
Sheng-Gao Liu, Haiying Liu, Krisanu Bandyopadhyay, Zhiqiang Gao, and Luis Echegoyen*

Department of Chemistry, University of Miami, Coral Gables, Florida 33124

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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 groups 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]-resorcinaranes,1,4 2,2′-thiobisacetoacetate,3 crown ethers,5 and cyclodextrins.6 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-mercaptalkyl tetrathiafulvalene-carboxylate 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.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 (TBAPF6) as the supporting electrolyte, which was recrystallized twice from ethanol and dried under vacuum. A glassy carbon (GC, Ø 3 mm) or the SAM-modified spherical gold electrodes were used as the working electrodes, and the counter electrode was a platinum

* To whom correspondence should be addressed. E-mail: eche-
goyen@miami.edu. Fax: 305 284 4571.

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Dithia-Crown-Annulated Tetraphiafulvalene Disulfides

P. P.; Gates, J. W., Jr.


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 TADDOL (80 mmol). After the addition, the mixture was stirred for an additional 5 h at 0 °C and then left unstered overnight. THF was removed, the mixture was extracted with ether and dried over MgSO4, 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 1H NMR, which agreed well with the published data12 and the proposed structure.

General Synthetic Procedure of 2b–d. To a 1000 mL round-bottom flask were added 2b–d (30.0 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 CH2Cl2 (3 × 100 mL). The organic solution was then washed with water (3 × 50 mL), separated, and dried over MgSO4, and the last fraction was the target compound and gave a 63% yield as a pale yellow solid. FT-IR (KBr, cm−1): 3249 (m, −OH), 1709 (s, C=O). UV–vis (CH2Cl2, λmax nm): 310, 331, 429. 1H NMR (DMSO-d6, ppm): 3.39 (s, 4H), 3.72 (s, 3H), 4.66 (d, 2H, J = 5.90 Hz), 6.21 (1H, J = 5.93 Hz). 13C NMR (DMSO-d6, 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). 1H NMR (CDCl3, ppm): 3.04 (t, J = 6.3 Hz, 4H), 3.67–3.72 (4H, 20MHz), 4.40 (d, J = 0.9 Hz, 2H), 6.24 (s, 1H). FAB-MS: m/z 544 (M+, 100). HRMS: found 544.0208, calcld for C24H40O4S10: 544.0210.

General Procedure for the Preparation of TTF Bis- and Monodisulfides 7a–f. To a 5 mL of CH2Cl2 were added the alcohol-functionalized TTF (0.1–0.2 mmol) and thiocetic acid (2.5 molar equiv for dialcohols 6a–d or 1.2 molar equiv for monodisulfides 6e–f). The mixture was stirred for 15 min at 0 °C (ice-water bath) under N2. Then 1,3-dicyclohexylcarbodiimide (DCC) (3 molar equiv for dialcohols or 0.3 molar equiv for monodisulfides 6e–f) in 5 mL of cold CH2Cl2 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 N2, 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 MgSO4, filtered, and evaporated, and the residue was subjected to column chromatography.


7b. Silica gel (230–400 mesh) eluting with hexane/ethyl acetate (1:1) afforded the compound as a red-orange solid. Yield: 89%. 1H NMR (CDCl3, 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 (2H, m), 1.94–1.85 (2H, m), 1.79–1.63 (8H, m). 11C NMR (CDCl3, ppm): 173.70, 173.17, 154.47, 140.12, 109.29, 128.82, 111.84, 108.38, 71.98, 71.51, 70.38, 60.38, 57.36, 56.36, 40.62, 38.95, 37.05, 36.19, 34.17, 26.72, 25.07. UV–vis (CHCl3, λmax nm): 327.5, 304. FAB-MS: m/z 862 (M+, 60). HRMS: found 862.0453, calcld for C27H19O6S10: 862.0451.

7c. Silica gel (230–400 mesh) eluting with hexane/CH2Cl2 afforded the compound as a red-orange solid. Yield: 80%. 1H NMR (CDCl3, ppm): 4.67–4.62 (t, J = 5.24 Hz, 2H), 4.22 (d, J = 6.2 Hz, 2H), 2.52–2.41 (4H, m), 1.90–1.85 (2H, m), 1.33–1.28 (2H, m), 1.05–1.00 (4H, m). 11C NMR (CDCl3, ppm): 27.42, 25.13, 25.81, 28.85, 33.92, 34.15, 34.76, 35.89, 37.82, 40.42, 49.31, 56.45, 58.16, 69.85.


(13) The synthesis of diester and alcohol functionalized TTFs 5b,d and 6a,b,d were reported in our recent paper: Liu, S.-G.; Echegoyen, L. Eur. J. Org. Chem., in press.
7d. Silica gel (230–400 mesh) eluting with hexane/ethyl acetate (1:2) afforded the compound as an orange solid. Yield: 85%. 1H NMR (CDCl₃, 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). UV–vis (CHCl₃, λmax, nm): 325.50, 304.00. FAB–MS: m/z 570 (M⁺, 100). HRMS (FAB–): m/z found 590.0797, calcld for C₈H₁₉O₄S₅ 590.0795.

7e. Silica gel (230–400 mesh) eluting with CH₃Cl₂ afforded the compound as a red oil. Yield: 85%. 7e was also prepared following the same procedure but using dry THF instead of CH₃Cl₂ to yield 83%. 1H NMR (CDCl₃, 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). UV–vis (CHCl₃, λmax, nm): 323.32, 305.60. FAB–MS: m/z 570 (M⁺, 100). HRMS (FAB–): m/z found 569.9283, calcld for C₈H₁₉O₄S₅ 569.9284.

7f. Silica gel (70–230 mesh) eluting with 10:1 CH₃Cl₂/acetone afforded a red-orange solid. Yield: 90%. 1H NMR (CDCl₃, ppm): 6.34 (s, 1H), 4.82 (s, 2H), 3.73–3.67 (2m, 4H), 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), 1.39–1.29 (m, 2H). FAB–MS: m/z 732 (M⁺, 100). HRMS: found 732.0539, calcld for C₁₂H₂₃O₈S₈ 732.0540.

**Monolayer Preparation.** A 0.250 mM gold wire (99.9999%) was deformed in boiling 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/O₂ 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. 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/O₂ flame again and cooled under an Ar atmosphere before monolayer preparation. The geometrical 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(NH₃)₆³⁺. We employed a diffusion coefficient of 7.5 × 10⁻⁶ cm²/s at 25 °C in 0.1 M NaCl. Typical values for the geometrical area of the electrode vary between 0.01 and 0.02 cm². Surface coverages of the SAMs of the TTF disulfides 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. To investigate the possibility of a solvent effect on the formation of the monolayers, DMSO and CH₃Cl₂ 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(R0/R), where R and R₀ 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 or from n-alkyl disulfides. 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. However, the yield is normally somewhat low, and the SAMs of these mono-thiols are typically electrochemically unstable upon repeated voltammetric cycling. 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. 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. For these reasons, the use of thioctic acid derivatives to anchor SAMs on metal surfaces has received considerable recent attention. 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. Thus, TTF disulfides 7a–f were prepared according to the procedures shown in Scheme 1 starting from 4,5-ethylidithio-1,3-dithiole-2-thione (3a), 5,8,11-trioxo-2,4,6,16-tetrathiabicyclo[13.3.0]octadec-1(15)-ene-17-thione (3b), 5,8,11,14-tetraoxa-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 with a slight modification (Scheme 1). The modification consisted of reacting bis(tetralpylaminommonium)-bis(1,3-dithiole-2-thione-4,5-dithiolate)-zincate (the Zn salt, only (n-Bu₂N)₂-Zn(dmit)₂), rather than the dithiolate salt reported by Becker et al., with the corresponding 1,2-dibromoethane or dibromo glycols 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 previously reported.
Becher's. It should be pointed out that the large scale synthesis of 2b 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 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-1,13-dithiatridecane-1,13-diyI)-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-diyI)-1,4,5,8-tetrathiafulvalene (10), or 1,4,5,6-tetrahydro-2(3),6(7)-bis-(4,7,10,13,16-penta氧a-1,19-dithianonadecene-1,19-diyI)-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 to self-coupling. Reduction of the two ester groups of 5 using NaBH4 and LiCl in a mixed solvent of THF and methanol (4:1 v/v) 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 monoacohol 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 CH2Cl2, separation was accomplished by washing the crude product mixture with cold CH2Cl2 (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 CH2Cl2/acetone mixture (6c: 2:1 CH2Cl2/acetone; 6d: 5:2 CH2Cl2/acetone). Finally, compounds 7a–f were synthesized in high yield by direct coupling between the corresponding alcohols with thioctic acid in CH2Cl2 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–TBAPF6 on a glassy carbon electrode, giving two pairs of well-defined redox peaks with ΔE1/2 < 80 mV, typical for TTFs. The oxidation potentials (except for the first oxidation of 7c),

### Table 1. Electrochemical Data of 7a–f in THF–TBAPF6 at Room Temperature with a Scan Rate of 100 mV s⁻¹

<table>
<thead>
<tr>
<th>compd</th>
<th>E1/2 (ΔE1/2)mV</th>
<th>E1/2 (ΔE1/2)mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>655 (55)</td>
<td>866 (52)</td>
</tr>
<tr>
<td>7b</td>
<td>644 (67)</td>
<td>832 (80)</td>
</tr>
<tr>
<td>7c</td>
<td>685 (58)</td>
<td>822 (56)</td>
</tr>
<tr>
<td>7d</td>
<td>637 (67)</td>
<td>790 (77)</td>
</tr>
<tr>
<td>7e</td>
<td>726 (66)</td>
<td>949 (38)</td>
</tr>
<tr>
<td>7f</td>
<td>637 (52)</td>
<td>799 (62)</td>
</tr>
</tbody>
</table>
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 thiocic
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\(^{1+}\)), while the second
reduction process (TTF\(^{1+}\)/TTF\(^{2+}\)) remains unchanged.
These observations are similar to those previously re-
ported 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\(^{1+}\).\(^{9}\) 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
reduction 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\(^{1+}\)) and +30 mV
(TTF\(^{1+}\)/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\(^+\) > 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 com-
ounds \(7b\) 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 complex-
ation 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.\(^{13}\)

Comparing the shifts observed for \(7b - d\) with those
obtained by Becher et al.\(^9\) for the analogous symmetric

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

<table>
<thead>
<tr>
<th>Ions</th>
<th>(E_{1/2}^{a})</th>
<th>(E_{1/2}^{b})</th>
<th>(E_{1/2}^{c})</th>
<th>(E_{1/2}^{d})</th>
<th>(E_{1/2}^{e})</th>
<th>(E_{1/2}^{f})</th>
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<tr>
<td>LiPF(_6)</td>
<td>0</td>
<td>0</td>
<td>+11</td>
<td>+10</td>
<td>+40</td>
<td>+20</td>
</tr>
<tr>
<td>NaPF(_6)</td>
<td>+10</td>
<td>0</td>
<td>+14</td>
<td>+11</td>
<td>+15</td>
<td>+20</td>
</tr>
<tr>
<td>KPF(_6)</td>
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<td>+11</td>
<td>+15</td>
<td>+20</td>
</tr>
</tbody>
</table>

Figure 1. CVs of 1.0 mM of \(7d\) in THF solution containing
0.1 M TBAPF\(_6\) in the presence and absence of 5 mM NaPF\(_6\).
The working electrode was a platinum electrode, and Ag/AgCl + 0.1 M TBAPF\(_6\) in THF was the reference electrode.

(24) Moore A. J.; Bryce, M. R.; Batsanov, A.-S.; Green, A.; Howard,
J. A. K.; McKervey, M. A.; McGuigan, P.; Ledoux, I.; Orti, E.; Viruela,
(26) Socrates, G. In Infrared Characteristic Group Frequencies; John
102, 4918.
The 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

<table>
<thead>
<tr>
<th>Transmission IR of 7b</th>
<th>RAIR of 7b</th>
<th>RAIR of 7c</th>
<th>RAIR of 7d</th>
<th>Assignment</th>
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<tr>
<td>2925</td>
<td>2928</td>
<td>2925</td>
<td>2925</td>
<td>$\nu_{as}$ (CH$_2$)</td>
</tr>
<tr>
<td>2852</td>
<td>2848</td>
<td>2851</td>
<td>2851</td>
<td>$\nu_{as}$ (CH$_2$)</td>
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<td>1731</td>
<td>1737</td>
<td>1731</td>
<td>1737</td>
<td>$\nu$ (C=C)</td>
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<td>1571</td>
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<td>1246</td>
<td>1245</td>
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<tr>
<td>1157</td>
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<td>1175</td>
<td>1178</td>
<td>$\nu_s$ (C$-$O$-$C$-$)</td>
</tr>
<tr>
<td>1129</td>
<td>1122</td>
<td>1122</td>
<td>1124</td>
<td>$\nu$ (C=S) from TTF</td>
</tr>
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<td>946</td>
<td>950</td>
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</tbody>
</table>

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 $\nu$C=O stretching at 1737 cm$^{-1}$. The peak due to the $\nu_{as}$ (C=O) from the rings and $\nu$ (C=O$-$C$-$) stretching are also very weak. On the other hand, the $\nu$ (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 $\nu$C=O groups and the $\nu$ (C=O$-$C$-$) from the anchoring chain as well as the $\nu$ (C=O$-$C$-$ in the rings are oriented almost parallel to the metal surface while the $\nu$ (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 $\nu$C=O stretching and a strong absorption due to the $\nu$ (C=O$-$C$-$ symmetric vibrations but none is observed for the $\nu$ (C=S) stretching. This observation strongly suggests that $\nu$C=O group in this case is oriented almost perpendicular to the surface. Calculations based on the $\nu$ (C=O$-$C$-$ vibration$^{29}$ suggest a $\sim 60^\circ$ inclination of the $\nu$ (C=O$-$C$-$) portion attached to the TTF moiety for the monolayer of 7d and $\sim 80^\circ$ for that of 7b, with respect to the surface. The corresponding angle is $68^\circ$ for the monolayer of 7c. These differences in orientation may be due to the changes in the size of the terminal crown ether group.

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


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 mV are observed (90.6 mV fwhm for a one-electron transfer).30 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. 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 −CO₂CH₃ group in 7e. The SAMs of 7a−d 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.31 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 stability 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.

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**Table 4.** Electrochemical Data of SAMs of the TTF Disulfides in THF–TBAPF₆ System at Room Temperature with a Scan Rate of 100 mV s⁻¹

| SAMs of the disulfides | E₁/₂¹ (ΔEₚ) (mV) | E₁/₂² (ΔEₚ) (mV) | coverage
|------------------------|-----------------|-----------------|------------|
| 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/cm²⁻².

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

<table>
<thead>
<tr>
<th>solvent</th>
<th>E₁/₂¹ (ΔEₚ) (mV)</th>
<th>E₁/₂² (ΔEₚ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>641 (12)</td>
<td>846 (5)</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>502 (22)</td>
<td>769 (9)</td>
</tr>
<tr>
<td>ODCB</td>
<td>557 (42)</td>
<td>828 (46)</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>543 (19)</td>
<td>799 (15)</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>solvent</th>
<th>E₁/₂¹ (ΔEₚ) (mV)</th>
<th>E₁/₂² (ΔEₚ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>644 (67)</td>
<td>832 (80)</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>550 (75)</td>
<td>875 (75)</td>
</tr>
<tr>
<td>ODCB</td>
<td>524 (62)</td>
<td>839 (72)</td>
</tr>
</tbody>
</table>

(a) Chidsey, C. E. D. Science 1991, 251, 919
(c) Feldberg, S. W.; Rubinstein, I. J. Electroanal. Chem. 1988, 240, 1.