New Crown Annelated Tetrathiafulvalenes: Synthesis, Electrochemistry, Self-Assembly of Thiol Derivatives, and Metal Cation Recognition

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The synthesis of new S_2O_4-crown annelated tetrathiafulvalene (TTF) derivatives substituted with one terminal thiol group is described. Self-assembled monolayers (SAMs) of these compounds have been assembled on gold and platinum surfaces, the latter substrate giving improved quality films. SAMs of TTF derivative **16b** are the most stable of those we have studied. Electrochemical data for SAMs of **5a**, **5b**, **8**, **16a**, and **16b** in acetonitrile reveal two reversible one-electron waves, typical of the TTF system; the current increased linearly with scan rate, indicating a surface wave response. SAMs of **8**, **16a**, and **16b** exhibited an electrochemical response in aqueous electrolytes, which was observed between 50 and 100 cycles. Moreover, if the potential scanned was limited to the first TTF oxidation, *the cyclic voltammetry response was observed for at least 1000 cycles*. Metal complexation by the crown ionophore of the SAMs in acetonitrile has been monitored by a positive shift in the first oxidation potential of the TTF unit (maximum $\Delta E_1^{1/2} = 80$ mV for Ag^+). We also report the X-ray crystal structure of TTF−crown derivative **21** bearing two hydroxymethyl substituents, synthesized during the course of this work. The structure is characterized by infinite chains of molecules linked by strong intrachain hydrogen bonds between the terminal hydroxy groups.

Introduction

Self-assembled monolayers (SAMs) of organic compounds provide chemically tailored substrate surfaces which have technological applications as sensors, devices, and switches.[1] There is current interest in the study of molecular recognition processes within SAM nanostructures.[2] Examples have been reported recently in which specific interactions of a guest analyte with a host SAM are transduced to a signaling unit which responds by undergoing a change in its electronic state, which is measured by spectroscopic, structural, or electrochemical techniques.[3]

It is well documented that crown annelated tetrathiafulvalene (TTF) derivatives function as metal cation sensors in organic media.[4] The presence of a bound metal cation imposes an inductive effect on the polarizable TTF system, resulting in a positive shift of the first oxidation potential as indicated by cyclic voltammetry (CV) experiments; the second oxidation potential is usually unchanged or shifts (also positively) only very slightly. Recent data imply that complete expulsion of the metal does not occur until the dication stage.[4e] Near planarity of the TTF system is a prerequisite for reversible redox behavior.[4a,d,e] Yip and Ward first reported that redox-active SAMs of TTF derivative **1** could be obtained on gold electrodes.[5] Subsequently, new TTF SAMs with increased stability have been described.[6] We now report the synthesis, electrochemistry, SAM formation, and metal cation recognition in a series of functionalized TTF−S_2O_4 crowns. Following our initial communication,[7] Echegoyen et al. described a different series of TTF−

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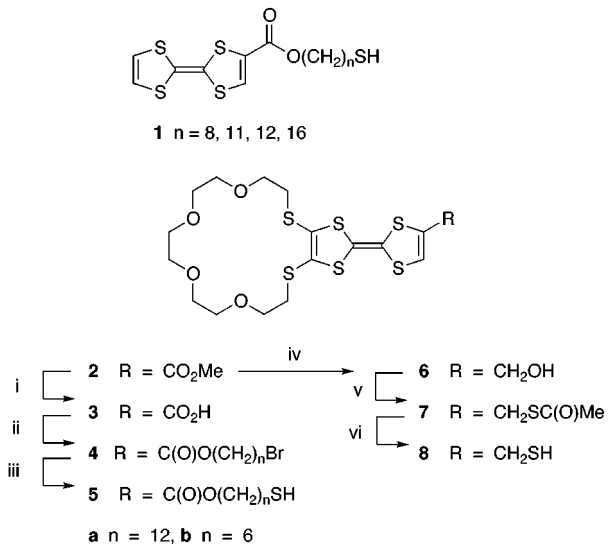
Scheme 1[a]



[a] Reagents and Conditions: (i) 1 M NaOH (aq), dioxane, reflux; then 1 M HCl (aq) (ref 4c); (ii) $Br(CH_2)_nOH$ (n = 12 or 6), DCC, DMAP, CH_2Cl_2, 20 °C; (iii) thiourea, EtOH, reflux; then 1 M KOH (aq); (iv) DIBAL-H, CH_2Cl_2, −80 °C; then HCl−MeOH (ref 4c); (v) DIAD, Ph_3P, THF, 20 °C; then compound **6**, THF, 20 °C; then MeC(O)SH, 20 °C; (vi) $LiAlH_4$, Et_2O, 20 °C; then aqueous hydrolysis.

crown SAMs and their alkali metal cation binding properties.[8]

Results and Discussion

Synthesis. The synthetic strategy described by Yip and Ward for the preparation of **1**[5] was adapted for compounds **5a** and **5b** as shown in Scheme 1. The key starting reagent is compound **2**,[4c] which was converted into the carboxylic acid derivative **3** (75% yield) as reported previously.[4c] Treatment of **3** with either 12-bromo-1-dodecanol or 6-bromo-1-hexanol in the presence of dicyclohexylcarbodiimide and *N*,*N*-(dimethylamino)-pyridine afforded bromoester derivatives **4a** and **4b** (75 and 85% yields, respectively). Subsequent conversion of the terminal bromide into a thiol group was achieved by treatment with thiourea followed by basic hydrolysis of the intermediate isothiouronium salt to afford the target derivatives **5a** and **5b** (42 and 33% yields, respectively). In both cases, this last step gave a complex reaction mixture containing unidentified byproducts; consequently, the purified yields for compounds **5a** and **5b** were significantly reduced as a result of repeated chromatography. The overall yields compare favorably with those reported by Yip and Ward for **1**.[5]

We considered the possibility that the ester linkage was contributing to the electrochemical inactivity of SAMs of compounds **5** in aqueous media (see below). Therefore, analogues without this linkage were synthesized as follows. The TTF−crown methanol derivative **6** (obtained by reduction of **2**, as described previously)[4c] was converted into thiol analogue **8**, using Volante's modification[9] of the Mitsunobu reaction.[10] Treatment of compound **6** with the diisopropylazodicarboxylate (DIAD)/triphenylphosphine complex in tetrahydrofuran and subsequent in situ displacement of the resulting leaving group with thioacetic acid cleanly afforded compound **7**. The thiol **8** was then obtained by reduction of **7** using lithium aluminum hydride in diethyl ether (70% overall yield for the two steps). During the course of this work, analogous methodology was utilized for the preparation of bis(sulfanylmethyl)TTF derivatives.[11] The instability of TTF−CH_2X systems (X = anionic leaving group, e.g., Br, tosyl)[12] precluded their use as intermediates in the synthesis of **8** from **6**.

We have also synthesized compounds **16a** and **16b** which possess two alkylsulfanyl chains appended to the TTF−crown, one of which is terminally substituted with a thiol group for self-assembly (Scheme 2). We considered that the steric bulk of the additional alkylsulfanyl chain should facilitate a more ordered monolayer packing within a SAM. Deprotection of the thiolate group in compounds **9a**[13] and **9b** with cesium hydroxide followed by in situ trapping with 6-bromohexan-1-ol afforded compounds **10a** and **10b** (90 and 82% yields, respectively). Reaction with *tert*-butyldiphenylsilyl chloride in the presence of imidazole in *N*,*N*-dimethylformamide afforded compounds **11a** and **11b** (96 and 89% yields, respectively). (This protection reaction was necessary as alcohol functionality is generally incompatible with the trialkyl phosphite-mediated cross-coupling reaction,[14] although there are exceptions.[15]) Reaction of compounds **11a** and **11b** with compound **12**[4a] in the presence of triethyl phosphite afforded TTF derivatives **13a** and **13b** (35 and 31% yields, respectively, after chromatographic separation from symmetrically coupled products). Deprotection of **13a** and **13b** with tetrabutylammonium fluoride gave alcohols **14a** and **14b** (95 and 76% yields, respectively). The two-step Mitsunobu protocol, as described for **5** and **8**, afforded compounds **16a** and **16b** as air-stable orange oils (63 and 65% yields, respectively, for the two-step reaction).

In light of the improved electrochemical response of SAMs of **16** compared to **5** and **8** (see below), we sought to attach two thiol-terminated chains to the TTF−crown framework, following the methodology for the monothiols above. The hydrolysis of diester **17**[4c] occurred readily under basic conditions (aqueous 1 M sodium hydroxide in refluxing dioxane) to afford diacid **18** (88% yield) which was insoluble in many organic solvents. Esterification of **18** with 2-bromohexanol in the presence of DCC and DMAP in refluxing dichloromethane using ultrasound afforded cleanly diester **19** (75% yield). However, all attempts to convert **19** into **20** under the conditions used for the preparation of **5** were unsuccessful (mass spec-

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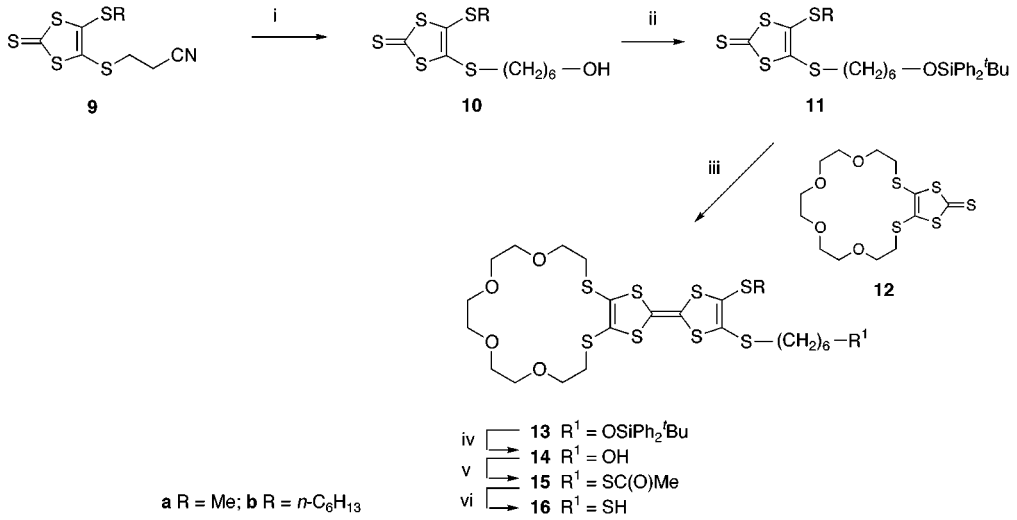
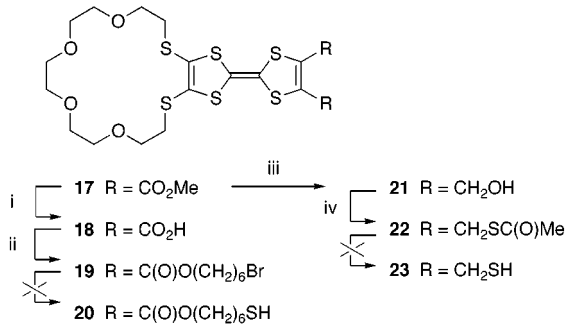
Scheme 2[a]



[a] Reagents and Conditions: (i) $CsOH{\cdot}H_2O$, MeOH, 20 °C; then $Br(CH_2)_6OH$, 20 °C; (ii) *t*-$BuPh_2SiCl$, imidazole, DMF, 20 °C; (iii) **12**, $P(OEt)_3$, 130 °C; (iv) TBAF, THF, 20 °C; (v) DIAD, Ph_3P, THF, 20 °C; then MeC(O)SH, 20 °C; (vii) $LiAlH_4$, Et_2O, 20 °C; then aqueous hydrolysis.

Scheme 3[a]



[a] Reagents and Conditions: (i) 1 M NaOH (aq), dioxane, reflux; then 1 M HCl (aq); (ii) $Br(CH_2)_6OH$, DCC, DMAP, CH_2Cl_2, reflux; (iii) $NaBH_4$, $ZnCl_2$, THF, reflux; then aqueous hydrolysis; (iv) DIAD, Ph_3P, THF, 20 °C; then **21**; then MeC(O)SH, 20 °C.

trometric and ^1H NMR evidence). Reduction of **17** using sodium borohydride/zinc chloride[16] in refluxing tetrahydrofuran gave **21** as a highly crystalline solid (55% yield). (In accord with the literature precedent,[16] attempted reductions of **17** with lithium aluminum hydride and diisobutyl aluminum hydride yielded complex reaction mixtures.) Compound **21** was converted into **22**, but all attempts to prepare dithiol derivative **23** (by analogy with the conversion of **7** into **8**) were unsuccessful; **22** was recovered unchanged.

X-ray Crystal Structure of 21. In view of the current interest in crystal structures of TTF crowns[4d,e] and in hydrogen-bonded networks in TTF derivatives,[17] we studied the crystal structure of **21** (Figure 1) which combines both these structural features. The TTF moiety is nearly planar, folding by 7° along the S(2)···S(3) vector. One of the hydroxymethyl groups is rotationally disordered between two orientations (in a 3:1 ratio), participating in different hydrogen bonds. The macrocycle adopts a crown conformation, favorable for metal coordination.[18] All four oxygen atoms and S(6) lie within ±0.25 Å from their mean plane (inclined by 43° to the TTF plane), with lone electron pairs pointing into the transannular cavity; S(5) lies 1.2 Å away from this plane. The molecules are linked by hydrogen bonds into an infinite double ribbon, parallel to the *x* axis of the crystal. The ribbons pack in a herringbone motif, so that the TTF planes in adjacent ribbons form a dihedral angle of 86°.

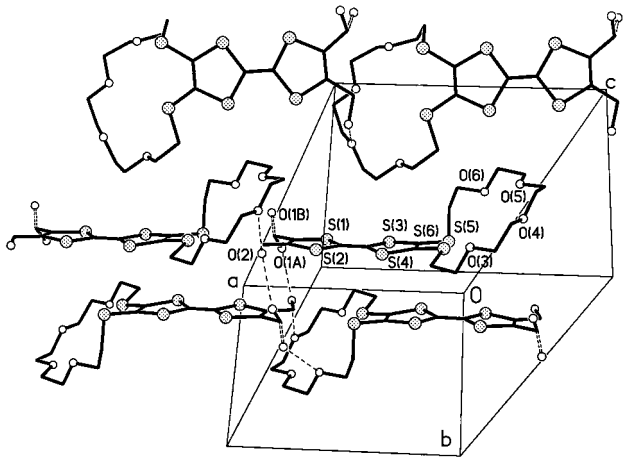


Figure 1. Crystal structure of **21** (H atoms are omitted for clarity), showing the disorder and hydrogen bonds (dashed lines).

Film Assembly. Monolayers of compounds **5a**, **5b**, **8**, **16a**, and **16b** were assembled from saturated acetonitrile or acetonitrile−benzene solutions onto silver, gold, or platinum surfaces (see Experimental Section for details). Initial proof of SAM formation was provided by FTIR and surface plasmon resonance data. We have previously reported[7] FTIR data for SAMs of **5a**, and these data will not be repeated here. A monolayer of compound **5a** self-

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Table 1. Redox Potentials in Various Media (As Indicated) for 5a, 5b, 8, 16a, and 16b in Solution and as Self-Assembled Films on Platinum

compound	$E_1^{1/2}$ (V)[a]	$E_2^{1/2}$ (V)[a]	electroactive coverage (10^{-10} molecules cm^{-2}) [b]	ΔE_1^{ox} (mV) + Ag^+ [c]
		solution[d] (MeCN)		
TTF	0.34	0.78		
5a	0.48	0.76		80
5b	0.52	0.76		65
8	0.42	0.63		65
16a	0.44	0.63		90
16b	0.45	0.63		85
		SAM[d] (MeCN)		
5a	0.52	0.76	3.5−5.0	75
5b	0.50	0.76	3.0−4.0	80
8	0.38	0.65	3.5−10.0	65
16a	0.41	0.62	3.0−4.0	70
16b	0.42	0.62	4.5	70
		SAM[e] (0.5 M $HClO_4$)		
5a				
5b				
8	0.35	0.65	3.0−5.0	
16a	0.40	0.62	3.0	
16b	0.40	0.63	4.0	

[a] Corrected to Fc/Fc^+ as 0.35 V vs Ag/AgCl in acetonitrile and measured directly against Ag/AgCl in aqueous solution. [b] Obtained by graphical integration of the first oxidation peak during the first scan, as described by Yip and Ward (ref 5); an electroactive coverage of 5×10^{-10} molecule cm^{-2} represents a monolayer coverage, as calculated from Langmuir−Blodgett film studies of compound **5a**. [c] Ag^+ added as $AgBF_4$ to a concentration of 0.02 M. Errors are estimated at ±5 mV. [d] 0.2 M Bu_4NBF_4 as supporting electrolyte. [e] Adsorbed onto platinum disk electrode (1.6 mm diameter, commercial BAS).

adsorbed on a Ag surface showed a shift in the surface plasmon resonance (SPR) minimum compared to a clean Ag surface indicating film formation. Fitting of the SPR curve gave a calculated monolayer thickness of ca. 2.2 nm. From space-filling models for compound **5a**, the molecular length (if the alkyl chain is normal to the substrate) is ca. 3.4 nm. This would indicate that the molecules in the SAM are tilted at ca. 40° to the substrate normal, in agreement with analysis of the FTIR data.[7] A similar tilt angle was calculated for a SAM of **16b** on silver from SPR data.

Electrochemistry. We have studied the solution electrochemistry of compounds **5a**, **5b**, **8**, **16a**, and **16b** in solution and as SAMs, both in the absence and in the presence of metal cations, by cyclic voltammetry (CV). All these compounds showed a CV response typical of the TTF system in acetonitrile solution and as SAMs in acetonitrile (i.e., two reversible one-electron redox couples) at potentials consistent with their substitution patterns (Table 1). Predictably, the electron-withdrawing ester substituent of **5a** and **5b** raises the oxidation potentials[19] relative to TTF and **8**; the additional alkylsulfanyl chains in **16a** and **16b** also slightly raise the oxidation potential (as observed for bis(ethylenedithio)tetrathiafulvalene−TTF in comparison with TTF).[20] The electrochemical response of the SAMs of all these compounds was stable if the potential was limited to the first TTF oxidation; however, as noted by Yip and Ward for SAMs of **1**,[5] the CV response gradually decreased when the potential was

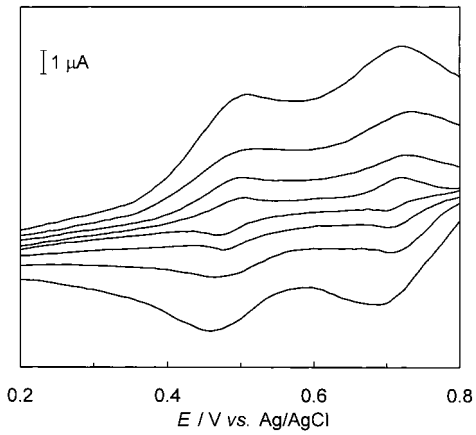

Figure 2. CV data for self-assembled monolayers of compound **5a** on a Pt 1.6 mm diameter electrode vs Ag/AgCl reference, 0.2 M $LiClO_4$/acetonitrile, at scan rates of 100 (lowest current), 200, 500, and 1000 mV s^{-1} (highest current).

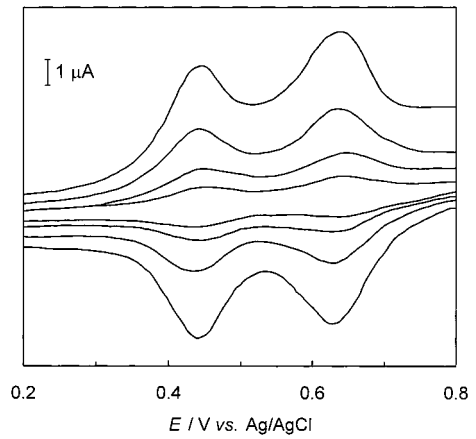

Figure 3. CV data for self-assembled monolayers of compound **16b** (same conditions as Figure 2).

scanned beyond the first oxidation. Compound **16b** was notably more stable in this respect than **5a**, **5b**, **8**, or **16a**, presumably as a result of the beneficial effect of the space-filling hexylsulfanyl chain. Adsorption onto platinum gave a slightly more reproducible electrochemical response (less variation in electroactive coverage between several different samples) than adsorption onto gold. The quality of the films obtained was unchanged by admixture of the TTF derivative with hexadecylthiol (2:1 or 1:1 molar ratio). For SAMs of **5a**, **5b**, **8**, **16a**, and **16b**, the peak current was observed to be proportional to the scan rate, indicating a "surface wave" response, and the peak potentials and peak-to-peak separations were independent of the scan rate at least up to 1 V s^{-1}, indicating that kinetic effects at the surface-confined redox centers were insignificant on the voltammetric time scale. These data for **5a** and **16b** are shown in Figures 2 and 3, respectively. It is notable that the peak shapes were significantly cleaner for **16b** than for the other compounds. The electroactive coverage for compound **8** was more varied than those for compounds **5a**, **5b**, and **16a**, ranging from submonolayer to multilayers, and the coverage for **16b** was by far the most reproducible (Table 1), which is consistent with the improved stability of SAMs of **16b** noted above. The response for **16b** was unchanged after storage of the films in air for several days. Preliminary X-ray photoelectron spectroscopy (XPS)

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data suggested submonolayer coverage on gold with compounds **5a** and **5b**, whereas almost complete coverage was achieved with **16b**.[21] Multilayer formation has been observed previously for a ferrocene derivative substituted with an alkylthiol chain;[22] the extensive variation with **8** is consistent with decreased order within the film structure because of the very short thiol chain, and hence the coverage for this compound is critically dependent on the pretreatment (and hence the roughness) of the electrode surface. The parent system TTF−CH_2−SH[23] showed similarly variable behavior. This is consistent with the report of Fujihara et al. that monolayers of the tetrathiol TTF[$S(CH_2)_3SH]_4$ are more stable than those of the monothiol TTF$S(CH_2)_3SH$.[6]

The SAMs of **5a** and **5b** were not electroactive in aqueous electrolytes (cf. compounds **1**, which have a similar ester linkage and also exhibited no CV response in water).[5] However, SAMs of **8**, **16a**, and **16b** exhibited an electrochemical response in aqueous electrolytes which was observed between 50 and 100 cycles. Moreover, if the potential scanned was limited to the first TTF oxidation, *the CV response was observed for at least 1000 cycles*. It should be noted that the peak separation ($E_1^{ox} - E_1^{red}$) in aqueous electrolyte was always larger (>80 mV) than that in acetonitrile, possibly because of a change in solvation after the redox reaction and/or a phase change in the SAM as suggested for other systems.[24]

Cation Recognition. Electrochemical recognition for compounds **5a**, **5b**, **8**, **16a**, and **16b** has been studied in solution and as SAMs in the presence of different metal cations. There was a small but highly reproducible positive response in the value of $E_1^{1/2}$ to Li^+ and K^+ (10−20 mV in solution), a significant response to Na^+ and Ba^{2+} (45−55 mV in solution), and a greater response to Ag^+ (65−90 mV in solution), whereas $E_2^{1/2}$ was essentially unaffected. Collectively, these data are consistent with previous observations of other S_2O_4-crown compounds.[4a,c]

For SAMs of **5a**, **5b**, **8**, **16a**, and **16b**, the CV response to metal cations in acetonitrile was similar to the solution result, with the largest response for Ag^+ (Table 1). It is notable that the response seems to be independent of the length of the thiol chain. Figure 4 shows the shift in both E_1^{ox} and E_2^{ox} for SAMs of **16b** in acetonitrile with added $AgClO_4$. For this compound (but not for **5a**, **5b**, **8**, or **16a**), a small shift in E_2^{ox} was also observed at higher [Ag^+]. This could be a consequence of surface aggregation or cooperativity effects between adjacent crowns in the more densely packed SAMs of this compound, as suggested by Liu and Echegoyen for SAMs of a TTF−S_2O_5-crown which showed a shift in both E_1^{ox} and E_2^{ox} in the presence of $NaPF_6$.[8] No voltammetric response to metal cations was observed for the SAMs of **8**, **16a**, and **16b** in aqueous media.

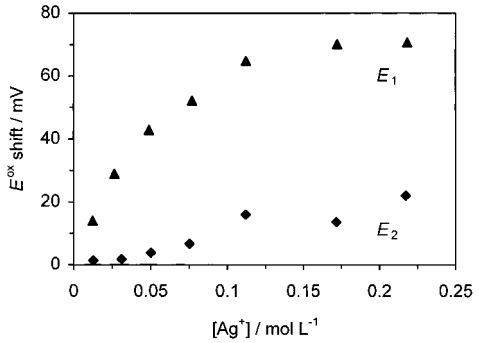

Figure 4. The shift in the potentials of E_1^{ox} and E_2^{ox} for SAMs of **16b** on a Pt 1.6 mm diameter electrode, 0.2 M $LiClO_4$/acetonitrile, scan rate 200 mV s^{-1}, with added $AgBF_4$.

The binding constants for the formation of 1:1 complexes **5a**·Ag^+ and **16b**·Ag^+ in acetonitrile solution were calculated from UV−vis and CV data, using procedures described previously for TTF crowns,[4c] to be log K_{obs} = 2.3−2.4 and 2.5−2.6, respectively. 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.[18]

Conclusions

Synthetic routes have been developed for S_2O_4-crown annelated TTFs bearing one terminal thiol group, and electrochemically active SAMs have been assembled. The stability and electrochemical behavior of the SAMs is enhanced by the presence of an additional space-filling alkyl chain (compounds **16a** and **16b**). Although multiple anchor points are certainly beneficial for the electrochemical stability of some SAMs,[8,25] it seems they are not necessarily a prerequisite for TTF derivatives which have a high propensity to form ordered stacks. SAMs of **5a**, **5b**, **8**, **16a**, and **16b** are voltammetric sensors for metal cations, and binding to the ionophore site can be monitored by a positive shift in the first oxidation potential of the TTF unit (maximum $\Delta E_1^{1/2}$ = 80 mV for Ag^+). These results and those of Echegoyen et al.[8] demonstrate that TTF is a suitable transducer unit for thin layer molecular devices for sensing applications.

Experimental Section

General Methods. Column chromatography was performed on Merck silica gel (70−230 mesh). All reagents were of commercial quality and were used as supplied unless otherwise stated; solvents were dried when necessary using standard procedures and were distilled for chromatographic use. The gold and platinum substrates for electrochemistry (disk electrodes, 1.6 mm diameter) were purchased from Bioanalytical System Inc. (BAS). Pretreatment of the metal surface for electrochemical experiments involved polishing with alumina (sequentially decreasing particle size, 1.00−0.05 mm) and washing sequentially with water, dilute sulfuric acid (2 min), distilled water, and distilled methanol before drying in a stream of nitrogen. Monolayers were assembled from saturated acetonitrile or acetonitrile/benzene solutions onto gold or platinum electrodes or freshly evaporated metal on a silicon wafer substrate. The electrode or wafer substrate was removed from the solution containing the TTF derivative after 24 h (Ag and Au) or 72 h (Pt) and then washed with dichloromethane and dried in a stream of nitrogen. Cyclic

(21) XPS data were obtained on films assembled on gold grown on a mica substrate as described by Nie et al.: Nie, H. Y.; Mizutani, W.; Tukumoto, H. *Surf. Sci. Lett.* **1994**, *311*, L649. Peaks from the gold surface were clearly visible in the XPS spectra of films of **5a** and **5b**, whereas their intensity was considerably reduced for films of **16b**.

(22) Creager, S. F.; Rowe, G. K. *J. Electroanal. Chem.* **1993**, *347*, 327.

(23) Moore, A. J.; Goldenberg, L. M.; Petty, M. C.; Bryce, M. R. Unpublished results. TTF−CH_2−SH was obtained from TTF−CH_2−OH (Garín, J.; Orduna, J.; Uriel, J.; Moore, A. J.; Bryce, M. R.; Wegener, S.; Yufit, D. S.; Howard, J. A. K. *Synthesis* **1994**, 489.) by analogy with the preparation of **8** from **6** and was isolated as a yellow solid. δ_H ($CDCl_3$): 6.31 (2 H, s), 6.17 (1 H, s), 3.48 (2 H, d, J = 7.9), 1.89 (1 H, t, J = 7.9).

(24) Reference 3, p 242.

(25) Beulen, M. W. J.; Kastenberg, M. I.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Langmuir* **1998**, *14*, 7463.

voltammetry was performed using an EG&G PARC model 273 potentiostat using *iR* compensation with an Advanced Bryans XY recorder. Pt mesh served as the counter electrode, and a saturated calomel electrode (in aqueous solution) or Ag/Ag^+ (in acetonitrile solution) served as the reference electrode. A ferrocene/ferrocenium couple was used as the internal reference to test that the reference electrode did not change potential with added metal salts. Experiments were performed using either 0.2 mol L^{-1} Bu_4NPF_6 (Fluka, electrochemical grade) in acetonitrile (Aldrich, HPLC grade) or 0.2 mol L^{-1} $HClO_4$ (Aldrich, ACS reagent) in ultrapure water. For solution studies, platinum disk electrodes (BAS, 1.6 mm diameter) were employed as the working electrodes; for studies on the self-assembled films, the electrodes with assembled layers described above were used directly. Metal salts 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). In the following discussion, values of *J* are given in Hz.

$1^{3'}$-(12-Bromo-1-dodecyloxycarbonyl)-5,8,11,14-tetraoxa,$1^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (4a). To a suspension of compound **3**[4c] (336 mg, 0.65 mmol) in dry dichloromethane (30 mL) was added dicyclohexylcarbodiimide (215 mg, 1.0 mmol), and the mixture was stirred at 0 °C under argon for 10 min. 12-Bromo-1-dodecanol (217 mg, 0.81 mmol) and 4-(dimethylamino)-pyridine (25 mg, 0.19 mmol) were then added, and the mixture was stirred at 20 °C for 48 h. The mixture was filtered, and the filtrate was evaporated. Chromatography of the residue (silica) eluting with dichloromethane/ethyl acetate (1:1 v/v) afforded the product initially as an orange oil. Compound **4a** was obtained as a yellow solid from a methanol solution stored at −5 °C overnight (371 mg, 74%); mp 49 °C (from diethyl ether/ethanol). Found: C, 45.8; H, 6.1; S, 25.0%. $C_{29}H_{45}BrO_6S_6$ requires: C, 45.7; H, 5.9; S, 25.2%. *m*/*z* (EI) (%): 762, 760 (M^+, 100 and 75), 683 (30), 514 (30), 446 (25), 383 (30). NMR ($CDCl_3$): δ_H 7.34 (1 H, s), 4.20 (2 H, t, $J = 6.5$), 3.73 (4 H, t, $J = 6.1$), 3.67−3.65 (12 H, m), 3.40 (2 H, t, $J = 6.8$), 3.04 (2 H, t, $J = 6.1$), 3.02 (2 H, t, $J = 6.1$), 1.86 (2 H, p, $J = 6.1$), 1.65 (2 H, p, $J = 6.1$), 1.27 (16 H, m).

$1^{3'}$-(6-Bromo-1-hexyloxycarbonyl)-5,8,11,14-tetraoxa,$1^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (4b). By analogy with the preparation of **4a**, compound **3** (500 mg, 0.97 mmol) in dry dichloromethane (75 mL), dicyclohexylcarbodiimide (320 mg, 1.6 mmol), 6-bromo-1-hexanol (0.16 mL, 1.25 mmol), and 4-(dimethylamino)-pyridine (25 mg, 0.19 mmol) were reacted to give a product mixture which was filtered, the filtrate was evaporated, and the excess 6-bromo-hexanol was removed by distillation using a Kugelröhr apparatus (125 °C at 1 mmHg). Chromatography of the residue (silica) eluting with dichloromethane/ethyl acetate (4:1 v/v) afforded compound **4b** as an orange oil (530 mg, 81%). Found: C, 41.0; H, 5.1; S, 28.1%. $C_{23}H_{33}BrO_6S_6$ requires: C, 40.8; H, 4.9; S, 28.4%. *m*/*z* (EI) (%): 678, 676 (M^+, 60 and 35), 599 (40), 446 (20). NMR ($CDCl_3$): δ_H 7.34 (1 H, s), 4.12 (2 H, t, $J = 6.5$), 3.71 (4 H, t, $J = 6.1$), 3.65−3.63 (12 H, m), 3.40 (2 H, t, $J = 6.6$), 3.02 (2 H, t, $J = 6.1$), 3.01 (2 H, t, $J = 6.1$), 1.86, (2 H, p, $J = 6.4$), 1.70 (2 H, p, $J = 6.5$), 1.44 (4 H, m).

$1^{3'}$-(12-Sulfanyl-1-dodecyloxycarbonyl)-5,8,11,14-tetraoxa,$1^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (5a). A mixture of compound **4a** (284 mg, 0.37 mmol) and thiourea (84 mg, 1.12 mmol) in dry ethanol (80 mL) was stirred at reflux under argon for 24 h. After the solution was cooled , the solvent was removed, 1 M potassium hydroxide (40 mL) was added to the residue, and the resultant mixture was stirred at reflux for 18 h. After the mixture was cooled, it was extracted with diethyl ether (4 × 50 mL), the combined extracts were dried ($MgSO_4$), and the solvent was evaporated. Chromatography of the residue (silica) eluting with dichloromethane/ethyl acetate (2:1 v/v) afforded compound **5a** as an orange oil (112 mg, 42%) (four columns were necessary in order to obtain a pure sample of the product). Found: C, 49.0; H, 6.6; S, 31.2%. $C_{29}H_{46}O_6S_7$ requires: C, 48.7; H, 6.5; S, 31.4%. *m*/*z* (DCI) (%): 732 ($M^+ + NH_4^+$, 45), 714 (M^+, 25), 470 (55). HRMS: found, 714.1323; calcd, 714.1329. NMR ($CDCl_3$): δ_H 7.34 (1 H, s), 4.20 (2 H, t, $J = 6.7$), 3.74 (4 H, t, $J = 6.0$), 3.68−3.66 (12 H, m), 3.04 (2 H, t, $J = 6.0$), 3.03 (2 H, t, $J = 6.0$), 2.68 (2 H, t, $J = 7.0$), 1.67 (4 H, m), 1.28 (16 H, m).

$1^{3'}$-(6-Sulfanyl-1-hexyloxycarbonyl)-5,8,11,14-tetraoxa,$1^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (5b). By analogy with the preparation of **5a**, compound **4b** (186 mg, 0.27 mmol) and thiourea (65 mg, 0.85 mmol) in dry ethanol (50 mL) and 1 M potassium hydroxide (40 mL) after workup and chromatography of the residue (silica) eluting with dichloromethane/ethyl acetate (1:1 v/v) afforded compound **5b** as an orange oil (40 mg, 23%) (three columns were necessary in order to obtain a pure sample of the product). Found: C, 43.5; H, 5.2; S, 35.9%. $C_{23}H_{34}O_6S_7$ requires: C, 43.8; H, 5.4; S, 35.6%. *m*/*z* (EI) (%): 630 (M^+, 25), 470 (10). HRMS: found, 630.0393; calcd, 630.0389. NMR ($CDCl_3$): δ_H 7.34 (1 H, s), 4.20 (2 H, t, $J = 6.5$), 3.72 (4 H, t, $J = 6.2$), 3.67−3.65 (12 H, m), 3.03 (2 H, t, $J = 6.2$), 3.02 (2 H, t, $J = 6.2$), 2.68 (2 H, t, $J = 7.2$), 1.69 (4 H, m), 1.42 (4 H, m).

$1^{3'}$-Methoxysulfanylmethyl-5,8,11,14-tetraoxa,$1^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (7). A mixture of diisopropyl azodicarboxylate (0.16 mL, 0.8 mmol) and triphenylphosphine (210 mg, 0.8 mmol) was stirred in dry tetrahydrofuran (30 mL) under argon at 0 °C for 1 h. A solution of compound **6**[4c] (200 mg, 0.4 mmol) in dry tetrahydrofuran (10 mL) was slowly added, and the mixture was stirred for 1 h at 20 °C. Thioacetic acid (0.06 mL, 0.8 mmol) was added, and the reaction was stirred for a further 12 h. After evaporation of the solvent, the residue was chromatographed (silica), eluting initially with dichloromethane to remove the fast-running impurities. Subsequent elution with ethyl acetate afforded compound **7** as an orange wax (160 mg, 72%). Found: C, 40.7; H, 4.5%. $C_{19}H_{25}O_5S_7$ requires: C, 40.9; H, 4.5%. *m*/*z* (DCI) (%): 576 ($M^+ + NH_4^+$, 20), 558 (M^+, 15), 286 (70), 267 (45), 103 (75). NMR ($CDCl_3$): δ_H 6.21 (1 H, s), 3.86 (2 H, s), 3.73 (4 H, t, $J = 6.2$), 3.68−3.66 (12 H, m), 3.02 (4 H, t, $J = 6.2$), 2.38 (3 H, s).

$1^{3'}$-Sulfanylmethyl-5,8,11,14-tetraoxa,$1^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (8). To a solution of compound **7** (120 mg, 0.21 mmol) in dry diethyl ether (25 mL) at 20 °C under argon was added lithium aluminum hydride (25 mg, 0.63 mmol), and the reaction was stirred for 4 h. After the reaction was quenched (ethyl acetate, 5 mL), water (100 mL) was added and the mixture was extracted with dichloromethane. The combined organic extracts were washed with water and dried ($MgSO_4$), and the solvent was evaporated. Chromatography of the residue (silica) eluting with ethyl acetate afforded compound **8** as a yellow solid (92 mg, 83%); mp 85 °C. Found: C, 39.9; H, 4.8%. $C_{17}H_{24}O_4S_7$ requires: C, 39.5; H, 4.7%. *m*/*z* (DCI) (%): 534 ($M^+ + NH_4^+$, 25), 516 (M^+, 10), 502 (25), 485 (20), 131 (70). HRMS: found, 515.9719; calcd, 515.9715. NMR ($CDCl_3$): δ_H 6.18 (1 H, s), 3.74 (4 H, t, $J = 6.3$), 3.68−3.66 (12 H, m), 3.49 (2 H, d, $J = 7.9$), 3.02 (4 H, t, $J = 6.3$), 1.89 (1 H, t, $J = 7.9$).

4-Methylthio-5-(6-hydroxyhexylthio)-1,3-dithiole-2-thione (10a). To a suspension of compound **9**[14] (3.0 g, 0.011 mol) in dry methanol (50 mL) under argon at 20 °C was added a solution of cesium hydroxide monohydrate (1.90 g, 0.011 mol) in dry methanol (10 mL), and the mixture was stirred for 2 h. 6-Bromohexanol (2.22 mL, 0.0165 mol) was added, and the reaction was stirred overnight. After evaporation of the solvent and removal of excess 6-bromohexanol by distillation using a Kugelröhr apparatus (160 °C, 1 mmHg), the residue was chromatographed (silica), eluting with dichloromethane to afford compound **10a** as an orange oil (3.12 g, 88%). Found: C, 38.5; H, 5.3%. $C_{10}H_{16}OS_5$ requires: C, 38.4; H, 5.2%. *m*/*z* (DCI): 313 (MH^+). HRMS: found, 311.9807; calcd, 311.9802. NMR ($CDCl_3$): δ_H 3.65 (2 H, t, $J = 6.0$), 2.87 (2 H, t, $J = 7.0$), 2.50 (3 H, s), 1.66 (2 H, m), 1.58 (2 H, m), 1.42 (4 H, m), 1.26 (1 H, s).

4-Hexylthio-5-(6-hydroxyhexylthio)-1,3-dithiole-2-thione (10b). By analogy with the preparation of **10a**, compound **9**[14] (5.0 g, 0.015 mmol) in dry methanol (75 mL),

cesium hydroxide monohydrate (2.50 g, 0.015 mol) in dry methanol (10 mL), and 6-bromohexanol (2.22 mL, 0.0165 mmol) after chromatography (silica) eluting with dichloromethane afforded compound **10b** as an orange oil (4.67 g, 82%). Found: C, 47.3; H, 7.0%. $C_{15}H_{26}OS_5$ requires: C, 47.1; H, 6.9%. *m*/*z* (DCI): 383 (MH^+). HRMS: found, 382.0577; calcd, 382.0582. NMR ($CDCl_3$): δ_H 3.62 (2 H, t, $J = 6.0$), 2.86 (4 H, t, $J = 7.2$), 1.67 (4 H, m), 1.57 (2 H, m), 1.42 (6 H, m), 1.31 (4 H, m), 0.88 (3 H, t, $J = 6.9$).

4-Methylthio-5-(6-diphenyl-*t*-butylsilyloxyhexylthio)-1,3-dithiole-2-thione (11a). To a solution of compound **10a** (2.60 g, 8.33 mmol) in dry dimethylformamide (50 mL) under argon at 20 °C was added imidazole (6.0 g, 88 mmol) and *tert*-butyldiphenylsilyl chloride (2.29 g, 8.33 mmol), and the mixture was stirred for 12 h. The solvent was evaporated in vacuo. The residue was dissolved in dichloromethane, washed with water, and dried ($MgSO_4$), and the solvent was evaporated. Chromatography of the residue (silica) eluting with dichloromethane afforded compound **11a** as an orange oil (4.45 g, 97%). Found: C, 57.0; H, 6.0%. $C_{26}H_{34}OS_5Si$ requires: C, 56.7; H, 6.2%. *m*/*z* (DCI) (%): 551 (MH^+, 100), 473 (80), 367 (70), 196 (80). NMR ($CDCl_3$): δ_H 7.68−7.64 (4 H, m), 7.42−7.38 (6 H, m), 3.65 (2 H, t, $J = 7.1$), 2.83 (2 H, t, $J = 7.1$), 2.47 (3 H, s), 1.68 (2 H, m), 1.56 (2 H, m), 1.36 (4 H, m), 1.05 (9 H, s).

4-Hexylthio-5-(6-diphenyl-*t*-butylsilyloxyhexylthio)-1,3-dithiole-2-thione (11b). This compound was prepared analogously to **11a** from **10b** (4.00 g, 10.5 mmol), dimethylformamide (50 mL), imidazole (5.0 g, 73.5 mmol), and *tert*-butyldiphenylsilyl chloride (2.73 mL, 10.5 mmol). Chromatography of the residue (silica) eluting with hexane/dichloromethane (1:1 v/v) afforded compound **11b** as an orange oil (5.78 g, 89%). Found: C, 59.7; H, 6.9%. $C_{31}H_{44}OS_5Si$ requires: C, 60.0; H, 7.1%. *m*/*z* (DCI): 621 (MH^+, 100%). NMR ($CDCl_3$): δ_H 7.68−7.64 (4 H, m), 7.43−7.37 (6 H, m), 3.65 (2 H, t, $J = 6.3$), 2.87 (2 H, t, $J = 7.2$), 2.84 (2 H, t, $J = 7.2$), 1.65 (4 H, m), 1.59 (2 H, m), 1.37 (6 H, m), 1.30 (4 H, m), 1.07 (9 H, s), 0.89 (3 H, t, $J = 6.9$).

1$^{3'}$-(6-Diphenyl-*t*-butylsilyloxy-1-hexylthio)-4′-methylthio-5,8,11,14-tetraoxa,1$^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (13a). A mixture of compound **11a** (1.0 g, 1.82 mmol) and compound **12**[4a] (0.75 g, 1.87 mmol) in triethyl phosphite (20 mL) was stirred at 130 °C for 5 h. After the mixture was cooled, the solvent was evaporated under reduced pressure and the residue was chromatographed (silica) eluting with dichloromethane/ethyl acetate (1:1 v/v) to afford in order of elution (i) the self-coupled product from **11a** (250 mg, 25%), (ii) compound **13a** as an orange oil (325 mg, 20%), and (iii) the self-coupled product from **12** (240 mg, 35%). **13a** Found: C, 53.0; H, 6.0%. $C_{39}H_{54}O_5S_8Si$ requires: C, 52.8; H, 6.1%. *m*/*z* (DCI) (%): 904 ($M^+ + NH_4^+$, 75), 887 (MH^+, 25), 295 (100). NMR ($CDCl_3$): δ_H 7.67−7.64 (4 H, m), 7.42−7.36 (6 H, m), 3.72 (4 H, t, $J = 6.1$), 3.68−3.66 (12 H, m), 3.61 (2 H, t, $J = 6.3$), 3.04 (2 H, t, $J = 6.1$), 3.02 (2 H, t, $J = 6.1$), 2.83 (2 H, t, $J = 6.4$), 2.47 (3 H, s), 1.61−1.53 (4 H, m), 1.35−1.31 (4 H, m), 1.04 (9 H, s).

1$^{3'}$-(6-Diphenyl-*t*-butylsilyloxy-1-hexylthio)-4′-hexylthio-5,8,11,14-tetraoxa,1$^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (13b). By analogy with the preparation of **13a**, **11b** (1.12 g, 1.82 mmol) and compound **12**[4a] (0.75 g, 1.87 mmol) in triethyl phosphite (20 mL) gave a residue which was chromatographed (silica), eluting with dichloromethane/ethyl acetate (3:1 v/v) to afford **13b** as an orange oil (535 mg, 31%) after separation from self-coupled products. Found: C, 55.3; H, 6.9%. $C_{44}H_{64}O_5S_8Si$ requires: C, 55.2; H, 6.7%. *m*/*z* (DCI) (%): 956 (MH^+, 35), 295 (100). NMR ($CDCl_3$): δ_H 7.67−7.64 (4 H, m), 7.41−7.37 (6 H, m), 3.72 (4 H, t, $J = 6.1$), 3.68−3.65 (12 H, m), 3.61 (2 H, t, $J = 6.3$), 3.04 (2 H, t, $J = 6.1$), 3.02 (2 H, t, $J = 6.1$), 2.87 (2 H, t, $J = 7.2$), 2.84 (2 H, t, $J = 7.2$), 1.65 (4 H, m), 1.59 (2 H, m), 1.37 (6 H, m), 1.29 (4 H, m), 1.03 (9 H, s), 0.87 (3 H, t, $J = 6.9$).

1$^{3'}$-(6-Hydroxy-1-hexylthio)-4′-methylthio-5,8,11,14-tetraoxa,1$^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (14a). To a solution of compound **13a** (300 mg, 0.34 mmol) in dry tetrahydrofuran (25 mL) under argon at 20 °C was added tetrabutylammonium fluoride (1 M in tetrahydrofuran, 2 mL, excess), and the mixture was stirred for 12 h. After evaporation of the solvent, the residue was chromatographed (silica), eluting with ethyl acetate to afford compound **14a** as an orange oil (200 mg, 91%). Found: C, 42.6; H, 5.7%. $C_{23}H_{36}O_5S_8$ requires: C, 42.6; H, 5.7%. *m*/*z* (DCI) (%): 668 ($M^+ + NH_4^+$, 85), 649 (MH^+, 80), 367 (60), 279 (100), 168 (95). NMR ($CDCl_3$): δ_H 3.74 (4 H, t, $J = 6.3$), 3.68−3.66 (12 H, m), 3.64 (2 H, t, $J = 6.2$), 3.03 (4 H, t, $J = 6.2$), 2.82 (2 H, t, $J = 7.1$), 2.43 (3 H, s), (1.66−1.25 8 H, m), OH not observed.

1$^{3'}$-(6-Hydroxy-1-hexylthio)-4′-hexylthio-5,8,11,14-tetraoxa,1$^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (14b). By analogy with the preparation of **14a**, **13b** (1.40 g, 1.46 mmol), tetrahydrofuran (50 mL), and tetrabutylammonium fluoride (1 M in tetrahydrofuran, 2 mL, excess) gave a product which was chromatographed (silica), eluting with dichloromethane/ethyl acetate (5:1 v/v) to afford compound **14b** as an orange oil (800 mg, 76%). Found: C, 46.6; H, 6.6%. $C_{28}H_{46}O_5S_8$ requires: C, 46.8; H, 6.5%. *m*/*z* (DCI) (%): 736 ($M^+ + NH_4^+$, 15), 719 (MH^+, 25), 473 (100). NMR ($CDCl_3$): δ_H 3.74 (4 H, t, $J = 6.3$), 3.68−3.63 (12 H, m), 3.60 (2 H, t, $J = 6.6$), 3.00 (4 H, t, $J = 6.2$), 2.78 (4 H, t, $J = 7.2$), 1.65−1.51 (6 H, m), 1.36−1.21 (10 H, m), 0.85 (3 H, t, $J = 6.5$), OH not observed.

1$^{3'}$-(6-Methoxysulfanyl-1-hexylthio)-4′-methylthio-5,8,11,14-tetraoxa,1$^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (15a). A mixture of diisopropyl azodicarboxylate (0.09 mL, 0.46 mmol) and triphenylphosphine (120 mg, 0.46 mmol) was stirred in dry tetrahydrofuran (50 mL) under argon at 0 °C for 1 h. A solution of compound **14a** (150 mg, 0.23 mmol) in dry tetrahydrofuran (10 mL) was slowly added, and the mixture was stirred for 1 h at 20 °C. Thioacetic acid (0.035 mL, 0.46 mmol) was added, and the reaction was stirred for a further 12 h. After evaporation of the solvent, the residue was chromatographed (silica), eluting initially with dichloromethane and subsequently with dichloromethane/ethyl acetate (1:1 v/v) to afford compound **15a** as an orange oil (117 mg, 71%). Found: C, 42.5; H, 5.2%. $C_{25}H_{38}O_5S_9$ requires: C, 42.5; H, 5.4%. *m*/*z* (DCI) (%): 724 ($M^+ + NH_4^+$, 30), 705 (MH^+, 15), 383 (35), 228 (60), 168 (100). NMR ($CDCl_3$): δ_H 3.71 (4 H, t, $J = 6.3$), 3.66−3.63 (12 H, m), 3.01 (4 H, t, $J = 6.1$), 2.84 (2 H, t, $J = 6.9$), 2.81 (2 H, t, $J = 6.9$), 2.40 (3 H, s), 2.30 (3 H, s), 1.61−1.53 (4 H, m), 1.40−1.33 (4 H, m).

1$^{3'}$-(6-Methoxysulfanyl-1-hexylthio)-4′-hexylthio-5,8,11,14-tetraoxa,1$^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (15b). By analogy with the preparation of **15b**, diisopropyl azodicarboxylate (0.13 mL, 0.62 mmol), triphenylphosphine (165 mg, 0.62 mmol), tetrahydrofuran (50 mL), compound **14b** (220 mg, 0.31 mmol) in dry tetrahydrofuran (10 mL), and thioacetic acid (0.045 mL, 0.62 mmol) gave a product which was chromatographed (silica), eluting initially with dichloromethane and subsequently with dichloromethane/ethyl acetate (3:1 v/v) to afford compound **15b** as an orange oil (218 mg, 92%) (ca. 90% pure by ^1H NMR and used directly in the next step). *m*/*z* (DCI) (%): 794 ($M^+ + NH_4^+$, 30), 777 (MH^+, 20), 531 (80), 383 (70), 222 (100). HRMS: found, 776.0982; calcd for $C_{30}H_{48}O_5S_9$, 776.0978. NMR ($CDCl_3$): δ_H 3.71 (4 H, t, $J = 6.2$), 3.66−3.64 (12 H, m), 3.00 (4 H, t, $J = 6.3$), 2.83 (2 H, t, $J = 6.9$), 2.81 (2 H, t, $J = 6.9$), 2.79 (2 H, t, $J = 6.9$), 2.29 (3 H, s), 1.63−1.54 (6 H, m), 1.38−1.27 (10 H, m), 0.88 (3 H, t, $J = 6.6$).

1$^{3'}$-(6-Sulfanyl-1-hexylthio)-4′-methylthio-5,8,11,14-tetraoxa,1$^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (16a). To a solution of compound **15a** (100 mg, 0.14 mmol) in dry diethyl ether (25 mL) at 20 °C under argon was added lithium aluminum hydride (10 mg, 0.26 mmol), and the reaction was stirred for 4 h. After the reaction was quenched (ethyl acetate, 1 mL), water (30 mL) was added and the mixture was extracted with dichloromethane. The combined organic extracts were washed with water and dried ($MgSO_4$), and the solvent was evaporated. Chromatography of the residue (silica) eluting with ethyl acetate afforded compound **16a** as yellow oil (80 mg, 88%).

Found: C, 41.7; H, 5.4; S, 43.6%. $C_{23}H_{36}O_4S_9$ requires: C, 41.5; H, 5.5; S, 43.4%. *m/z* (DCI) (%): 682 ($M^+ + NH_4^+$, 35), 665 (MH^+, 10), 372 (90), 317 (70), 279 (100). HRMS: found, 664.0099; calcd, 664.0093. NMR ($CDCl_3$): δ_H 3.73 (4 H, t, J = 6.2), 3.68−3.66 (12 H, m), 3.03 (4 H, t, J = 6.2), 2.81 (2 H, t, J = 7.5), 2.68 (2 H, t, J = 7.2), 2.42 (3 H, s), 1.72−1.60 (4 H, m), 1.50−1.39 (4 H, m), SH not observed.

$1^{3'}$-(6-Sulfanyl-1-hexylthio)-$^{4'}$-hexylthio-5,8,11,14-tetraoxa,$1^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (16b). By analogy with the preparation of **16a**, compound **15b** (200 mg, 0.14 mmol, ca. 90% pure from previous reaction), diethyl ether (25 mL), and lithium aluminum hydride (10 mg, 0.26 mmol) gave a product that when chromatographed (silica) eluting with dichloromethane/ethyl acetate (6:1 v/v) afforded compound **16b** as an orange oil (134 mg, 71%). Found: C, 46.0; H, 6.2%. $C_{28}H_{46}O_4S_9$ requires: C, 45.7; H, 6.3; S, 39.3%. *m/z* (DCI) (%): 752 ($M^+ + NH_4^+$, 45), 735 (MH^+, 10), 368 (30), 280 (100). NMR ($CDCl_3$): δ_H 3.73 (4 H, t, J = 6.2), 3.68−3.66 (12 H, m), 3.03 (4 H, t, J = 6.3), 2.81 (4 H, t, J = 7.1), 2.67 (2 H, t, J = 7.1), 1.66−1.60 (6 H, m), 1.43−1.29 (10 H, m), 0.89 (3 H, t, J = 6.6), SH not observed.

$1^{3',4'}$-Bis(carboxy)-5,8,11,14-tetraoxa,$1^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (18). A stirred solution of compound **17**[4c] (1.0 g, 1.7 mmol) in a mixture of dioxane (80 mL) and 1 M sodium hydroxide (10 mL) was refluxed for 24 h. After the mixture was cooled, the solvent was evaporated and the residue was dissolved in water (125 mL). The aqueous phase was washed with dichloromethane and acidified with 1 M hydrochloric acid to precipitate the product as a red solid. The solid was collected by filtration, washed sequentially with water, ethanol, and diethyl ether, and air-dried at 60 °C, affording compound **18** as a red solid of sufficient purity for further reaction (660 mg, 70%). (Because of insolubility in a wide range of solvents, an analytically pure sample could not be obtained.) NMR [$(CD_3)_2SO$]: δ_H 4.52 (2 H, br s, OH), 3.62 (4 H, t, J = 5.8), 3.59−3.51 (12 H, m), 3.02 (4 H, t, J = 5.8).

$1^{3',4'}$-Bis(2-bromoethoxycarbonyl)-5,8,11,14-tetraoxa,$1^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (19). To a suspension of compound **18** (200 mg, 0.36 mmol) in dry dichloromethane (75 mL) at 20 °C under argon was added dicyclohexylcarbodiimide (215 mg, 1.0 mmol), and the mixture was stirred with ultrasound for 0.5 h. 2-Bromohexanol (0.5 mL, excess) and 4-(dimethylamino)-pyridine (25 mg, 0.2 mmol) were added, and the mixture was refluxed with ultrasound for 24 h. After the mixture was cooled, the reaction was filtered and the filtrate was evaporated. Chromatography of the residue (silica) eluting with dichloromethane/ethyl acetate (1:1 v/v) afforded compound **19** as a red oil (185 mg, 67%). Found: C, 34.5; H, 3.6%. $C_{22}H_{28}Br_2O_8S_6$ requires: C, 34.2; H, 3.7%. *m/z* (EI) (%): 770 (M^+, 85), 622 (60). NMR ($CDCl_3$): δ_H 4.55 (4 H, d, J = 6.2), 3.73 (4 H, t, J = 6.2), 3.68−3.66 (12 H, m), 3.56 (4 H, t, J = 6.2), 3.03 (4 H, t, J = 6.2).

$1^{3',4'}$-Bis(hydroxymethyl)-5,8,11,14-tetraoxa,$1^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (21). To a solution of compound **17**[4c] (250 mg, 0.43 mmol) in dry tetrahydrofuran (50 mL) under argon was added sodium borohydride (65 mg, 1.7 mmol) and zinc chloride (232 mg, 1.7 mmol), and the mixture was refluxed for 4 h. After the mixture was cooled, the reaction was quenched (ethyl acetate, 5 mL), water was added (100 mL), and the mixture was extracted with dichloromethane. The combined organic extracts were washed with water and dried ($MgSO_4$), and the solvent was evaporated. Chromatography of the residue (silica) eluting with acetone afforded compound **21** as an orange solid (115 mg, 50%); mp 148−149 °C (from acetone). Found: C, 40.7; H, 4.9%. $C_{18}H_{26}O_6S_6$ requires: C, 40.7; H, 4.9%. *m/z* (EI): 530 (M^+, 80%). NMR ($CDCl_3$): δ_H 4.41 (4 H, d, J = 5.7), 3.73 (4 H, t, J = 6.2), 3.68−3.66 (12 H, m), 3.02 (4 H, t, J = 6.2), 2.48 (2 H, t, J = 5.7).

$1^{3',4'}$-Bis(Methoxysulfanylmethyl)-5,8,11,14-tetraoxa,$1^{2,2',5,5'}$,2,17-hexathia-1(3,4)-bicyclopent-3-en-1-ylidena)cycloheptadecane (22). A mixture of diisopropyl azodicarboxylate (0.15 mL, 0.75 mmol) and triphenylphosphine (200 mg, 0.75 mmol) was stirred in dry tetrahydrofuran (50 mL) under argon at 0 °C for 1 h. A solution of compound **21** (100 mg, 0.19 mmol) in dry tetrahydrofuran (10 mL) was slowly added, and the mixture was stirred for 1 h at 20 °C. Thioacetic acid (0.06 mL, 0.8 mmol) was added, and the reaction was stirred for a further 12 h. After evaporation of the solvent, the residue was chromatographed (silica), eluting initially with dichloromethane and subsequently with dichloromethane/ethyl acetate (1:1 v/v) to afford compound **22** as an orange solid (90 mg, 73%); mp 96−97 °C. Found: C, 41.0; H, 4.6%. $C_{22}H_{30}O_6S_8$ requires: C, 40.8; H, 4.7%. *m/z* (EI): 646 (M^+, 100%). NMR ($CDCl_3$): δ_H 3.94 (4 H, s), 3.71 (4 H, t, J = 6.3), 3.67−3.65 (12 H, m), 3.00 (4 H, t, J = 6.3), 2.37 (6 H, s).

X-ray Crystallography. A single crystal (0.2 × 0.2 × 0.3 mm) of **21** suitable for the X-ray diffraction study was grown from acetone. The experiment was carried out on a SMART 3-circle diffractometer with a 1K charge-coupled device area detector, using Mo Kα radiation (0.710 73 Å). The structure was solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELX-97 software (G. M. Sheldrick, Göttingen University, 1997). Crystal data: $C_{18}H_{26}O_6S_6$, fw 530.75, monoclinic, space group $P2_1/c$ (No. 14), a = 12.517(3) Å, b = 10.073(3) Å, c = 20.220(4) Å, β = 107.14(2)°, U = 2436(1) Å^3, Z = 4, μ = 0.59 mm^{-1}, 12 075 reflections ($2\theta \leq 51°$), 4084 unique, R_{int} = 0.059, 280 refined parameters (H atoms 'riding'), R = 0.072 [2695 data with $F^2 \geq 2\sigma(F^2)$], wR(F^2) = 0.144, max residual $\Delta\rho$ = 0.45 e Å^{-3}. Full structural data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142587.

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