# Dithia-Crown-Annelated Tetrathiafulvalene Disulfides: Synthesis, Electrochemistry, Self-Assembled Films, and Metal Ion Recognition

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The synthesis and electrochemistry of a series of tetrathiafulvalene (TTF) and dithia-crown-TTF derivatives attached with one or two disulfide group(s) **7a**−**f** are reported. The self-assembled monolayers (SAMs) of these TTF disulfides on gold were prepared and characterized by reflection−absorption infrared spectroscopy. The SAMs are extremely stable under a wide variety of conditions and over extended periods of time and show remarkable electrochemical stability upon repeated potential scans. SAMs of the crown-TTF disulfides **7c**,**d**,**f** can recognize alkali metal ions, and the process can be monitored following the electrochemical potential shift of the surface-confined TTF group.

## Introduction

Functionalized self-assembled monolayers (SAMs) have received considerable attention because of their ability to easily modify the chemical and physical properties of the substrate surfaces to which they are bound and to provide a variety of chemically tailored surfaces.[1−3] SAMs also offer an easy route to prepare active and fast-responding sensors if appropriate receptor groups are linked to a transduction element (such as a redox center or an optically absorbing group).[4−6] Molecular recognition events on the surfaces of these well-organized assemblies can thus be used to monitor and sense specific analytes in solution. Illustrative examples of receptor molecules that have been incorporated in SAMs include calix[4]-resorcinarenes,[1,4] 2,2′-thiobisethylacetoacetate,[3] crown ethers,[5] and cyclodextrins.[6−8] In the present work, we are particularly interested in the use of immobilized crown ether groups as potential ion sensors in SAMs, employing the redox active tetrathiafulvalene (TTF) as the transduction group.[5b] The overall concept is based on the following observations: (i) Becher et al. reported that appropriate dithia-crown-TTFs can recognize alkali metal ions in homogeneous solution due to an inductive effect on the polarizable TTF system.[9] (ii) Ward et al. described SAMs on gold electrodes of *n*-mercaptoalkyl tetrathiafulvalenecarboxylate terminated in a thiol group, even though the SAMs were relatively unstable.[10] (iii) Recently, Reinhoudt et al.[5a] and Moore et al.[5b] reported the incorporation of crown-ether groups into SAMs and their responses as potential metal ion sensors. 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 the ion binding events on the surface.[5a] The other reported dithia-crown-annelated TTF derivatives that also contained single alkyl chains terminated in a thiol group.[5b] This work exploited the direct electrochemical response of the crown-TTF to measure the effect of ion complexation, similar to the work in homogeneous solution reported by Becher et al.[9] However, these SAMs were apparently not very stable under several conditions, and the electrochemical responses observed were rather weak and ill-resolved.[5b] Very recently, we reported very stable SAMs of bis-thioctic ester derivative of TTFs which exhibit well-resolved, surface-confined electrochemistry.[11] Here we report the synthesis, electrochemistry, SAM formation and characterization, and alkali metal cation recognition properties of the SAMs of a series of TTF and dithia-crown annelated TTF derivatives containing one or two surface active disulfide group(s) to anchor the systems to the metal surfaces.

## Experimental Section

**Electrochemistry.** All electrochemical experiments were performed on a BAS 100W electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN) at room temperature with a three-electrode configuration containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte, which was recrystallized twice from ethanol and dried under vacuum. A glassy carbon (GC, ∅ 3 mm) or the SAM-modified spherical gold electrodes were used as the working electrodes, and the counter electrode was a platinum

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wire (∅ 1 mm). An aqueous Ag/AgCl or nonaqueous Ag/Ag$^+$ electrode served as reference. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. The scan rate was generally 100 mV s$^{-1}$ unless otherwise specified.

**General Synthetic Procedure of 2b−d.**[12] To a −10 °C mixture of ethylene glycol (tri-, tetra-, or penta-) (0.1 mol), dry THF (70 mL), and pyridine (3 mL, 37 mmol) was added dropwise (ca. 30 min) 7.5 mL of $PBr_3$ (80 mmol). After the addition, the mixture was stirred for an additional 5 h at 0 °C and then left unstirred overnight. THF was removed, the mixture was extracted with ether and dried over $MgSO_4$, and the solvent was removed to give a yellow oil, which was distilled under high vacuum to yield a colorless oil fraction at ca. 220 °C. The yield was around 60%. The compounds were characterized by FAB$^+$-MS and $^1$H NMR, which agreed well with the published data[12] and the proposed structure.

**General Synthetic Procedure of 3b−d.** To a 1000 mL round-bottom flask were added **2b**−**d** (10.0 mmol), the Zn salt **1** (5.0 mmol), and acetone (500 mL). The mixture was bubbled with nitrogen for about 10 min and then heated to reflux under nitrogen for 2 days. After removal of the solvent, the mixture was extracted with $CH_2Cl_2$ (3 × 100 mL). The organic solution was then washed with water (3 × 50 mL), separated, and dried over $MgSO_4$ and the solvent removed to give a red oil, which was subjected to column chromatography on silica gel (230−400 mesh), eluting with a $CH_2Cl_2$/acetone mixture. The yield was about 60−75%. Characterization of compounds **3b**−**d** agreed well with that reported by Becher et al., who synthesized the compounds using the dithiolate salts rather than **1**.[9]

**Synthesis of 5c.**[13] To a 50 mL round-bottom flask were added **3c** (1.87 g, 4.66 mmol), **4** (1.10 g, 4.66 mmol), and 10 mL of freshly distilled triethyl phosphite. The mixture was stirred and heated to 110 °C (oil temperature) under Ar for a period of 2 h. After the excess triethyl phosphite was evaporated under high vacuum, the residue was then subjected to column chromatography on silica gel (70−230 mesh) eluting with 2:1 $CH_2Cl_2$/hexane. After the first fraction was eluted, the eluent was changed to 10:1 $CH_2Cl_2$/acetone. The last fraction was the target compound and gave a 63% yield as a purple solid. FT-IR (KBr, cm$^{-1}$): 1722 (vs, C=O). $^1$H NMR ($CDCl_3$, ppm): 3.01 (t, $J$ = 6.3 Hz, 4H), 3.64−3.66 (m, 12H), 3.70−3.75 (m, 4H), 3.83 (s, 6H). $^{13}$C NMR ($CDCl_3$, ppm): 35.92, 53.57, 69.84, 70.66, 70.96, 70.98, 108.93, 112.86, 128.39, 132.10, 160.07. FAB$^+$-MS: $m/z$ 586 (M$^+$, 100). HRMS: found 585.9954, calcd for $C_{20}H_{26}O_8S_6$ 585.9952.

**Synthesis of 6c.**[13] To a 100 mL three-necked round-bottom flask were added **5c** (0.8 g, 1.36 mmol), 30 mL of dry THF, and 7.5 mL of methanol. The mixture was stirred and cooled to 0 °C. Then, $NaBH_4$ (0.415 g, 10.97 mmol) and LiCl (0.51 g, 12.03 mmol) were added under nitrogen. After being stirred at 0 °C for about 4 h, the cooling bath was removed and stirring was continued for an additional 1 h at room temperature. Then the reaction mixture was cooled again, and 25 mL of saturated $NH_4Cl$ aqueous solution was added dropwise at 0 °C. After the addition, the mixture was extracted with AcOEt (3 × 80 mL), and the combined organic layers were washed with brine (2 × 40 mL), separated, and dried over $Na_2SO_4$. After removal of the solvent, most of the dialcohol TTF **6c** was collected as a pale yellow solid and purified by washing the mixture with $CH_2Cl_2$. The filtrate was subjected to flash chromatography on silica gel (70−230 mesh) eluting with 2:1 (v/v) $CH_2Cl_2$/acetone. The total yield was 85%. FT-IR (KBr, cm$^{-1}$): 3340 (br, s, −OH), 1090 (s, CO). $^1$H NMR (DMSO-$d_6$, ppm): 3.02 (t, $J$ = 6.3 Hz, 4H), 3.51−3.55 (m, 12H), 3.62 (t, $J$ = 6.2 Hz, 4H), 4.24 (d, $J$ = 5.7 Hz, 4H), 5.51 (t, $J$ = 5.7 Hz, 2H). $^{13}$C NMR (DMSO-$d_6$, ppm): 34.93, 56.58, 68.94, 69.56, 70.01, 70.03, 103.56, 115.03, 127.24, 131.48. FAB$^+$-MS: $m/z$ 530 (M$^+$, 100). HRMS: found 530.0049, calcd for $C_{18}H_{26}O_6S_6$ 530.0054.

**Synthesis of 6e,f.** Monoalcohols **6e**−**f** were prepared by controlled reduction of one of the two ester groups of the corresponding diester-TTF derivatives using $NaBH_4$−LiCl in a mixed solvent of dry THF and absolute ethanol (4:1 v/v),[14] similar to the preparation of **6c** as described above, or separated as a minor byproduct during the preparation of **6a** and **6d**, respectively. It should be pointed out that only **6f** was separated as a byproduct in the preparation of **6d**. **6e**: pale yellow solid. FT-IR (KBr, cm$^{-1}$): 3249 (m, −OH), 1709 (s, C=O). UV−vis ($CH_2Cl_2$, $\lambda_{max}$, nm): 310, 331, 429. $^1$H NMR (DMSO-$d_6$, ppm): 3.39 (s, 4H), 3.72 (s, 3H), 4.66 (d, 2H, $J$ = 5.90 Hz), 6.21 (t, 1H, $J$ = 5.93 Hz). $^{13}$C NMR (DMSO-$d_6$, ppm): 29.51, 52.79, 59.91, 104.64, 112.85, 112.95, 113.20, 115.07, 158.52, 159.38. MS (FAB$^+$): 382 (M$^+$, 100). **6f**: pale yellow solid. FT-IR (KBr, cm$^{-1}$): 3250 (m, −OH), 1050 (m, CO). $^1$H NMR ($CDCl_3$, ppm): 3.04 (t, $J$ = 6.3 Hz, 4H), 3.67−3.72 (m, 20H), 4.40 (d, $J$ = 0.9 Hz, 2H), 6.24 (s, 1H). FAB$^+$-MS: $m/z$ 544 (M$^+$, 100). HRMS: found 544.0208, calcd for $C_{19}H_{28}O_6S_6$ 544.0210.

**General Procedure for the Preparation of TTF Bis- and Monodisulfides 7a−f.** To a 5 mL of $CH_2Cl_2$ were added the alcohol-functionalized TTF (0.1−0.2 mmol) and thioctic acid (2.5 molar equiv for dialcohols **6a**−**d** or 1.2 molar equiv for monoalcohols **6e**−**f**). The mixture was stirred for 15 min at 0 °C (ice/water bath) under $N_2$. Then 1,3-dicyclohexylcarbodiimide (DCC) (3 molar equiv for dialcohols **6a**−**d** or 1.5 molar equiv for monoalcohols **6e**−**f**) and 4-(dimethylamino)pyridine (DMAP) or 4-pyrrolidinopyridine (0.6 molar equiv for dialcohols **6a**−**d** or 0.3 molar equiv for monoalcohols **6e**−**f**) in 5 mL of cold $CH_2Cl_2$ were added, and the mixture was stirred for another 15 min at 0 °C. The cooling bath was then removed and the solution allowed to warm to room temperature. After being stirred for 48 h under $N_2$, the reaction mixture was filtered through a fine glass frit to yield a clear filtrate and the insoluble urea byproduct as a fine white-gray powder. The clear filtrate was washed with water (3 × 50 mL), 5% acetic acid aqueous solution (3 × 20 mL), and finally again with water (3 × 30 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated, and the residue was subjected to column chromatography.

**7a.** Silica gel (230−400 mesh) eluting with $CH_2Cl_2$ afforded the compound as a red oil. Yield: 84%. $^1$H NMR ($CDCl_3$, ppm): 4.90 (4H, s), 3.56−3.54 (2H, m), 3.29 (4H, s), 3.23−3.15 (4H, m), 2.51−2.41 (2H, m), 2.38−2.33 (4H, m), 1.93−1.90 (2H, m), 1.76−1.71 (8H, m), 1.58−1.55 (4H, m). $^{13}$C NMR ($CDCl_3$, ppm): 173.10, 140.17, 129.95, 114.39, 114.36, 106.91, 60.31, 58.30, 56.29, 55.17, 37.00, 35.28, 33.58, 30.60, 25.81, 25.07, 24.18, 23.35. UV−vis ($CHCl_3$, $\lambda_{max}$, nm): 335, 309. FAB$^+$-MS: $m/z$ 731 (M$^+$, 100). HRMS: found 730.9735, calcd for $C_{26}H_{34}O_4S_{10}$ 730.9742.

**7b.** Silica gel (230−400 mesh) eluting with hexane/ethyl acetate (1:1) afforded the compound as a red-orange solid. Yield: 87%. $^1$H NMR ($CDCl_3$, ppm): 4.91 (4H, s), 3.91 (4H, t, $J$ = 5.34 Hz), 3.74−3.67 (12H, m), 3.58 (4H, t, $J$ = 5.40 Hz), 3.19−3.14 (4H, m), 2.99 (2H, t, $J$ = 5.90 Hz), 2.45−2.37 (4H, m), 1.94−1.85 (2H, m), 1.79−1.63 (8H, m), 1.49−1.46 (4H, m). $^{13}$C NMR ($CDCl_3$, ppm): 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. UV−vis ($CHCl_3$, $\lambda_{max}$, nm): 327.5, 304.0. FAB$^+$-MS: $m/z$ 862 (M$^+$, 60). HRMS: found 862.0453, calcd for $C_{32}H_{46}O_7S_{10}$ 862.0451.

**7c.** Silica gel (230−400 mesh) eluting with 20:1 $CH_2Cl_2$/acetone afforded the compound as a red-orange solid. Yield: 80%. $^1$H NMR ($CDCl_3$, ppm): 1.46−1.48 (m, 4H), 1.65−1.72 (m, 8H), 1.90−1.95 (m, 2H), 2.33−2.38 (m, 4H), 2.44−2.53 (m, 2H), 3.02 (t, $J$ = 6.3 Hz, 4H), 3.13−3.18 (m, 4H), 3.51−3.60 (m, 2H), 3.66−3.68 (m, 12H), 3.70−3.76 (m, 4H), 4.89 (s, 4H). $^{13}$C NMR ($CDCl_3$, ppm): 24.72, 25.13, 25.81, 28.85, 33.92, 34.15, 34.76, 35.89, 38.72, 40.42, 49.31, 56.45, 58.16, 69.85,

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70.70, 71.02, 108.43, 111.29, 128.35, 129.78, 133.13, 172.95. FAB$^+$-MS: *m/z* 906 (M$^+$, 100). HRMS: found 906.0709, calcd for $C_{34}H_{50}O_8S_{10}$ 906.0713.

**7d.** Silica gel (230−400 mesh) eluting with hexane/ethyl acetate (1:2) afforded the compound as an orange solid. Yield: 85%. $^1$H NMR (CDCl$_3$, ppm): 4.90 (s, 4H), 4.07 (4H, t, $J = 6.0$ Hz), 3.73−3.67 (20H, m), 3.49−3.46 (2H, m), 3.13−3.04 (4H, m), 2.45−2.39 (2H, m), 2.37−2.34 (4H, m), 1.96−1.91 (2H, m), 1.67−1.61 (8H, m), 1.38−1.29 (4H, m). UV−vis (CHCl$_3$, $\lambda_{max}$, nm): 325.50, 304.00. FAB$^+$-MS: *m/z* 950 (M$^+$, 100). HRMS (FAB$^+$) *m/z* found 950.0977, calcd for $C_{36}H_{54}O_9S_{10}$ 950.0975.

**7e.** Silica gel (230−400 mesh) eluting with $CH_2Cl_2$ afforded the compound as a red oil. Yield: 85%. **7e** was also prepared following the same procedure but using dry THF instead of $CH_2Cl_2$ to yield 83%. $^1$H NMR (CDCl$_3$, ppm): 5.34 (2H, s), 3.81 (3H, s), 3.61−3.56 (1H, m), 3.30 (4H, s), 3.19−3.14 (1H, m), 2.88−2.66 (1H, m); 2.42−2.38 (2H, m), 1.95−1.90 (2H, m), 1.72−1.64 (4H, m), 1.53−1.48 (2H, m). $^{13}$C NMR (CDCl$_3$, ppm): 172.55, 160.17, 147.14, 121.62, 114.36, 112.62, 108.53, 60.99, 56.66, 56.10, 53.05, 40.59, 38.90, 35.31, 34.96, 34.08, 30.65, 29.02, 25.87, 25.03, 24.93. UV−vis (CHCl$_3$, $\lambda_{max}$, nm): 432, 332, 305. FAB$^+$-MS: *m/z* 570 (M$^+$, 100). HRMS (FAB$^+$): *m/z* found 569.9283, calcd for $C_{19}H_{22}O_4S_8$ 569.9284.

**7f.** Silica gel (70−230 mesh) eluting with 10:1 $CH_2Cl_2$/acetone afforded a red-orange solid. Yield: 90%. $^1$H NMR (CDCl$_3$, ppm): 6.34 (s, 1H), 4.82 (s, 2H), 3.73−3.67 (m, 20H), 3.49−3.46 (m, 1H), 3.17−3.14 (m, 2H), 3.06−3.02 (m, 4H), 2.45−2.39 (m, 1H), 2.37−2.34 (m, 2H), 1.96−1.91 (m, 1H), 1.67−1.61 (m, 4H), 1.38−1.29 (m, 2H). FAB$^+$-MS: *m/z* 732 (M$^+$, 100). HRMS: found 732.0539, calcd for $C_{27}H_{40}O_7S_8$ 732.0540.

**Monolayer Preparation.** A ∅ 250 $\mu$m gold wire (99.9999%) was cleaned by boiling in 37% nitric acid overnight and rinsed with copious amounts of 18 MΩ water (Barnstead). Spherical gold electrodes were prepared by heating the wire in a natural gas/O$_2$ flame until a small gold sphere formed on the end of the wire followed by cooling in the water (Barnstead). This process leads to the formation of well-defined Au(111) facets, as described in earlier reports.[15] The gold wire was then sealed into a glass capillary leaving only the gold sphere exposed. The gold sphere was annealed in the natural gas/O$_2$ flame again and cooled under an Ar atmosphere before monolayer preparation. The geometric areas of the gold electrodes were calculated from the slopes of the linear plots of the cathodic peak current versus the square root of the scan rate obtained for the diffusion-controlled reduction of $Ru(NH_3)_6^{3+}$. We employed a diffusion coefficient of $7.5 \times 10^{-6}$ cm$^2$/s (at 25 °C in 0.1 M NaCl).[10] Typical values for the geometric area of the electrode varied between 0.01 and 0.02 cm$^2$. Surface coverages of the SAMs of the TTF derivatives were calculated by integration of the current during the first scan.

Monolayers were typically prepared by immersing the freshly prepared gold-bead electrodes into a THF solution containing the appropriate disulfides in mM concentrations for 24−48 h.[11,16] To investigate the possibility of a solvent effect on the formation of the monolayers, DMSO and $CH_2Cl_2$ were also employed. After removal from solution, the gold-bead electrodes were rinsed with the appropriate solvent and dried in air.

**Infrared Spectroscopy.** For monolayer characterization, the reflection−absorption infrared spectra (RAIRs) were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer, equipped with a grazing angle (80°) infrared reflection accessory and a ZnSe wiregrid polarizer from International Crystal Laboratory. The spectra were recorded with a liquid nitrogen cooled MCT detector and the measurement chamber was continuously purged with nitrogen gas during the measurements. Typically 1000 scans with 4 cm$^{-1}$ resolution were performed to get the average spectra. A clean and freshly prepared gold plate was used to record the reference spectra. The RAIRs are reported as $-\log(R/R_0)$, where $R$ and $R_0$ are the reflectivities of the sample and reference, respectively.

The transmission infrared spectra of the compounds **7b−d** were recorded for thin films prepared by putting a drop of the solution of the compound on a quartz cell and then evaporating with a flow of Ar in the same spectrometer using 500 scans with 4 cm$^{-1}$ resolution.

## Results and Discussion

**Synthesis.** Generally speaking, most of the reported SAMs on gold are derived from alkanethiols[5] or from *n*-alkyl disulfides.[17−19] To generate the thiol group(s), a well-established method is to convert −Br to −SH by refluxing RBr with thiourea in ethanol followed by hydrolysis with potassium hydroxide.[5b,10,20] However, the yield is normally somewhat low, and the SAMs of these mono-thiols are typically electrochemically unstable upon repeated voltammetric cycling.[5b,10] Very recently a novel TTF compound containing four thiol groups was reported, which formed very robust SAMs on gold electrodes, and these were remarkably stable after repeated voltammetric cycling.[21] 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.[22] For these reasons, the use of thioctic acid derivatives to anchor SAMs on metal surfaces has received considerable recent attention.[17−19] In addition, thioctic acid is commercially available and easy to incorporate into a wide variety of structures via simple condensation reactions, as reported in the present work. This method is much easier and more effective, involving a single reaction and affording high yields by attaching thioctic acid to TTF derivatives incorporating hydroxy group(s) (Scheme 1), which affords a mild and direct introduction of the disulfide group(s) to the TTF derivatives. Moreover, the SAMs of the TTF disulfides are much more stable than those previously reported.[10,5b] Thus, TTF disulfides **7a−f** were prepared according to the procedures shown in Scheme 1 starting from 4,5-ethylenedithio-1,3-dithiole-2-thione (**3a**), 5,8,11-trioxa-2,14,16,18-tetrathiabicyclo[13.3.0]octadec-1(15)-ene-17-thione (**3b**), 5,8,11,14-tetraoxa-2,17,19,21-tetrathiabicyclo[16.3.0]hexaicos-1(18)-ene-20-thione (**3c**), or 5,8,11,14,17-pentaoxa-2,20,22,24-tetrathiabicyclo[19.3.0]tetraicos-1(21)ene-23-thione (**3d**), all of which were synthesized according to well-established procedures[9] with a slight modification (Scheme 1). The modification consisted of reacting bis(tetrabutylammonium)-bis(1,3-dithiole-2-thione-4,5-dithiolate)-zincate(II), the Zn salt **1**, $(n\text{-}Bu_4N)_2$-Zn(dmit)$_2$, rather than the dithiolate salt reported by Becher et al.[9] with the corresponding 1,2-dibromoethane (**2a**) or dibromo glycols (**2b−d**) in acetone at reflux for about 2 days under nitrogen using high-dilution techniques (see Experimental Section). The yields (60−75%) for **3b−d** are reasonably high compared to those of

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**Scheme 1. Synthetic Procedures for Compounds 7a−f**

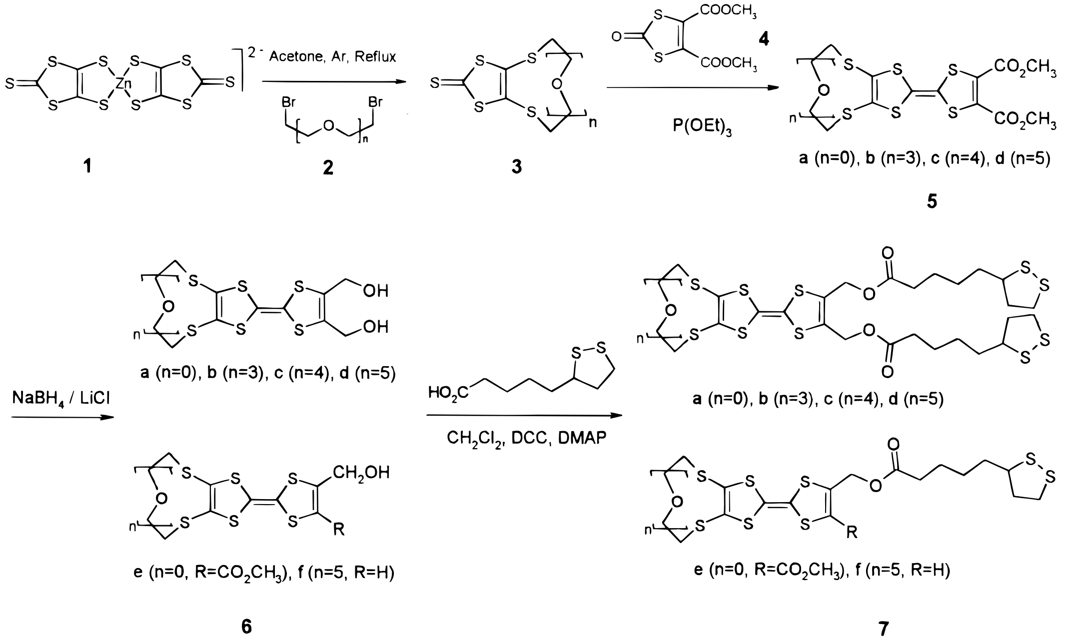

**Chart 1**

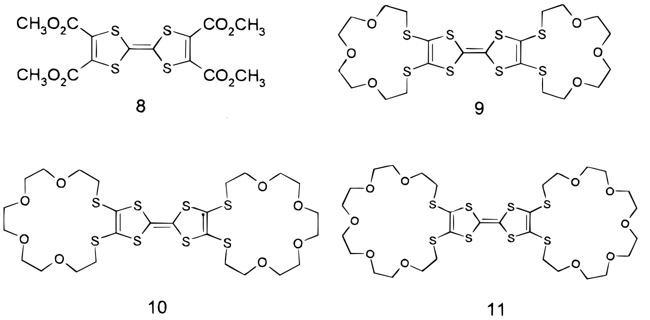

**Table 1. Electrochemical Data of 7a−f in THF−TBAPF$_6$ at Room Temperature with a Scan Rate of 100 mV s$^{-1}$**

| compd | $E_{1/2}{}^1$ ($\Delta E_p$)/mV | $E_{1/2}{}^2$ ($\Delta E_p$)/mV |
|---|---|---|
| **7a** | 655 (55) | 866 (52) |
| **7b** | 644 (67) | 832 (80) |
| **7c** | 685 (58) | 822 (56) |
| **7d** | 637 (67) | 790 (77) |
| **7e** | 726 (66) | 949 (58) |
| **7f** | 637 (52) | 799 (62) |

Becher's.[9] It should be pointed out that the large scale synthesis of **2b**−**d** was reported long ago. Our procedure was slightly different, since THF was used as the solvent and the reaction gave higher yields. Cross coupling between the 1,3-dithiole-2-thione **3a**−**d** and 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-one (**4**) in neat triethyl phosphite at 110−140 °C afforded the unsymmetrically substituted crown-ether TTF diester **5** in reasonably high yields (40−60%). Theoretically speaking, symmetric TTF derivatives (Chart 1) tetramethoxycarbonyltetrathiafulvalene (**8**) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), or 1,4,5,6-tetrahydro-2(3),6(7)-bis(4,7,10-trioxa-1,13-dithiatridecane-1,13-diyl)-1,4,5,8-tetrathiafulvalene (**9**), or 1,4,5,6-tetrahydro-2(3),6(7)-bis(4,7,10,13-tetraoxa-1,16-dithiahexadecane-1,16-diyl)-1,4,5,8-tetrathiafulvalene (**10**), or 1,4,5,6-tetrahydro-2(3),6(7)-bis-(4,7,10,13,16-pentaoxa-1,19-dithianonadecene-1,19-diyl)-1,4,5,8-tetrathiafulvalene (**11**) could be formed in addition to the unsymmetrical ones (**5a**−**d**) during such cross-coupling reactions. However, except for **8** which was formed in all cases and for a small amount BEDT-TTF formed during the preparation of **5a**, we did not observe any symmetric dithia-crown annelated TTF derivatives (**9**, **10**, or **11**, Chart 1) during the preparation of **5b**−**d**. This reflects the low reactivity of the 1,3-dithiole-2-thione **3b**−**d** to self-coupling.[11] Reduction of the two ester groups of **5** using NaBH$_4$ and LiCl in a mixed solvent of THF and methanol (4:1 v/v)[14] gave the corresponding dialcohol TTF derivatives **6**. In general, the reduction products should be mixtures of mono- and dialcohol TTFs and the separation could be difficult. However, only trace amount of the monoalcohol TTF was present in the reaction mixture for all the cases and, due to the great differential solubility between the mono- and dialcohol products in CH$_2$Cl$_2$, separation was accomplished by washing the crude product mixture with cold CH$_2$Cl$_2$ (**6a**−**c**). Alternatively, due to their polarity difference, analytically pure di-alcohols were readily obtained by a flash column chromatography on silica gel (70−230 mesh) eluting with a CH$_2$Cl$_2$/acetone mixture (**6c**: 2:1 CH$_2$Cl$_2$/acetone; **6d**: 5:2 CH$_2$Cl$_2$/acetone). Finally, compounds **7a**−**f** were synthesized in high yield by direct coupling between the corresponding alcohols with thioctic acid in CH$_2$Cl$_2$ in the presence of DCC and DMAP or 4-pyrrolidinopyridine. It should be stressed that this direct coupling reaction to prepare TTF disulfides is general, straightforward and gives high yields (>80%).

**Electrochemistry and Complexation Studies in Solution.** The electrochemistry and the complexation properties of compounds **7a**−**f** with alkali metal ions (Li$^+$, Na$^+$, and K$^+$) in solution were investigated by cyclic voltammetry.

As shown in Table 1, TTF derivatives **7a**−**f** undergo two, one-electron, redox processes in THF−TBAPF$_6$ on a glassy carbon electrode, giving two pairs of well-defined redox peaks with $\Delta E_p$<80 mV, typical for TTFs.[9,23,24] The oxidation potentials (except for the first oxidation of **7c**),

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(23) (a) For a recent review, see: Bryce, M. R. *J. Mater. Chem.* **1995**, *5*, 1481. (b) Devonport, W.; Bryce, M. R.; Marshallsay, G. J.; Moore, A. J.; Goldenberg, L. M. *J. Mater. Chem.* **1998**, *8*, 1361.

**Table 2. Electrochemical Recognition for 7b,c,d (1.0 mM) in the Presence of Different Alkali Metal Ions (ca. 5 mM) in THF Solution**

| | 7b | | 7c | | 7d | |
|---|---|---|---|---|---|---|
| ions | $E_{1/2}^1$ | $E_{1/2}^2$ | $E_{1/2}^1$ | $E_{1/2}^2$ | $E_{1/2}^1$ | $E_{1/2}^2$ |
| $LiPF_6$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $NaPF_6$ | +10 | 0 | +11 | +10 | +40 | +30 |
| $KPF_6$ | 0 | 0 | +14 | +11 | +15 | +20 |

especially for the second oxidation, show a small but evident trend: **7a** > **7b** > **7c** > **7d**. This correlates with the electron-donating ability of the crown-ether group.[13] In addition, the current varies linearly with the square root of the scan rate indicative of diffusion controlled processes and the peak-to-peak separation increases slightly with the scan rate indicating a slow electron-transfer process.

Complexation in homogeneous solution was also studied by cyclic voltammetry. As discussed above, **7a**−**f** exhibit two, one-electron, reversible oxidation waves. The CVs were also recorded after addition of ca. 5 molar equiv of $MPF_6$ ($M^+ = Li^+$, $Na^+$, or $K^+$) to THF−$TBAPF_6$ solutions. The results are summarized in Table 2. As can be seen the addition of 5 mM $LiPF_6$, $NaPF_6$, or $KPF_6$ to a 1.0 mM solution of **7a** or **7e** in THF−$TBAPF_6$ system had no effect on the observed potentials, indicating that the alkali metal ions do not interact with the thioctic acid−TTF moieties. Addition of 5 mM $NaPF_6$ to a 1.0 mM THF solution of **7b** results in a 10-mV positive potential shift of the first redox peak ($TTF/TTF^{\bullet+}$), while the second reduction process ($TTF^{+\cdot}/TTF^{2+}$) remains unchanged. These observations are similar to those previously reported for analogous compounds **9**−**11** (Chart 1) in homogeneous solution and could be interpreted in terms of complex dissociation due to a repulsive interaction after initial formation of $TTF^{+\cdot}$.[9] However, the $Na^+$ or $K^+$ induced potential shift for either **7c** or **7d** in THF solution is between +10 and +40 mV for both the first and second redox processes (Table 2). This is different from previous observations with similar compounds.[9]

As an example, in the case of **7d**, the shifts in the presence of $Na^+$ are +40 mV ($TTF/TTF^{\bullet+}$) and +30 mV ($TTF^{\bullet+}/TTF^{2+}$), for the first and second oxidations, respectively (Figure 1). $K^+$ also causes a positive potential shifts, but smaller than those caused by $Na^+$ (Table 2). As shown in Table 2, the affinity sequence for **7d** is $Na^+ > K^+ > Li^+$, for **7c**, it is $Na^+ \sim K^+ > Li^+$.

On the whole, it can be concluded that (i) the observed shifts, as expected, were always anodic (more positive); (ii) the shifts, if any, of the first oxidation peak were always larger than those for the second one; (iii) no $Li^+$ effect was observed with any of the compounds; (iv) the shifts for compound **7d** are larger than those for compounds **7b** or **7c**; and (v) the largest shifts observed for compound **7d** were found in the presence of sodium ions, with a general order of $Na^+ > K^+ > Li^+$.

Evidence that the shifts observed arise from complexation comes from the fact that **7a** and **7e** (no crown ether present in either) showed no cation effects and **5b** and **5d**, which do possess a crown-ether moiety, showed almost the same behavior.[13]

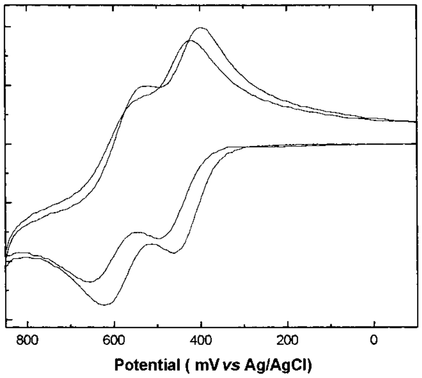

**Figure 1.** CVs of 1.0 mM of **7d** in THF solution containing 0.1 M $TBAPF_6$ in the absence and presence of 5.0 mM $NaPF_6$. The working electrode was a platinum electrode, and Ag/AgCl + 0.1 M $TBAPF_6$ in THF was the reference electrode.

Comparing the shifts observed for **7b**−**d** with those obtained by Becher et al.[9] for the analogous symmetric crown-ether annelated TTFs **9**, **10**, and **11** (Chart 1) shows that for **7b** the shifts are identical to those observed for **9**, while those of **7c**,**d**, are different from those of **10** or **11**. Both $E_{ox}^1$ and $E_{ox}^2$ changed for **7c**,**d** upon metal ion additions, but only the first oxidation potentials were positively shifted for **10** or **11**. The potential shifts for **7c** follow the order $Na^+ \sim K^+ > Li^+$, for **7d** it is $Na^+ > K^+ > Li^+$, but for **10**, the trend is $Na^+ > K^+ > Li^+$ and for **11**, the order is $K^+ > Na^+ > Li^+$.

**Characterization of Monolayers by Reflection−Absorption Infrared Spectroscopy (RAIR).** RAIR spectroscopy was used to provide information about monolayer formation and also about the degree of organization. The conventional transmission spectrum of compound **7b** (spectrum not shown here) shows peaks at 2925 and 2852 $cm^{-1}$ due to the asymmetric and symmetric stretching modes of the $-CH_2$ in the alkyl chains, respectively.[25] A strong band is observed at 1731 $cm^{-1}$ that is due to the ester $-C{=}O$ group.[26] Peaks at 1157 and 1129 $cm^{-1}$ are assigned to the symmetric −C−O−C− stretching from the anchoring chain.[27] Moreover, a peak at 1232 $cm^{-1}$ is due to the antisymmetric −C−O−C− band. The transition dipole of the former band should be aligned parallel to the axis bisecting the C−O−C angle while that of the latter should be perpendicularly aligned. Besides these, absorbances at 891, 783, 731, and 668 $cm^{-1}$ are assigned to various −C−S stretching modes of the TTF moiety and the peak at 1540 $cm^{-1}$ corresponds to the C=C ring stretch of the TTF ring.[10] Since compounds **7** (**b**, **c**, and **d**) are structurally similar, only data for **7b** are presented, both from the conventional transmission spectrum along with those of the SAM on a gold surface; see Table 3.

Figure 2 shows the RAIR spectra of monolayers of three different compounds at two different frequency ranges. Comparisons of the conventional transmission spectrum with those of the monolayers in the higher frequency region reveal that for all three monolayers the peak positions for the $-CH_2$ symmetric and antisymmetric stretching are the same or shifted to higher wavenumber, suggesting a disordered or liquidlike packing environment of the methylene chains in the monolayers.[28]

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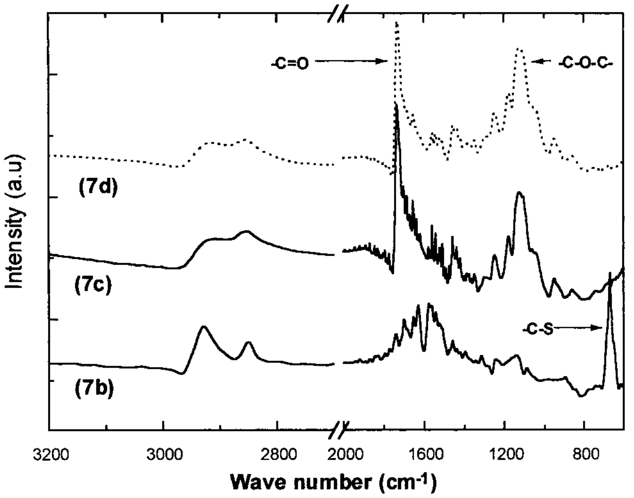

**Figure 2.** RAIR spectra of the monolayers of **7b**,**c**,**d** in two different frequency ranges.

**Table 3. Vibrational Mode Assignment ($cm^{-1}$) of Major Peaks Observed by Transmission IR Spectra of 7b and by RAIR Spectroscopy of Different Monolayers on a Gold Surface**

| transmission IR of **7b** | RAIR of **7b** | RAIR of **7c** | RAIR of **7d** | assignment |
|---|---|---|---|---|
| 2925 | 2928 | 2925 | 2925 | $\nu_{as}(-CH_2)$ |
| 2852 | 2848 | 2851 | 2851 | $\nu_{a}(-CH_2)$ |
| 1731 | 1737 | 1731 | 1737 | $\nu$ (−C=O) |
| 1540 | 1571 | | | $\nu$ (C=C) central |
| 1232 | 1241 | 1246 | 1245 | $\nu_{as}$ (−C−O−C−) |
| 1157 | 1175 | 1175 | 1178 | $\nu_{s}$ (−C−O−C−) |
| 1129 | 1122 | 1122 | 1124 | |
| 974 | | 946 | 950 | $\nu$ (C−S) from TTF |
| 891 | 893 | 859 | 860 | |
| 783 | | 740 | 744 | |
| 731 | | | | |
| 668 | 666 | 672 | 670 | |

This is expected since molecules with short alkyl chains are known to form disordered monolayers. Moreover, the presence of crown ether terminal groups is probably also responsible for the less ordered structure of these monolayers. It is apparent from the peak positions that increasing the size of the appended crown results in more disordered monolayers, as expected.

Comparison of the RAIR spectra in the lower frequency range (1800−600 $cm^{-1}$) provides information about the orientation of the molecules. For the monolayer of **7b**, a very weak peak was observed for the −C=O stretching at 1737 $cm^{-1}$. The peak due to the −C=C− from the rings and −C−O−C− stretching are also very weak. On the other hand, the −C−S stretching at 666 $cm^{-1}$ is very intense (Figure 2) compared to the one observed in the conventional transmittance spectrum. From the surface selection rule this differential spectral intensity indicates that the two −C=O groups and the −C−O−C− from the anchoring chain as well as the −C=C− in the rings are oriented almost parallel to the metal surface while the −C−S− part from the crown ether is more perpendicular.

In contrast, the RAIR spectra of the monolayers of **7c** and **7d** show an intense peak for the −C=O stretching and a strong absorption due to the −C−O−C− symmetric vibrations but none is observed for the −C−S stretching. This observation strongly suggests that −C=O group in this case is oriented almost perpendicular to the surface. Calculations based on the −C−O−C− vibration[29] suggest a ~60° inclination of the −C−O−C− portion attached to the TTF moiety for the monolayer of **7d** and ~80° for that of **7b,** with respect to the surface. The corresponding angle is 68° for the monolayer of **7c**. These differences in orientation may be due to the changes in the size of the terminal crown ether group.

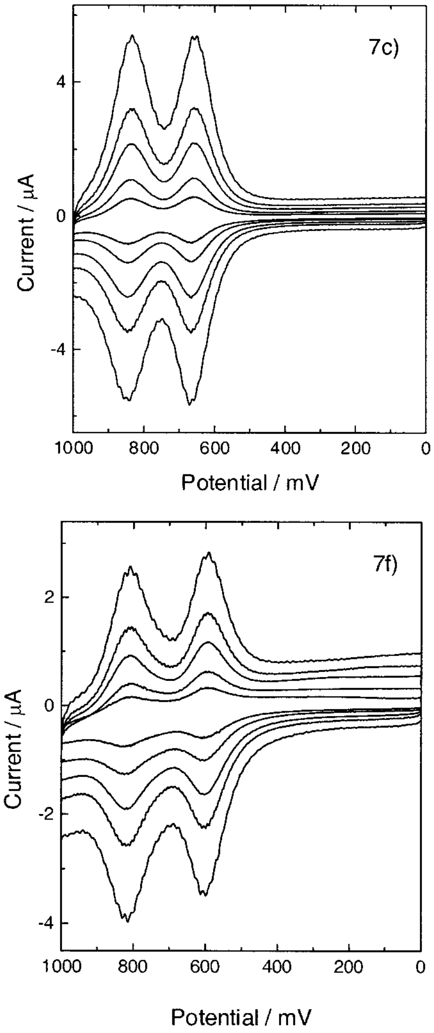

**Figure 3.** CVs of SAMs of **7c**,**f** in THF solution containing 0.1 M $TBAPF_6$ at different scan rates of 100 (the lowest current), 200, 400, 600, and 1000 (the highest current) mV $s^{-1}$.

**Electrochemical and Recognition Properties of the SAMs of the Disulfides.** Figure 3 presents two typical surface-confined CVs of the SAMs of TTF disulfides **7c** and **7f**. The electrochemical data are collected in Table 4. As can be seen in Figure 3 and Table 4, for all cases studied the redox peak currents are proportional to the scan rate and the peak shapes, peak potentials and peak-to-peak separations are independent of the scan rate up to 1000 mV $s^{-1}$, indicative of well-behaved surface-confined electrochemical processes. The anodic and cathodic peak-to-peak separations are less than 20 mV in all cases, and the full width at half-maximum (fwhm) is 95−110 mV in THF solution. For surface-confined redox centers where no lateral interactions exist

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**Table 4. Electrochemical Data of SAMs of the TTF Disulfides in THF−TBAPF$_6$ System at Room Temperature with a Scan Rate of 100 mV s$^{-1}$**

| SAMs of the disulfides | $E_{1/2}{}^1$ ($\Delta E_p$)/mV | $E_{1/2}{}^2$ ($\Delta E_p$)/mV | coverage[a] |
|---|---|---|---|
| **7a** | 654 (25) | 904 (15) | 1.58 |
| **7b** | 641 (12) | 846 (5) | 1.16 |
| **7c** | 661 (9) | 841 (7) | 1.79 |
| **7d** | 623 (20) | 798 (15) | 0.86 |
| **7e** | 719 (9) | 996 (13) | 2.21 |
| **7f** | 597 (7) | 817 (7) | 1.07 |

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

**Table 5. Solvent Effect on the Electrochemistry of the SAMs of 7b at Room Temperature with a Scan Rate of 100 mV s$^{-1}$**

| solvent | $E_{1/2}{}^1$ ($\Delta E_p$)/mV | $E_{1/2}{}^2$ ($\Delta E_p$)/mV |
|---|---|---|
| THF | 641 (12) | 846 (5) |
| $CH_2Cl_2$ | 502 (22) | 769 (9) |
| ODCB[a] | 557 (42) | 828 (46) |
| $CHCl_3$ | 543 (19) | 799 (15) |

[a] *o*-Dichlorobenzene.

**Table 6. Solvent Effect on the Electrochemistry of 7b in Solution at Room Temperature with a Scan Rate of 100 mV s$^{-1}$**

| solvent | $E_{1/2}{}^1$ ($\Delta E_p$)/mV | $E_{1/2}{}^2$ ($\Delta E_p$)/mV |
|---|---|---|
| THF | 644 (67) | 832 (80) |
| $CH_2Cl_2$ | 550 (75) | 875 (75) |
| ODCB | 524 (62) | 839 (72) |

**Table 7. Electrochemical Shift for the SAMs of 7b−d in the Presence of Different Alkali Metal Ions (ca. 5 mM)**

| metal ions | SAMs of **7b** | | SAMs of **7c** | | SAMs of **7d** | |
|---|---|---|---|---|---|---|
| | $E_{1/2}{}^1$ | $E_{1/2}{}^2$ | $E_{1/2}{}^1$ | $E_{1/2}{}^2$ | $E_{1/2}{}^1$ | $E_{1/2}{}^2$ |
| $LiPF_6$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $NaPF_6$ | +10 | 0 | +40 | +35 | +60 | +55 |
| $KPF_6$ | 0 | 0 | +45 | +38 | +20 | +30 |

between them and in rapid equilibrium with the electrode, identical surface waves with a zero peak-to-peak separation and a peak width of 90.6/*n* mV are observed (90.6 mV fwhm for a one-electron transfer).[30−32] The fact that the peak-to-peak separations are nonzero but independent of scan rate indicates that slow charge transfer kinetics are not the cause of the observed results. Similar behavior has been previously observed for surface-confined redox centers, and explained on the basis of nonequilibrium states due to slow rate processes, such as electron transfer from the TTF redox center to the gold electrode via tunneling.

The formal potentials of the SAMs of **7d** are slightly shifted cathodically compared with those of the SAMs of **7b**,**c**. The formal potentials of the SAMs of **7a** are higher than those of **7b**. The formal potentials of SAMs of **7e** are 60 mV higher than those of the SAMs of **7a**, surely the result of the $-CO_2CH_3$ group in **7e**. The SAMs of **7a**−**f** are very stable and their electrochemical responses remain essentially unchanged, especially for those of **7a**−**d**, after more than 100 scans because the four sulfurs can bind strongly to the gold surface. By far these are the most robust monolayers that we have ever worked with.

It should be pointed that the electrochemical behavior of the SAMs of the TTF disulfides is highly solvent dependent (Table 5), similar to what is observed in solution, typical of TTF electrochemistry.[33] In aqueous solution, it is impossible to detect a CV response for any of the SAMs studied.

For comparison, solution electrochemical data of **7b** are summarized in Table 6 in different solvents.

The alkali metal cation recognition abilities of the SAMs of **7a**−**f** were checked by CV in the presence of different alkali metal ions and the data are summarized in Table 7. The results of **7f** are almost identical to those of **7d**, which contain the same dithia-crown ether. As reported in homogeneous solution, a significant anodic shift was observed for both the first and second redox processes of the SAMs of **7b**,**c**,**d**,**f** in THF solution when Na$^+$ was added. However, there is no potential shift observed for the SAMs of **7a** or **7e**, in which no crown ether group is present. These results indicate that the potential shifts result from the interaction of M$^+$ with the dithia-crown ether of **7b**,**c**,**d**,**f**. The affinity sequence for the SAMs of **7b**,**d**,**f** was Na$^+$ > K$^+$ > Li$^+$. However, for **7c**, the order is Na$^+$ ∼ K$^+$ > Li$^+$, similar to the solution behavior.

## Conclusions

A general, effective and straightforward synthetic procedure has been developed to prepare dithia-crown annelated TTF disulfides with high yields. The self-assembled monolayers (SAMs) of these TTF disulfides on gold spheres have been prepared and characterized by reflection−absorption infrared spectroscopy, which show different orientations due to changes in the terminal crown size. These electrochemically active SAMs showed well-defined surface confined redox waves characteristic of the TTF moiety, extreme stablity under a wide variety of conditions and over extended periods of time and especially, remarkable electrochemical stability upon repeated potential scans. SAMs of the crown-TTF disulfides **7c**,**d**,**f** can recognize alkali metal ions and the process can be easily monitored following the potential shift of the surface-confined TTF group. These recognition properties and almost indefinite stability show promise as potential thin-film sensors for electrochemically inactive metal ions.

**Acknowledgment.** This work was supported by the National Science Foundation, grant CHE-9816503.

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