# Polymer films on electrodes. 21. Electrochemical behavior of tetramethyltetraselenafulvalene incorporated into a Nafion-coated electrode[§]

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**Abstract.** The cyclic voltammetry of tetramethyltetraselenafulvalene (TMTSF) in $CH_2Cl_2$ is described. Controlled potential coulometry yielded a suspension of $(TMTSF)_2ClO_4$ crystals. The incorporation of TMTSF onto a Pt electrode coated with the perfluorinated ion exchange polymer Nafion and the electrochemical behavior of the electrode in aqueous $NaClO_4$ is described and compared to the related compound tetrathiafulvalene (TTF). A pair of peaks separated by about 400 mV is observed and is ascribed to the couple $TMTSF/(TMTSF)_2^+ ClO_4^-$. However, formation of the needle-like crystals found with Nafion/TTF was not seen with TMTSF.

**Keywords.** Tetramethyltetraselenafulvalene; cyclic voltammetry; controlled potential coulometry; Nafion; tetrathiafulvalene.

## 1. Introduction

Considerable attention has been directed towards the modification of the electrode surface by attachment of a thin layer of the perfluorinated cation exchange polymer Nafion[†] (Rubinstein and Bard 1980, 1981; White *et al* 1982; Martin *et al* 1982a, b; Buttry and Anson 1982, 1983, 1984; Prieto and Martin 1984; Leddy and Bard 1985; Leddy *et al* 1985). Electroactive molecules can be preconcentrated in the polymer film, which can exhibit novel electrochemical behavior. In a previous study from this laboratory, tetrathiafulvalenium ($TTF^+$) was incorporated into a Nafion-coated Pt electrode (Henning *et al* 1981, 1982; Henning and Bard 1982) (denoted Pt/Naf, $TTF^+$). Electrochemical cycling of this electrode resulted in the growth of electrically conductive domains and crystals of $TTF^+Br_{0.7}$ inside the polymer matrix. The recent report of the superconducting properties of a compound related to TTF, $(TMTSF)_2ClO_4$ (TMTSF = tetramethyltetraselenafulvalene) (Bechgaard 1982; Engler *et al* 1982; Lee *et al* 1982) led us to explore the electrochemical behavior of a Pt/Naf, $TMTSF^+$ electrode, with the goal of growing crystals of the superconducting salt in the Nafion film. In this paper, the electrochemical behavior of a Pt/Naf, $TMTSF^+$ electrode is described. We were guided in our study by the previous work with TTF; however, the properties of the system involving TMTSF were very different, and no conductive crystal could be produced by the electrochemical procedure.

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[§] Dedicated to Prof. K S G Doss on his eightieth birthday.
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[†] Nafion is the registered trademark of E I duPont de Nemours and Co, Inc.

R    X       X     R

R    X       X     R
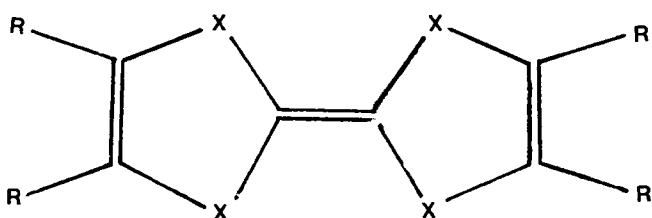
TTF: R=H, X=S
TMTSF: R=CH₃, X=Se

**Chart 1.**

## 2. Experimental

### 2.1 Materials

Tetramethyltetraselenafulvalene (TMTSF) was prepared as previously described (Wudl and Nalewajek 1980) and was stored under $N_2$ at 5°C. (TMTSF)$Cl_x$ was prepared photochemically from TMTSF and $CCl_4$ as previously described (Scott *et al* 1976). Aqueous solutions were made from $NaClO_4$ (Fischer Scientific) and triply distilled water. 970 equivalent weight Nafion dissolved in ethanol (2% by weight) was a gift from E I duPont de Nemours and Co.

### 2.2 Electrochemical synthesis of (TMTSF)₂ClO₄

50 mg TMTSF were dissolved in 20 ml $CH_2Cl_2$/0·4 M TBAP and cyclic voltammetry performed at a Pt disk. The solution showed two well-formed oxidation waves. Controlled potential coulometry at a Pt mesh electrode at a potential midway between the waves resulted in the consumption of 0·49 Faradays/eq. The purple solution immediately began to darken with a suspended crystalline precipitate, which was collected after the coulometry was complete by decanting the solution. The precipitate was washed several times with $CH_2Cl_2$ and air dried. The total yield was 43 mg (77%).

### 2.3 Apparatus

All electrochemical measurements employed a Princeton Applied Research (PAR) Model 175 universal programmer, Model 173 potentiostat and Model 179 digital coulometer. The working electrode was a platinum disk (area = 0·05 cm²) imbedded in a glass rod. A platinum mesh was used as a counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The cell was of a two-compartment design, as discussed previously (Malpas *et al* 1979).

### 2.4 Procedure

Two methods were employed to incorporate TMTSF into a Nafion film on the electrode surface. Method A: The Pt electrode was polished with 0·05 $\mu$m alumina on a felt pad and the electrode was then rinsed with water and covered with a 5 $\mu$L aliquot of the Nafion solution mixed with a solution of (TMTSF)₂ClO₄ dissolved in MeCN. The amount of TMTSF solution was controlled to give equal stoichiometry of the (TMTSF)₂⁺ and sulfonate groups in the polymer. The liquid layer on the

electrode was then allowed to evaporate for 15 min before the electrode was immersed in solution. The thickness of the film created in this manner was measured with a Sloan–Dektak profile measuring device. Films of dry thickness of 0·5 μm tended to be the most reproducible. Method B: 5 μL of a solution of Nafion in EtOH was deposited onto an electrode allowed to dry for 10 min. The electrode was then immersed in an aqueous solution of TMTSF $Cl_x$ to extract $(TMTSF)^+$. After 30 min, the electrode was removed and placed in the cell, and electrochemical experiments were begun immediately to avoid ion exchange with :he electrolyte $(NaClO_4)$.

## 3. Results

### 3.1 *TMTSF in solution*

The electrochemical behavior of TTF and its analogues in nonaqueous solution has been studied (Chambers *et al* 1977; Coffen *et al* 1971; Kaufman *et al* 1976; Kacemi and Lamache 1985). Both tetrathia- and tetraselenafulvalenes are oxidized in two distinct processes to the +1 and +2 oxidation states. Each oxidation has been ascribed to the removal of an electron from a formally $7e^-$ ring to form an aromatic cationic heterocycle (Perlstein 1977; Engler *et al* 1975). Electrochemical methods have been employed in the synthesis of the conductive salts of TMTSF (Bechgaard 1982; Engler *et al* 1982; Lee *et al* 1982), but apparently no detailed study of the voltammetry has been reported. We therefore examined the redox behavior of TMTSF for comparison with that previously reported to TTF and its analogues.

TMTSF shows two reversible oxidation waves by cyclic voltammetry in $CH_2Cl_2$/ 0·4 M TBAP (figure 1). The peak potentials of the waves were estimated vs an aqueous standard hydrogen electrode by adding ferrocene to the solution as an internal standard (Gritzner and Kuta 1982), and were found to be +0·543 and +0·917 V vs NHE. The values are somewhat different from the values reported in $CH_2Cl_2$/0·1 M $TBABF_4$ (Wudl *et al* 1981). Evidently, complexation or ion pair formation with the supporting electrolyte anion is important in the stability of the
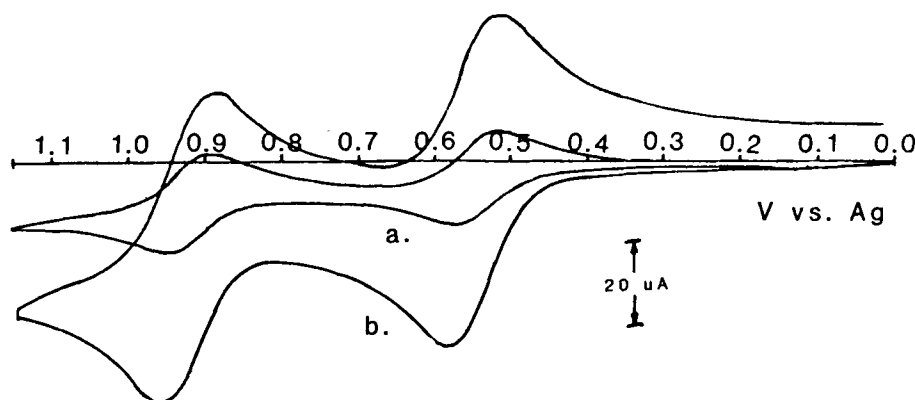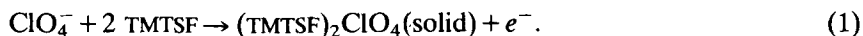


**Figure 1.** Cyclic voltammetry of 4·0 mm TMTSF in $CH_2Cl_2$/0·4 M TBAP (a) 50 mV/sec, (b) 200 mV/sec at a Pt electrode.

mixed valence salts. The controlled potential coulometry experiments yielded $n_{app} = 0.49$ with the formation of a precipitate (see § 2); the overall reaction at the electrode can be represented by

$$ClO_4^- + 2 \text{ TMTSF} \rightarrow (\text{TMTSF})_2ClO_4(\text{solid}) + e^-. \tag{1}$$

However, on the time scale of cyclic voltammetry, the oxidation is reversible with no loss of material due to precipitation (figure 2a). Precipitation of the product must therefore occur on a time scale intermediate between that of the voltammetry and coulometry. experiments. To determine at what point nucleation occurs, the following experiment was performed: After a scan over the first oxidation wave, the potential was held constant for different periods of time $(\tau)$, and then the reverse (cathodic scan) carried out (figure 2b–d). If the potential of the electrode was held at the first oxidation wave for $\tau > 10$ sec, a decrease was observed in the cathodic peak current with the appearance of "noise" in the voltammogram, especially at potentials following the cathodic peak. Visual examination of the solution showed a cloud of dark material near the electrode at this time. If the potential was held for longer times, the cathodic peak. current was further decreased and the "noise" became more noticeable. The results suggest that nucleation occurs after about 10 sec so that the cathodic peak current decreases
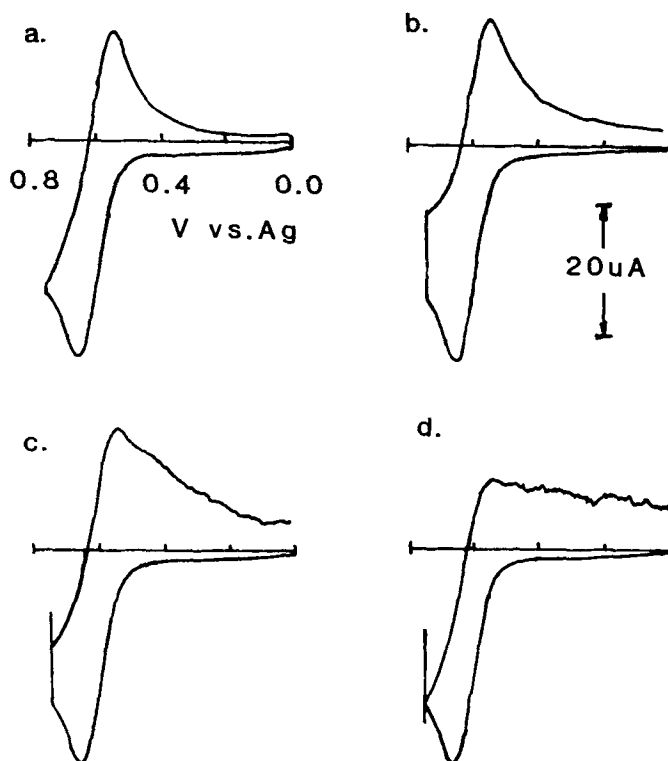


**Figure 2.** Single scan voltammograms of 5·0 mm TMTSF in $CH_2Cl_2/0.4$ M TBAP$_4$. Scan rate = 100 mV/sec, with the electrode held at the switching potential (+0.75 V) for (a) 0, (b) 10, (c) 20, (d) 40 sec.

because of loss of dissolved TMTSF$^+$ by precipitation of $(TMTSF)_2ClO_4$. The "noise" is attributed to small individual crystals of the salt that encounter the electrode and are reduced in a process aided by the electrical conductivity of the crystal. Because the nucleation process is slow, most crystals do not precipitate on the electrode surface.

## 3.2 *Behavior of TMTSF in Nafion*

The redox behavior of a Pt/Naf, TMTSF electrode in aqueous $NaClO_4$ prepared by the two methods is similar; the observed currents were larger when the electrode was prepared using method A (see above). On the first reductive scan, a large wave was seen (figure 3). This wave typically showed some diffusional tailing, especially at high scan rates or with thick films. On the subsequent scans, a small oxidation wave appeared at 0·35 V, and on reversal, a new reduction peak appeared at $-0·05$ V. The area under these waves suggests that $< 10\%$ of the $(TMTSF)_2^+$ reduced on the first scan remained electroactive. Continued cycling shows a small change in the peak potentials and a steady decrease in peak currents was observed over several hours. The pair of peaks found after the first reduction scan are separated by about 400 mV and are perhaps slightly sharper than the theoretical 90 mV ($n = 1$) width at half-maximum expected for a nernstian thin layer process (Bard and Faulkner 1980).

An attempt was made to characterize the nature of the peaks by studying the effect of scan rate and electrolyte concentration on peak potential and current. Unfortunately, the observed waves were not reproducible, so that unambiguous data to determine the exact stoichiometry of the processes could not be obtained.

## 3.3 *Effect of changing the electrolyte*

An electrode prepared by method A was cycled in 5 M $NaClO_4$ until essentially steady state behavior was obtained. The electrode was removed from solution in the oxidized state and placed in a 5 M NaCl solution. The first reduction showed a large peak similar to that seen on the scan of a freshly prepared electrode (figure 4). Continued cycling showed new electrochemical behavior in which the reduction
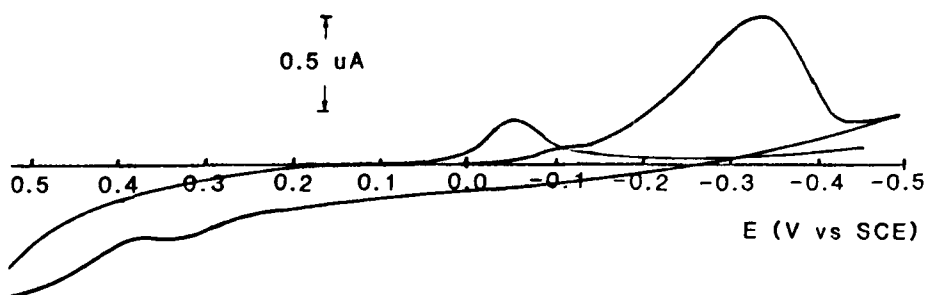


**Figure 3.** First scan and second scan of a Pt/Naf, TMTSF electrode in 5 M $NaClO_4$. Scan rate, 2 mV/sec; film thickness, 0·5 $\mu$m.
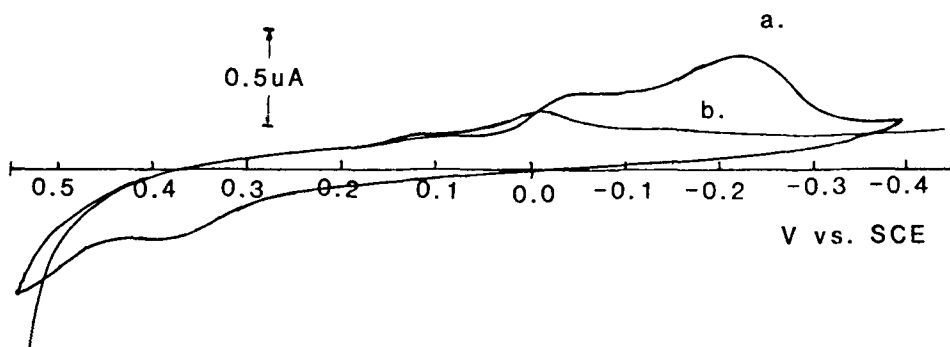
**Figure 4.** First (a) and second (b) scans of a Pt/Naf, TMTSF electrode previously cycled in 5 M $NaClO_4$ and then placed in 5 M NaCl. Film thickness, 0·5 $\mu$m, scan rate, 2 mV/sec. The electrode was prepared by the same procedure as in figure 3 (method A).
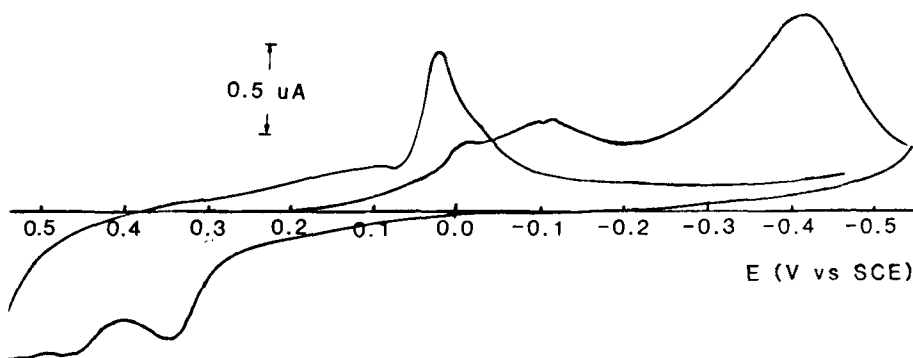
**Figure 5.** First scan and second scan in 5 M $NaClO_4$ of a Pt/Naf, TMTSF electrode made by method A and with benzonitrile as the solvent. Scan rate = 2 mV/sec; film thickness, 0·5 $\mu$m.

peak was shifted to positive potentials by ca. 50 mV and the amount of electroactive TMTSF was observed to be smaller – less than 50% of that previously observed in $NaClO_4$.

To establish that $(TMTSF)_2^+$ was not being expelled from the Nafion film by exchange with $Na^+$ from the 5 M NaCl solution, the electrode was replaced in the original $NaClO_4$ solution. After 1 cycle, essentially steady state behavior was observed as before. The electroactivity had returned to the previous level, confirming that the compound had not left the film.

### 3.4 *Effect of trapped solvent in the film*

An electrode prepared by method A showed that < 10% of TMTSF reduced on the first scan remained electroactive. However, if the film was cast from a benzonitrile solution, rather than an acetonitrile solution, the amount of TMTSF which remained electroactive on the second and following cycles was much greater (figure 5). The potential of the reduction peak was also shifted to positive values by 75 mV.

The difference in the films prepared by the two methods is probably a result of the effects of trapped benzonitrile in the film. Whereas method A involving acetonitrile gave reproducible films as described above following evaporation of
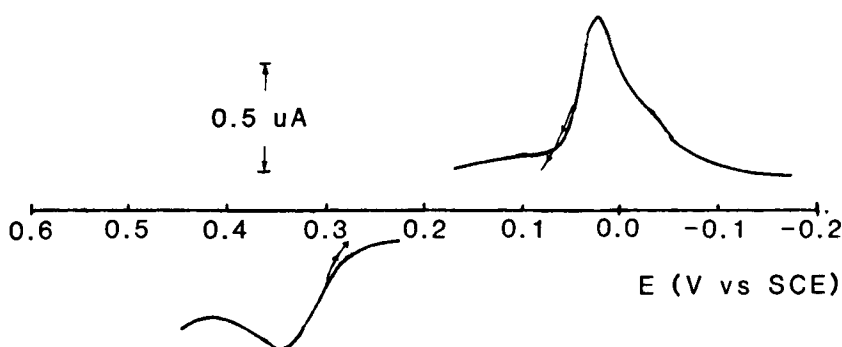
**Figure 6.** Scan reversal experiment of the electrode shown in figure 5. Reversal occurred at the steepest part of the rising portion of each wave. Scan rate, 2 mV/sec.

the solvent for 15 min, the use of benzonitrile required evaporation overnight to achieve the same degree of reproducibility. Even after 12 hr, some of the benzonitrile used to cast the film probably remained trapped in pockets inside the Nafion.
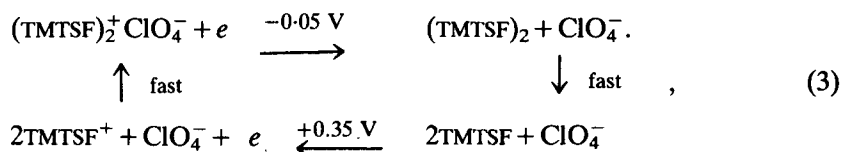
### 3.5 *Effect of switching potential*

The presence of strong positive interactions between molecules (as between monomers in a one-dimensional conductor) can be demonstrated by a scan reversal at points less extreme than the peak potential of a CV wave (Laviron 1975, 1981; Angerstein-Kazlowaska *et al* 1977). This technique was used previously to show that strong interactions exist between TTF molecules in Pt/Naf, TTF (Henning and Bard 1983). A similar experiment is shown in figure 6. As the potential of the scan approached the peak potential, the scan was reversed. The current on the reverse scan slightly exceeded that on the forward scan for a few seconds. This crossover pattern suggests that, as with $TTF^+Br^-$, there are interactions in the $(TMTSF)^+ClO_4^-$ that decrease upon reduction of part of the lattice, allowing the remaining molecules to be reduced more easily. A similar effect, however, was not observed in the oxidation of Nafion-bound TMTSF. The strength of the interactions in the $TMTSF^+ClO_4^-$ lattice is less than that with $TTF^+Br^-$ and TTF in Pt/Naf, $TTF^+$, since the crossover pattern was much less pronounced.

### 4. Discussion

Comparison of the electrochemical behavior of a Pt/Naf, $TMTSF^+$ electrode to the previously described Pt/Naf, $TTF^+$ electrode leads to some qualitative similarities. The first reductive scan shows a broad wave, which disappears on subsequent scans in favor of a pair of slightly sharper waves at widely separated potentials. The initial scan is assigned to the reduction of $TMTSF^+$ [or $(TMTSF)_2^+$] bound to the sulfonate groups of the Nafion film to neutral TMTSF. Continued cycling results in the incorporation of $ClO_4^-$ into the film, and we propose for the overall redox reaction in the film

$$2\, TMTSF + ClO_4^- \rightleftarrows (TMTSF)_2^+ ClO_4^- + e^-. \tag{2}$$
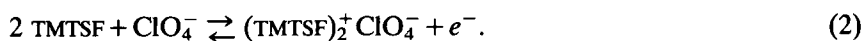
We propose a "square scheme" to explain the behavior of the Nafion/TMTSF system, by analogy to that previously deduced for Nafion/TTF (Henning *et al* 1981, 1982; Henning and Bard 1983). The first cathodic wave represents reduction of $(TMTSF)_2^+$ associated with sulfonate groups to neutral TMTSF. The oxidation of this species occurs with incorporation of $ClO_4^-$ to form $(TMTSF)_2^+ClO_4^-$. Subsequent reductions involve this species to TMTSF as shown in (3).

$$(TMTSF)_2^+ClO_4^- + e \xrightarrow{-0.05\ V} (TMTSF)_2 + ClO_4^-.$$

$$\uparrow \text{fast} \qquad\qquad \downarrow \text{fast} \qquad , \qquad (3)$$

$$2TMTSF^+ + ClO_4^- + e \xleftarrow{+0.35\ V} 2TMTSF + ClO_4^-$$

where $(TMTSF)_2$ and $2\,TMTSF^+ + ClO_4^-$ imply structures different from the equilibrium ones, TMTSF and $(TMTSF)_2^+ClO_4^-$, respectively.

One can also contrast the behavior of TMTSF with TTF in Nafion. Visual examination of a Pt/Naf, TMTSF electrode before and after cycling does not show formation of the needles of crystalline TMTSF in the film, as found during electrochemical formation of $TTFBr_{0.7}$ in Pt/Naf, TTF. The failure to achieve this goal may be attributed to the lack of a high concentration of electroactive TMTSF in the film. Even when benzonitrile is present in the film, which increases by several times the electroactivity of the TMTSF in the film, the concentration is evidently too low to initiate nucleation (to form bulk solid phase $(TMTSF)_2ClO_4$); TMTSF is also less hydrophilic than $TTF^\dagger$, so that it may preferentially migrate to hydrophobic zones of the Nafion (Yeo and Eisenberg 1977; Falk 1980; Yeager and Steck 1981), where it can no longer participate in electron transfer to the Pt substrate. This could account for the progressive loss of electroactivity even when the TMTSF is apparently not leached from the film, and the better waves observed when the film contains benzonitrile. Unfortunately, this difference in behavior prevents the electrochemical growth of microcrystals of conductive material.

## Acknowledgements

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† There is less charge density on the heteroatoms of TMTSF than TTF and the Me-groups decrease the hydrophilicity further. See Engler and Patel 1975.

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