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Synthesis, Electrochemistry and Self-Assembled Monolayers of Novel Tetrathiafulvalene (TTF) and π-Extended TTF (*ex*TTF) Disulfides

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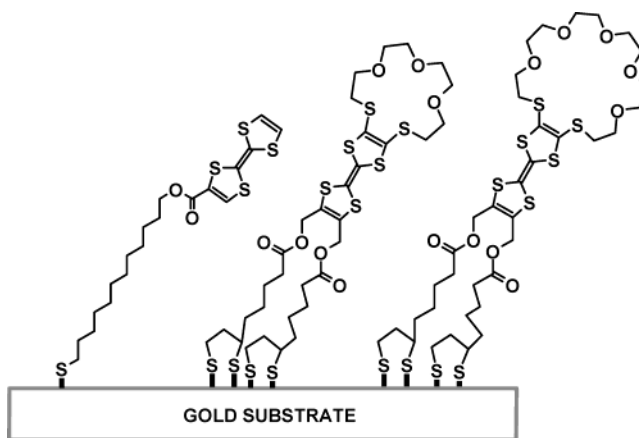
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The synthesis of a new series of tetrathiafulvalene (TTF) and π-extended TTF (*ex*TTF) disulfides and the electrochemical properties of self-assembled monolayers derived from these compounds are described. When the intermediate bromides **3** and **7** were reacted with thiourea, followed by basic hydrolysis, the expected thiol formation was not observed and only disulfides were obtained. A mechanism is proposed to explain the self-oxidation process of these compounds. For the first time SAMs of *ex*TTF derivatives were prepared. Electrochemical data for SAMs of **6** and **8** reveal a single two-electron chemically reversible oxidation process to form a dicationic state, typical of the *ex*TTF system. The SAMs are stable over extended periods of time and show electrochemical stability upon repeated potential scans.

Introduction

During the past few years, the construction of redox-active supramolecular systems for potential applications in different areas such as electroactive sensors, molecular switches, and molecular shuttles has been a burgeoning field of study.[1] Self-assembled monolayers (SAMs) are an attractive method for the assembly of electroactive molecular systems on solid supports, because they are easy to prepare and possess good stabilities.[2] Examples have been reported recently in which specific interactions of a guest species with a host SAM are transduced to a signaling unit that responds by undergoing a change in its electronic state, which is then detected by spectroscopic, structural, or electrochemical techniques.[2]

The redox-active TTF[3] can exists in three stable redox states (TTF°, TTF•+, and TTF²+), and for this reason TTF derivatives have been extensively used in materials chemistry.[3] Yip et al.[4] first reported SAMS on gold electrodes of *n*-mercaptoalkyl tetrathiafulvalenecarboxylate terminated in a thiol group, even though the SAMs were relatively unstable (see Chart 1 for examples of

CHART 1

GOLD SUBSTRATE

TTF-based SAMs). Subsequently, a TTF incorporating four thiol groups, which form very robust SAMs on gold, was described.[5] Moore et al.[6] were the first ones to incorporate crown-ether groups into TTF-SAMs, and their use as potential metal ion sensors was clearly demonstrated. Positive potential shifts of the first oxidation wave of the TTF unit were observed upon metal binding, similar to those observed in solution, e.g., $\Delta E^{1/2}$ for Na+ and Ba²+ = 45 mV. In these monolayers, if the potential scanned was limited to the first wave, the CV response was recorded for at least 1000 cycles. However,

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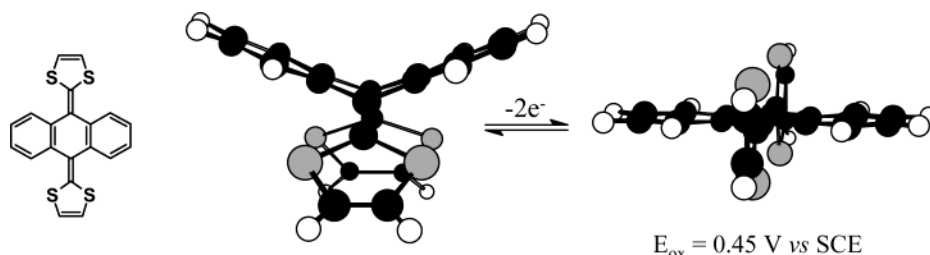(3) For recent TTF reviews, see: (a) Bryce, M. R. *J. Mater. Chem.* **2000**, *10*, 589. (b) Nielsen, M. B.; Lomholt, C.; Becher, J. *Chem. Soc. Rev.* **2000**, *29*, 153. (c) Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372.
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CHART 2

$E_{ox} = 0.45$ V *vs* SCE

the electroactivity gradually decreased when the potential was scanned beyond the first oxidation.[6]

New TTF SAMs have been reported by other research groups.[7] Notably, we showed how bis-thioctic ester derivatives of crown ether annelated TTFs form remarkably stable SAMs with surface confined electrochemistry.[8] SAMs of these crown-TTF disulfides can recognize alkali metal ions, and they possess almost indefinite stability.[9]

A particularly interesting class of TTF derivatives is the *p*-quinodimethane analogues of TTF (Chart 2), which oxidize at lower potentials than TTF as a result of charge delocalization and a decreased Coulombic repulsion in the dicationic state. The latter contains a planar anthracene moiety and two (also planar) orthogonal dithiole rings and is essentially aromatic; see Chart 2.[10] Because of these particular electronic and geometrical features, these *ex*TTFs are attractive for the preparation of new CT complexes[11] or C_{60}-based dyads.[12] Only recently, the π-radical cation species of these quinonoid *ex*TTFs have been generated and spectroscopically characterized by means of time-resolved and steady-state irradiation techniques.[13]

In this paper, we describe the synthesis, solution electrochemistry, and SAM formation of novel TTF and *ex*TTF derivatives containing two different types of surface active disulfide groups to anchor the systems to the gold surfaces. The formation of SAMs containing *ex*TTF derivatives has been carried out for the first time, and the electrochemical properties of the monolayers were studied by means of cyclic voltammetry.

Results and Discussion

Synthesis. The use of multiple anchoring sites provides very strong adherence of organic compounds to

metal surfaces, especially when sulfur atoms are contained within the same ring structure, in which case they exhibit a chelate effect.[14] For this reason, in addition to its commercial availability, the use of thioctic acid derivatives to anchor SAMs on metal surfaces has become frequent during the past years.[15–17] Thioctic acid based TTF disulfides **2** and **6** were prepared according to the procedure shown in Scheme 1. Starting from 4-hydroxymethyl TTF,[18] TTF **2** was synthesized in high yield following the previously described esterification procedure with thioctic acid in the presence of DCC/DMAP.[19] The preparation of the *ex*TTF analogue **6** was carried out starting from the 2-hydroxymethyl-*ex*TTF **5**,[20] again by direct coupling with thioctic acid in CH_2Cl_2 and in the presence of DCC and DMAP.[8] As observed previously, this direct coupling reaction to prepare TTF disulfides is straightforward and gives high yields, 95% (**2**) and 86% (**6**).

Generally speaking, SAMs of monothiol TTF derivatives have surface coverages nearer to an idealized close-packed monolayer,[4] though they are typically electrochemically unstable upon repeated voltammetric cycling.[6] For comparative purposes, we decided to carry out the preparation of the analogue thiol-derivatives of disulfides **2** and **6**, to analyze the differences (if any) in the electrochemical and structural properties of the monolayers formed. To generate the thiol groups, we decided to follow the well-established method that converts -Br to -SH by refluxing Br-derivatives with thiourea in ethanol followed by hydrolysis with potassium hydroxide.[4,6,21] The corresponding alcohols **1**[18] or **5**[20] were monoalkylated with a small excess of 1,6-dibromohexane to form **3** and **7**, respectively. Subsequent conversion of the terminal bromide into a thiol group was attempted by treatment with thiourea, followed by basic hydrolysis of the intermediate isothioureonium salt to afford the target thiol (not isolated). Surprisingly, what was observed was immediate self-oxidation to the disulfide **4** or **8**, respectively. The full-synthetic pathway is very clean for the TTF series, but in the case of the *ex*TTF analogue series, the basic hydrolysis of the intermediate

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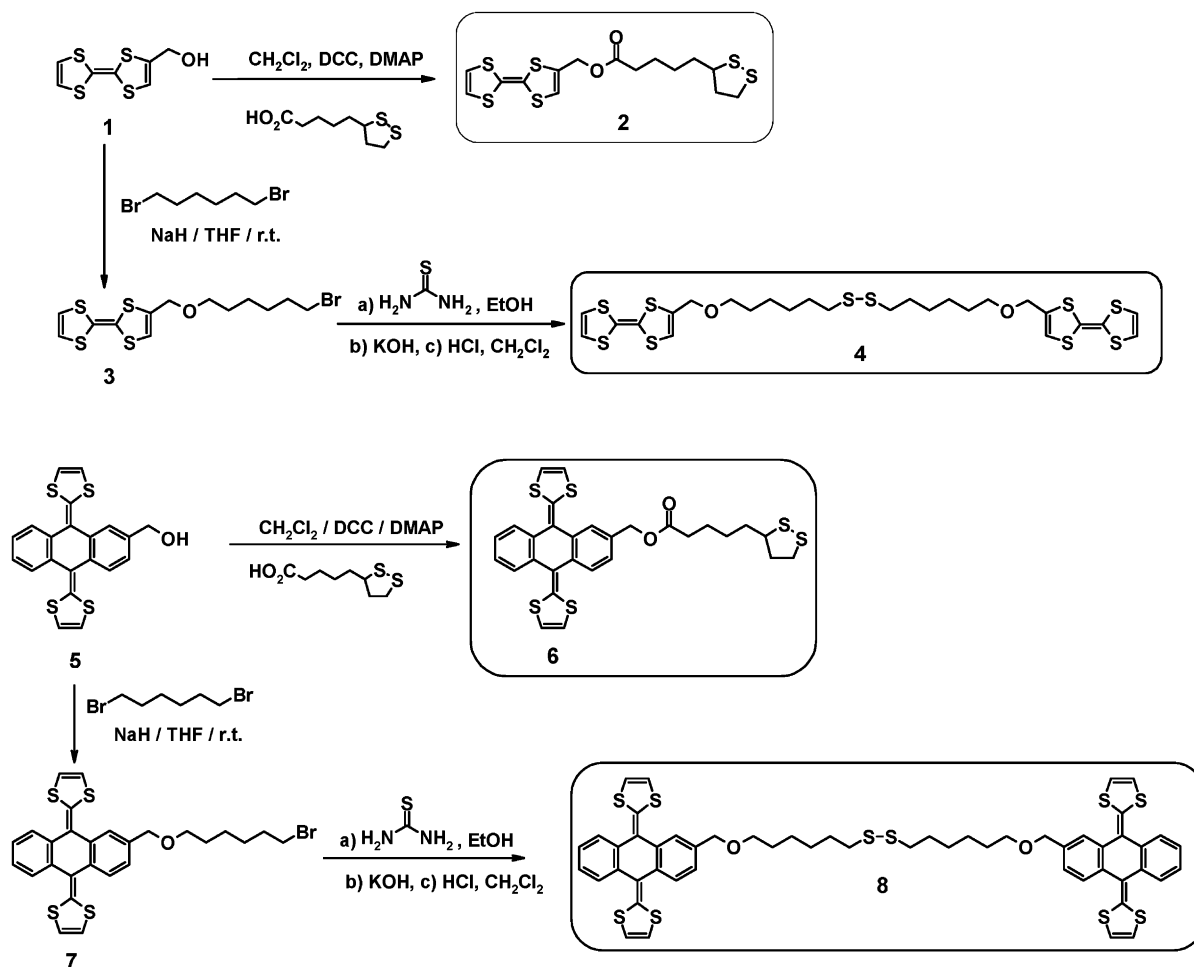(18) Garín, J.; Orduna, J.; Uriel, S.; Moore, A. J.; Bryce, M. R.; Wegener, S.; Yufit, D. S.; Howard, A. K. J. *Synthesis* **1994**, 489
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SCHEME 1

isothioureonium salt gave a complex mixture containing unidentified byproducts, as previously observed by other authors.[6] The thiol, just as in the case of the TTF analogue, forms the disulfide immediately even under an argon atmosphere.

Compounds **4** and **8** totally lack the presence of the typical SH symmetric stretch mode usually observed around 2550 cm^{-1} in the FTIR spectrum. The structures were clearly established by matrix-assisted laser desorption ionization (MALDI) and field desorption (FD) mass spectrometry, since the parent peaks corresponded to the disulfides, 698 amu for **4** and 1050 amu for **8**.

It is well-known that TTF derivatives are oxidized to the radical cation in acid media[22] but can also form protonated species, depending on the conditions and substituents present, if any.[23,24] In the present case, the thiol derivatives obtained from **3** and **7** are most probably irreversibly oxidized to the disulfides **4** and **8** following TTF cation-radical formation through acidic treatment (see Scheme 2).

Solution Electrochemistry. The solution electrochemistry of compounds **2**−**4** and **6**−**8** was investigated by cyclic voltammetry in CH$_3$CN and THF. A Ag/AgNO$_3$ reference electrode was used, Pt wire was the counter electrode, and different working electrodes (platinum, gold, and glassy carbon (GC)) were employed.

As shown in Table 1, predictably, TTF derivatives **2**−**4** undergo two one-electron, redox processes on a glassy carbon electrode, giving two pairs of well-defined redox couples, typical of TTFs.[25] The electron-withdrawing ester substituent of **2** increases slightly the oxidation potential of this derivative compared to that of **3** or **4**.[26] For compound **2**, another one-electron oxidation assigned to the cyclic disulfide oxidation was observed, and this electrochemical process is reversible in CH$_3$CN ($E_{1/2}$ = 827 mV) (see Figure 1). In general, the electrochemistry of disulfides has not been extensively studied.[27] Typically, disulfides undergo irreversible oxidation at potentials in the range of 0.9−1.5 V vs a Ag/Ag$^+$ reference electrode. However, some cyclic 1,2-dithioles generally show reversible one-electron oxidations in CH$_3$CN.[27,28]

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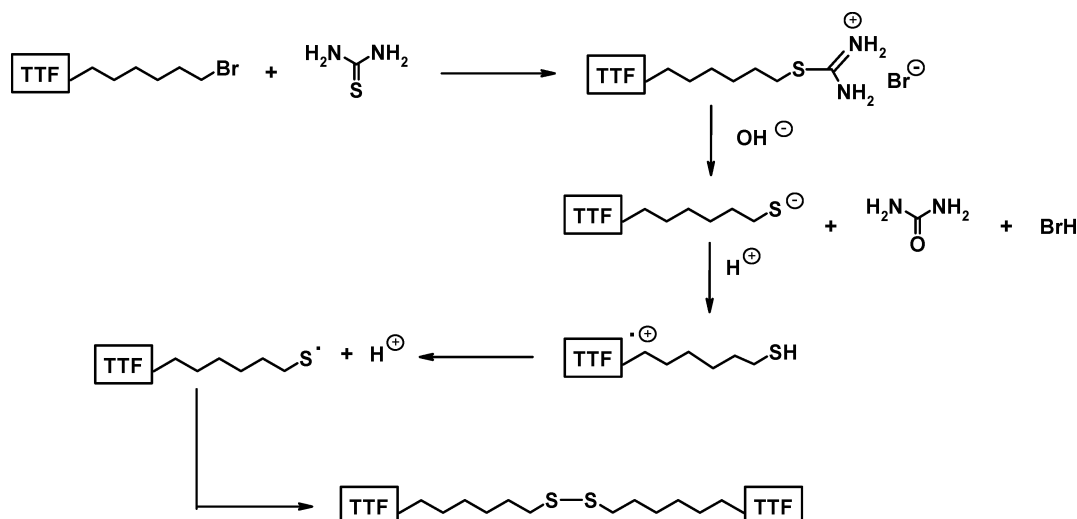(27) Glass, R. *Top. Curr. Chem.* **1999**, *205*, 1

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SCHEME 2

TABLE 1. Electrochemical Potentials (in mV) of 2−4 and 6−8 in THF−TBAPF₆ and CH₃CN−TBAPF₆[a]

	working electrode					
	glassy carbon		platinum		gold	
compound	THF	CH₃CN	THF	CH₃CN	THF	CH₃CN
TTF[b]	176 (83)	55 (58)	173 (66)	54 (62)	169 (72)	51 (65)
	447 (84)	443 (59)	441 (63)	444 (62)	440 (70)	441 (58)
2[b]	202 (78)	106 (59)	196 (61)	102 (59)	200 (70)	101 (58)
	464 (68)	489 (59)	463 (64)	499 (68)	465 (65)	490 (69)
	827 (103)	827 (69)	840 (110)	862 (60)	860 (108)	887 (47)
3[b]	186 (62)	69 (58)	178 (65)	67 (61)	174 (62)	68 (62)
	445 (64)	448 (64)	441 (60)	448 (63)	440 (64)	451 (66)
4[b]	156 (56)	62 (52)	154 (55)	60 (52)	153 (53)	65 (57)
	462 (56)	450 (62)	453 (56)	454 (60)	458 (53)	461 (58)
*ex*TTF[c]	133	34	187	66	202	33
6[c]	145	29	246	131	299	63
	840 (91)[b]	818 (58)[b]	844 (59)[b]	896 (91)[b]	861 (95)[b]	874 (69)[b]
7[c]	109	10	201	121	189	57
8[c]	99	17	238	77	232	74
	914 (irrev)					
thioctic acid[b]	870	785	898	783	873	783

[a] At room temperature with a scan rate of 100 mV s⁻¹; potentials vs Ag/AgNO₃. Values in parentheses correspond to the peak-to-peak separation. [b] $E_{1/2}$ reported. [c] E_{pc} reported, because of electrochemical irreversibility ($\Delta E_p \gg 80$ mV).

For all compounds (**2−4**), both the oxidation peak potentials and the ΔE_p values in CH₃CN are generally less than those in THF using the same working electrode. The oxidation potentials are very close in the three different working electrodes tested, although a weak trend is observed following the order GC > Pt > Au.[29] 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. *ex*TTFs **6−8**, unlike TTF, exhibit a single two-electron chemically reversible oxidation process to form a dicationic state.[29] For all *ex*TTF compounds the oxidation potentials are very close and both the E_{pa} and E_{pc} values are a function of the scan rate, the temperature, and the working electrode (Pt > Au ≫ GC). The *ex*TTF-based oxidation process has been analyzed as an electron transfer (ET) reaction with significant inner reorganization energy with the first ET having a larger barrier than

the second.[30] This results in the coalescence of the first and second electron oxidations into a single two-electron wave, and this is accompanied by a drastic geometric change, from a highly distorted butterfly-like geometry in the neutral state to a planar, aromatic hydrocarbon skeleton in the dicationic state.[10]

SAMs Electrochemistry. The CVs of the SAMs obtained with the model compounds **2** and **4** show the expected two one-electron oxidation processes corresponding to the formation of the radical-cation and dication of TTF, respectively (Figure 2a).[6,8] The electrochemical response of these SAMs is consistent with a redox system confined to the electrode surface, as shown by the proportionality of both oxidative peak currents with the scan rate (ν) (sweep rate varied from 50 mV s⁻¹ to 2 V s⁻¹). The peak-to-peak separation (ΔE_p) varies from 23 to 32 mV, indicating an electrochemically reversible process on the surface, and the heterogeneous electron-transfer rate constant (k_{et}) obtained for these monolayers

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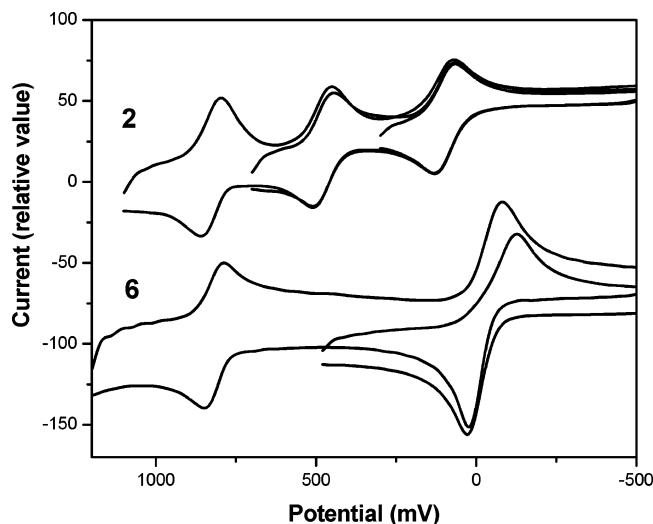(30) Ryan, M. R. *J. Electrochem. Soc.* **1978**, *125*, 547.

FIGURE 1. Cyclic voltammograms for 0.5 mM solutions of the cyclic disulfides **2** and **6** in CH_3CN at $v = 100$ mV s^{-1}. TBAPF$_6$ (0.1 M) was used as supporting electrolyte, GC as working electrode, Pt as counter electrode, and a Ag/AgNO$_3$ electrode in a CH_3CN solution as quasi-reference electrode, $T = 25$ °C.

was about 13.3 s^{-1}, which confirmed a very fast charge-transfer process.[31]

Repeated electrochemical cycling of **4**, as noted for other SAMs formed with TTF-thiol derivatives,[4,6] results in a gradual decrease of the current. Additionally, it is obvious that the surface charge transfer for the second redox reaction of TTF disulfides **2** and **4** bonded to the substrate leads to a cyclic voltammetric peak sharper than that for the first oxidation. This is an interesting effect recently noticed by Yuge and co-workers[7a] and also observed in TTF-silane derivatives on Ru or Pt electrodes.[32] Brown and Anson have proposed that such broadening is affected not by the surface concentrations but by surface activities.[33]

CVs of the SAMs formed with the *ex*TTF derivatives **6** and **8** show one pair of redox peaks, which correspond to the two-electron oxidation described in the solution electrochemistry. We did not observe stabilization of the *ex*TTF radical cation on the gold surface even when the experiments were done at temperatures as low as −78 °C. All peak potentials are proportional to the sweep rate, which was varied from 50 mV s^{-1} to 2 V s^{-1} (Figure 2b), indicating that the electroactive *ex*TTF was immobilized on the surface of the gold beads. ΔE_p for **6** and **8** are very large (more than 100 mV when $v = 100$ mV s^{-1}) and grow rapidly with increasing sweep rate, indicating an irreversible electrochemical process. The heterogeneous electron-transfer rate constants (k_s) were around 1 s^{-1}, which as expected, are much smaller than those of the TTF analogues and other well-known reversible redox couples such as ferrocene/ferrocinium ($k_{et} = 10$ s^{-1}).[31]

For both *ex*TTFs **6** and **8** SAMs, lowering the temperature results in an increase of the oxidation peak potentials, as shown in Figure 3, similar to the results obtained in homogeneous solution.[8] In fact, low-temperature measurements show that both compounds become more difficult to oxidize, and the corresponding reduction peaks in the reverse scan are remarkably shifted to more negative potentials (Figure 3). This behavior has been interpreted as an indication of the high stability of the dications in solution,[10c,11] and this is also observed for the SAMs.

The surface coverage of SAMs of **2**, **4**, **6**, and **8** were determined to be 1.09×10^{-10}, 0.73×10^{-10}, 1.32×10^{-10}, and 0.45×10^{-10} mol/cm^2, respectively. The coverages of the compounds with thioctic acid are larger than those with disulfide, which may indicate a slightly better lateral packing in the case of the thioctic acid derivatives.

It should be pointed out that the SAMs of **4**, **6**, and **8** are very stable and their electrochemical responses remain essentially unchanged, especially those of **4** and **8**, after more than 100 scans. Further work is underway in our group to fully characterize the SAMs formed with *ex*TTF disulfides and to exploit the tuneability of the oxidation potentials of *ex*TTF moieties in the preparation of other monolayers structures.
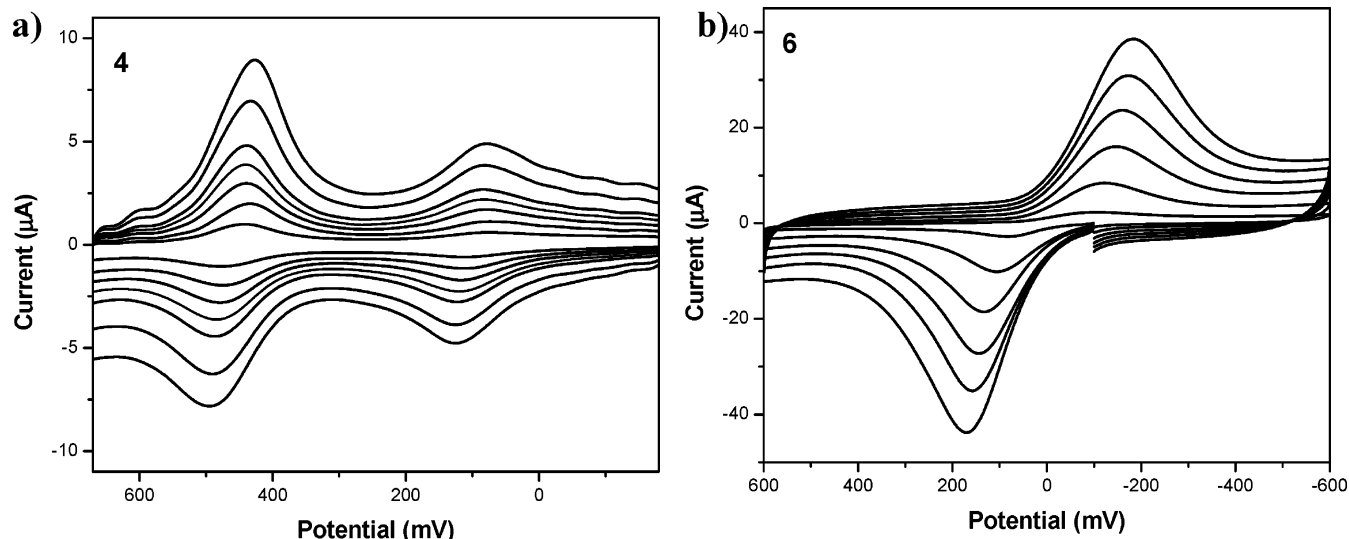

FIGURE 2. CVs of SAMs of **4** (a) and **6** (b) in THF solution containing 0.1 M TBAPF$_6$ at different scan rates (50 mV s^{-1} to 2 V s^{-1}).
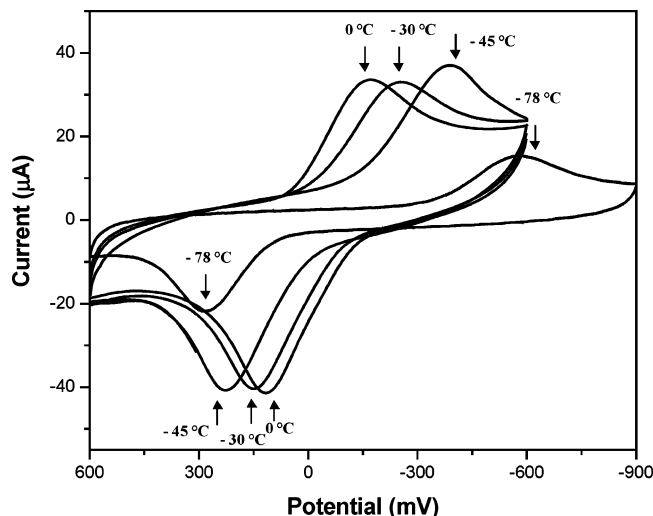
FIGURE 3. Temperature-dependent CVs of SAMs of compound **6**.

Conclusions

Novel TTF and *ex*TTF disulfides have been synthesized, and electrochemically active SAMs have been assembled with them. Following the known procedure for the preparation of thiol derivatives from the analogue Br-derivatives, no thiol formation was observed, and only disulfide derivatives were obtained instead. The formation of TTF cation radicals in acid media seems to be responsible for the efficient conversion of thiols into disulfides.

*ex*TTF derivatives have been successfully employed for the preparation of SAMs for the first time. The electrochemically active SAMs showed well-defined surface confined redox characteristics and are reasonably stable upon repeated potential scans. The electrochemical data of the SAMs formed is very similar to the solution electrochemistry observed for these derivatives, a single two-electron chemically reversible oxidation wave.

Experimental Section

General Methods. All reagents were of commercial quality and were used as supplied unless otherwise stated; solvents were dried using standard procedures. 4-(Hydroxymethyl)-tetrathiafulvalene (**1**)[18] and 2-(Hydroxymethyl)-9,10-bis(1,3-dithiol-2-ylidine)-9,10-dihydroanthracene (**5**)[20] were synthesized according to literature procedures.

Column chromatography was done on silica gel (60 Å, 32–63 μm). ^{1}H NMR and ^{13}C NMR were recorded at 500 and 125 MHz respectively, in deuterated chloroform with TMS as internal reference. MS spectra were obtained using MALDI or FD. A Varian ProStar high-performance liquid chromatography (HPLC) system, equipped with a ProStar 330 photodiode array detector, was used to determine the purity of the compounds synthesized. A semipreparative SiO$_2$ column (column dimensions, 25 cm × 10 mm; flow rate, 2.0 mL min^{-1}; injection volume, 20 μL; mobile phase, toluene) was employed. The retention time (t_R) and the peak area (PA) reported were determined at a wavelength of 310 nm.

Electrochemistry. Unless otherwise specified, electrochemical measurements were performed 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 (3 mm ϕ) or the SAM-modified spherical gold electrodes were used as the working electrodes, and a platinum wire and a Ag/AgNO$_3$ electrode were employed as the counter and the reference electrodes, respectively. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. The surface of the working electrode was polished with commercial alumina prior to use. Solutions were stirred and deaerated by bubbling argon for a few minutes prior to each voltammetric measurement.

Monolayer Preparation. Gold beads were prepared by the well-developed procedure described in previous work.[8,9,34] Monolayers were typically obtained by immersing the freshly prepared gold-bead electrodes into a ca. 1 mM THF solution of compound **2**, **4**, **6**, or **8**. The gold beads were rinsed thoroughly with THF after 24 h, and then the CVs of the SAMs were measured in a solution of THF containing 0.1 M TBAPF$_6$. The electrolyte solution was purged with argon for 15 min before every experiment.

Synthesis of TTF and *ex*TTF Disulfides 2 and 6. To 5 mL of CH$_2$Cl$_2$ were added the alcohol-functionalized **1**[18] or **5**[20] (0.05 mmol) and thioctic acid (1.2 molar equiv). The mixture was stirred for 15 min at 0 °C (ice/water bath) under N$_2$. Then 1,3-dicyclohexylcarbodiimide (DCC) (1.5 molar equiv) and 4-(dimethylamino)-pyridine (DMAP) (0.3 molar equiv) in 5 mL of CH$_2$Cl$_2$ 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 24 h under N$_2$, the reaction mixture was washed with water (3 × 50 mL). The organic layer was dried over MgSO$_4$, filtered, and evaporated. The residue was subjected to column chromatography in CH$_2$Cl$_2$ for further purification.

5-[1,2]Dithiolan-3-ylpentanoic Acid [2,2′]Bi(1,3-dithiolyliden-4-ylmethyl Ester (2).[19] 95% yield; HPLC (analytical) t_R = 11.15 min, PA = 99%; FTIR (PE) cm^{-1} 2731, 1736, 1651, 1543, 1512, 1432, 1381, 1342, 1265, 1126, 1026, 964, 794, 732, 648; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 6. 26 (1H, s), 6.25 (2H, s), 4.75 (2H, s) 3.50 (1H, m), 3.10−3.03 (2H, m), 2.39 (1H, m), 2.30 (1H, t, J = 7.35 Hz), 1.85 (2H, m), 1.72−1.60 (3H, m), 1.45−1.37 (2H, m); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 172.9, 131.3, 119.4, 119.2, 119.1, 111.9, 109.3, 60.7, 56.4, 40.3, 38.6, 34.6, 33.9, 28.7, 24.7; UV−vis (CHCl$_3$) λ_{max} (nm) (log ϵ) 314 (4.58), 394 (4.00), 466 (3.43), 540 (2.92), 612 (1.86), 710 (2.86); MS m/z (MALDI) 421 (M$^+$); HRMS m/z found 421.9630, calcd for C$_{15}$H$_{18}$S$_6$O$_2$ 421.9631.

5-[1,2]Dithiolan-3-ylpentanoic Acid 9,10-Bis[1,3]dithiol-2-ylidene-9,10-dihydroanthracen-2-ylmethyl Ester (6). 86% yield; HPLC (analytical) t_R = 12.96 min, PA = 99%; FTIR (PE) cm^{-1} 2740, 1727, 1597, 1543, 1511, 1450, 1419, 1380, 1280, 1257, 1164, 1126, 1088, 1026, 964, 833, 802, 756, 648; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.68 (4H, m), 7.27−7.25 (3H, m), 6.29 (4H, s), 5.16 (2H, s), 3.54 (1H, q, J = 6.4 Hz), 3.13−3.05 (2H, m), 2.39 (1H, t, J = 7.35), 1.86−1.82 (1H, m), 1.70−1.63 (4H, m), 1.55−1.42 (4H, m); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 173.4, 136.2, 136.1, 135.8, 135.3, 133.7, 126.1, 125.9, 125.2, 125.0, 124.8, 121.9, 121.8, 117.4, 117.3, 117.2, 66.1, 56.4, 40.2, 38.6, 34.7, 34.2, 28.8, 24.8; UV−vis (CHCl$_3$) λ_{max} (nm) (log ϵ) 273 (4.38), 318 (3.79), 365 (4.28), 417 (4.45), 432 (4.51); MS m/z (MALDI) 598 (M$^+$); HRMS m/z found 598.0254, calcd for C$_{29}$H$_{26}$S$_6$O$_2$ 598.0257.

Synthesis of TTF and *ex*TTF Bromo-Derivatives 3 and 7. A mixture of the corresponding alcohol (**1** or **5**) (0.5 mmol) and NaH (60% in mineral oil) (1.4 mmol) in anhydrous THF (100 mL) was stirred at room temperature under a stream of

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argon. After 30 min, 1,6-dibromohexane (3 mmol) was added, and the mixture was stirred for 16 h. After addition of MeOH the solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and washed with H_2O (3 × 100 mL). Purification by column chromatography in hexane/CH_2Cl_2 (1:1) afforded the expected compounds.

4-(6-Bromo-hexyloxymethyl)-2,2′bi[1,3]dithiolyli-dene (3). 43% yield; HPLC (analytical) t_R = 8.70 min, PA = 99%; FTIR (PE) cm^{-1} 2740, 1578, 1543, 1475, 1452, 1350, 1261, 1224, 1116, 1084, 794, 777, 735, 642, 557; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.24 (2H, s), 6.11 (1H, s), 4.15 (2H, s), 3.37−3.33 (4H, m), 1.82−1.77 (2H, m), 1.55−1.50 (2H, m), 1.41−1.29 (4H, m); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 135.1, 119.3, 119.1, 115.9, 110.9, 109.9, 70.2, 68.1, 34.1, 32.8, 29.5, 28.1, 25.4; UV−vis (CHCl$_3$) λ_{max} (nm) (log ϵ) 312 (4.18), 386 (3.41), 452 (3.01); MS m/z (MALDI) 414 (M$^+$ + 16); HRMS m/z found 395.9348, calcd for C$_{13}$H$_{17}$S$_4$OBr 395.9345.

4-(6-Bromo-hexyloxymethyl)-9,10-bis[1,3]dithiol-2-ylidene-9,10-dihydroanthracene (7). 36% yield; HPLC (analytical) t_R = 8.75 min, PA = 82%; FTIR (PE) cm^{-1} 1651, 1543, 1512, 1458, 1419, 1373, 1265, 1095, 1026, 956, 872, 802, 756, 648, 563; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.62−7.58 (4H, m), 7.21−7.18 (3H, m), 6.21 (4H, s), 4.47 (2H, s), 3.43−3.40 (2H, m), 3.32 (2H, t, J = 6.90 Hz), 1.79−1.75 (2H, m), 1.63−1.54 (2H, m), 1.38−1.33 (4H, m); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 136.5, 135.7, 135.6, 135.5, 135.4, 134.8, 131.0, 128.9, 126.0, 125.3, 125.1, 125.0, 124.2, 122.3, 122.1, 117.3, 117.2, 72.8, 70.2, 34.0, 32.9, 29.7, 28.1, 25.5; UV−vis (CHCl$_3$) λ_{max} (nm) (log ϵ) 275 (4.32), 312 (3.72), 363 (4.19), 412 (4.37), 430 (4.43); MS m/z (MALDI) 573 (M$^+$); HRMS m/z found 571.9980, calcd for C$_{27}$H$_{25}$S$_4$OBr 571.9971.

Synthesis of TTF and *ex*TTF Disulfides 4 and 8. A mixture of compound **3** or **7** (0.18 mmol) and thiourea (0.88 mmol) in dry ethanol (100 mL) was stirred and refluxed under an argon atmosphere for 24 h. After the solution was cooled, the solvent was removed, 1 M potassium hydroxide (4 mL) was

added to the residue, and the resultant mixture was stirred for 2 h. The reaction mixture was acidified with HCl, and CH_2Cl_2 (100 mL) was added. Washing with H_2O (3 × 100 mL) and purification by column chromatography in hexane/CH_2-Cl$_2$ (1:1) afforded **4** or **8** respectively.

Di[6-([2,2′]bi[[1,3]dithiolylidene]-4-ylmethoxy)-hex-yl] Disulfide (4). 37% yield; HPLC (analytical) t_R = 10.08 min, PA = 89%; FTIR (PE) cm^{-1} 2740, 1722, 1580, 1543, 1471, 1350, 1262, 1112, 1068, 1019, 794−734 (S−S), 647; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.24 (2H, s), 6.11 (1H, s), 4.15 (2H, s), 3.37 (2H, t, J = 6.40 Hz), 2.62 (2H, t, J = 7.30 Hz), 1.65−1.59 (2H, m), 1.55−1.49 (2H, m), 1.36−1.28 (4H, m); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 135.1, 119.2, 119.1, 115.8, 110.9, 110.0, 70.3, 68.1, 39.1, 29.5, 29.2, 28.4, 25.8; UV−vis (CHCl$_3$) λ_{max} (nm) (log ϵ) 252 (4.66), 329 (3.79), 379 (3.33), 456 (3.06); MS m/z (MALDI) 698 (M$^+$), 349 (thiol); (FD) 698 (M$^+$), 349 (thiol).

Di[6-(9,10-bis[1,3]dithiol-2-ylidene-9,10-dihydroanthra-cen-2-ylmethoxy)-hexyl] Disulfide (8). 33% yield; HPLC (analytical) t_R = 12.48 min, PA = 86%; FTIR (PE) cm^{-1} 1724, 1546, 1512, 1454, 1419, 1358, 1280, 1261, 1095, 1022, 802, 756, 675, 648, 551, 505; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.2−7.58 (4H, m), 7.21−7.19 (2H, m), 7.16 (1H, dd, J_1 = 7.78 Hz, J_2 = 1.85 Hz), 6.20 (4H, s), 4.47 (2H, s), 3.41 (2H, q, J = 6.40 Hz), 2.58 (2H, t, J = 7.30 Hz), 1.63−1.53 (4H, m), 1.36−1.28 (4H, m); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 136.5, 135.7, 135.6, 135.5, 135.4, 134.7, 126.0, 125.2, 125.1, 125.0, 124.2, 122.2, 117.3 (2C), 117.2 (2C), 72.8, 70.3, 39.1, 29.8, 29.3, 28.4, 26.0; UV−vis (CHCl$_3$) λ_{max} (nm) (log ϵ) 259 (4.09), 364 (4.22), 414 (4.34), 433 (4.37); MS m/z (MALDI) 1050 (M$^+$), 526 (thiol); (FD) 1050 (M$^+$), 526 (thiol).