oxidation of the TTF unit to its electron deficient states, a rapid and reversible decomplexation occurs. In the present work, we show for the first time using cyclic voltammetry (CV) that the reversible host–guest complexation can also occur at a solid/liquid interface of a SAM between an immobilised TTF disulfide **3** and the tetracationic cyclophane **2**.

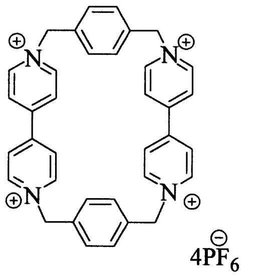
---

* Corresponding author. Fax: 0131 451 3180; e-mail: G.Cooke@hw.ac.uk

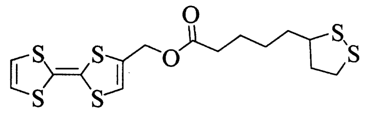
PII: S0040-4039(00)01424-6



1



2



3

TTF disulfide **3** was synthesised in high yield from 4-hydroxymethyl-TTF[4] and thioctic acid using DCC/DMAP-catalysed esterification procedures.[5] The solution electrochemistry of this system gave rise to two reversible oxidations at $E_{1/2}{}^{1} = +0.40$ V and $E_{1/2}{}^{2} = +0.76$ V corresponding to the formation of $\mathbf{3}^{+\bullet}$ and $\mathbf{3}^{2+}$, respectively (Fig. 1(a)).[6] Upon the addition of a 10-fold excess of **2** to the CV cell, the oxidation giving rise to the $\mathbf{3}^{+\bullet}$ species is immediately displaced by 19 mV to a more positive potential, whilst the oxidation due to the formation of **3**(++) is unaffected (Fig. 1(b)). Although this shift is somewhat smaller than that reported for [**1**·**2**], the shift is considerably greater than shifts attributed to experimental error commonly associated with CV measurements (±3 mV).[3c] The complexation behaviour is consistent with previously reported CV data for [**1**·**2**] and suggests that [**2**·**3**] reversibly decomplexes when the **3**(0) guest experiences its first electrochemical oxidation.[3c] Solution-phase complexation between **2** and **3** was further confirmed by UV-vis and ^{1}H NMR spectroscopic studies.[3] Mixing **2** and **3** in equimolar proportions in MeCN resulted in an immediate formation of an emerald green-coloured solution as a result of the appearance of a charge-transfer absorption band centred at 843 nm. The ^{1}H NMR spectrum of the green-coloured complex [**2**·**3**] shows small, but significant, changes in chemical shifts relative to those of non-complexed **2** and **3** (Table 1). The changes in chemical shifts of ^{1}H NMR signals for the bipyridinium unit of [**2**·**3**] are remarkably similar to that obtained for [**1**·**2**]; however, the changes in the chemical shift for the TTF protons of the former are less pronounced.[3c]

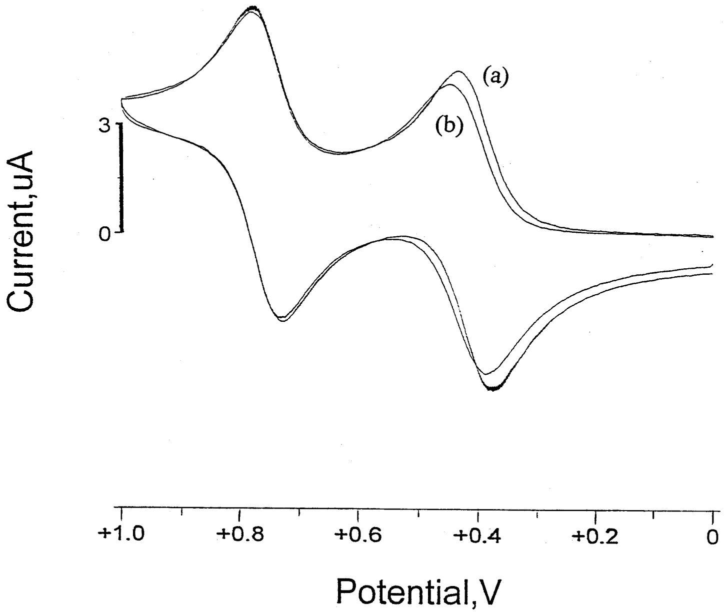


Figure 1. Cyclic voltammograms (MeCN, 0.1 M Bu_4NClO_4, 298 K, scan rate 100 mV s^{-1}) of compound **3** (a) and in the presence of **2** (b)

Table 1
The ^{1}H NMR chemical shift data (δ and $\Delta\delta$) for **2**, **3** and [**2**·**3**] in CD_3CN at ambient temperatures

Compound or complex	α-Bipy-CH	β-Bipy-CH	C_6H_4	$^+NCH_2$	TTF[a]	TTF[b]
2	8.86	8.16	7.52	5.74		
3					6.52	6.47
[**2**·**3**]	8.94	7.92	7.68	5.73	6.43	6.37
$\Delta\delta$	(+0.08)	(−0.24)	(+0.16)	(−0.01)	(−0.09)	(−0.10)

[a] Refers to the proton attached to the functionalised 1,3-dithiole ring.

[b] Refers to the protons on the non-functionalised 1,3-dithiole ring. α and β are with respect to N in the cyclophane.

With solution complexation between **2** and **3** unequivocally verified, we turned our attention to complexation at a solid/liquid interface of a SAM. Mixed monolayers were fabricated by immersing a gold wire (99.9999%, length 50 mm, diameter 0.25 mm) into an equimolar mixture of **3** (5 mmol) and 1-butanethiol (5 mmol) in MeCN for 12 hours. After washing the electrode with THF and MeCN and allowing it to dry in air, the SAM modified electrode was placed into a solution of 0.1 M Bu_4NClO_4–MeCN and their CV's were recorded (Fig. 2(a)). In accordance with previously reported work using a thioctic acid anchoring unit, the resultant SAM's were remarkably stable to repeated electrochemical oxidation/reduction cycles.[2d] Indeed, repeated electrochemical cycling of several days resulted in negligible change in peak currents. The CV's following the addition of an excess of **2** to the CV cell directly mirrored the solution-phase studies, as the first oxidation process was immediately anodically shifted by 19 mV, whilst the second oxidation process remained unaffected (Fig. 2(a)). The displacement of the first oxidation process of immobilised **3** is consistent with donor–acceptor interactions occurring between this

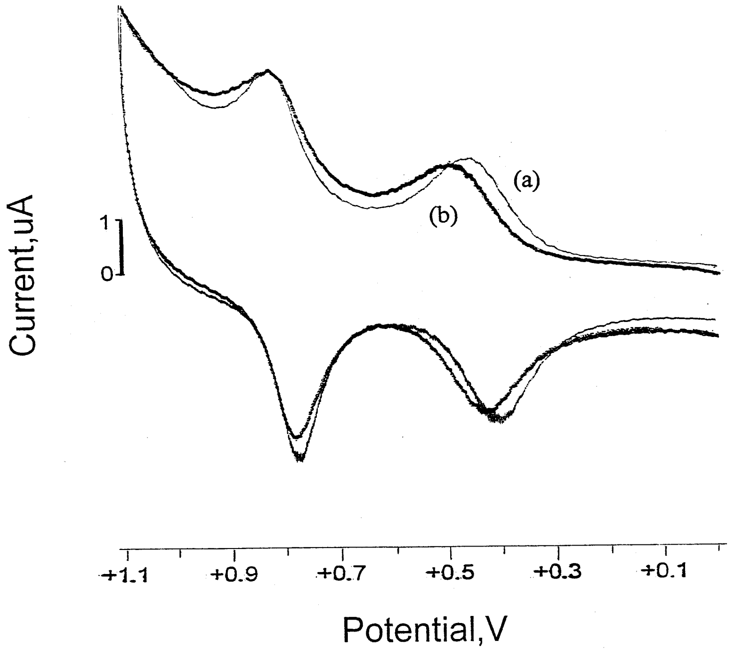


Figure 2. Cyclic voltammograms (MeCN, 0.1 M Bu_4NClO_4, 298 K, scan rate 500 mV s^{-1}) of SAM's of **3** (a) and in the presence of **2** (b)

unit and **2**. This result mirrors the solution-phase studies and shows that one-electron oxidation causes very fast (compared with the scan rate used, 100–1000 mV s^{-1}) reversible dethreading of the complex, and successive one-electron reduction causes a very fast re-formation.[7] The remarkably similar changes in the electrochemical properties of SAM's of **3**, following complexation with **2**, clearly illustrates that electrochemically controlled host–guest complexation, which we have confirmed in solution for **2** and **3**, can also be observed in the solid/liquid interface of a SAM.

In summary, we have shown that we can exploit the multi-stage redox properties of SAM's of **3** to produce electrochemically controlled host–guest complexes with the tetracationic cyclophane **2**. Further work is underway in our group to maximise the interaction between the immobilised TTF unit and **2**, and exploit the tuneability of TTF moieties oxidation potentials to create addressable SAM's.

Acknowledgements

G.C. gratefully acknowledges the EPSRC and the Royal Society of Chemistry for supporting this work. We thank Dr. Gunter Mattersteig for providing a sample of **2**.

References

1. Goldenberg, L. M.; Bryce, M. R.; Petty, M. C. *J. Mater. Chem.* **1999**, *9*, 1957.
2. (a) Hansen, T. K.; Jorgensen, T.; Stein, P. C.; Becher, J. *J. Org. Chem.* **1992**, *57*, 6403; (b) Yip, C.; Ward, M. D. *Langmuir* **1994**, *10*, 549; (c) Moore, A. J.; Goldenberg, L. M.; Bryce, M. R.; Petty, M. C.; Monkman, A. P.; Morenco, C.; Yarwood, J.; Joyce, M. J.; Port, S. N. *Adv. Mater.* **1998**, *10*, 395. (d) Liu, H.; Liu, S.; Echegoyen, L. *Chem. Commun.* **1999**, 1493. (e) Fibbioli, M.; Bandyopadhyay, K.; Liu, S.-G.; Echegoyen, L.; Enger, O.; Diederich, F.; Buhlmann, P.; Pretsch, E. *Chem. Commun.* **2000**, 339. (f) Liu, S.-G.; Liu, H.; Bandyopadhyay, K.; Gao, Z.; Echegoyen, L. *J. Org. Chem.* **2000**, *65*, 3292.
3. (a) Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Chem. Commun.* **1991**, 1584; (b) Devonport, W.; Blower, M. A.; Bryce, M. R.; Goldenberg, L. M. *J. Org. Chem.* **1997**, *62*, 885. (c). Ashton, P. R; Balzani, V.; Becher, J.; Credi, A.; Fyfe, M. C. T.; Mattersteig, G.; Menzer, S.; Nielsen, M. B.; Raymo, F. M.; Stoddard, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 3951.
4. Garin, J.; Orduna, J.; Uruiel, S.; Moore, A. J.; Bryce, M. R.; Wegner, S.; Yufit, D. S.; Howard, J. A. K. *Synthesis* **1994**, 489.
5. *Selected data* for **3**: isolated as a yellow wax in 86% yield. δ_H (CD_3CN/TMS) 6.51 (s, 1H), 6.47 (s, 2H), 4.83 (s, 2H), 3.56 (m, 1H), 3.16 (m, 2H), 2.42 (m, 1H), 2.35 (t, 2H), 1.94 (m, 1H), 1.63 (m, 4H), 1.46 (m, 2H); MS (EI) $m/z=422$; exact mass calc. for $C_{15}H_{18}S_6O_2$: 421.9631. Found: 421.9627.
6. All electrochemical experiments were performed using a BAS-100W system. Electrolyte solutions were prepared from recrystallised Bu_4NClO_4 using spectroscopic grade MeCN and purged with nitrogen prior to use. A three electrode configuration was used with an Ag/AgCl reference electrode and a platinum wire as the counter electrode.
7. Asakawa, M.; Ashton, P. R.; Balzani, V.; Credi, A.; Mattersteig, G.; Matthews, O. A.; Montalti, M.; Spencer, N.; Stoddart, J. F.; Venturi, M. *Chem. Eur. J.* **1997**, *3*, 1992.