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Chemical and Electrochemical Investigations on Thiazolium Salts: a Route to Powerful Donors in the Dithiadiazafulvalene Series

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Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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Thiazolium salts have been investigated, chemically and electrochemically, in order to access to the redox properties of dithiadiazafulvalenes (DTDAF). As these donor molecules are oxygen-sensitive, it is more advisable to isolate them in their oxidized form as dicationic salts. Starting from a tetrathiazolium cation including two precursors groups, linked together with a conjugated spacer, a bis-DTDAF was formed and its electrochemical behavior studied.

Dithiadiazafulvalenes (DTDAF) are excellent π-donor molecules but, as a consequence, they are air-sensitive and the presence of oxygen induces the formation of a ten-membered ring: a dithiadiazecinedione.[1,2] Isolation and characterisation of the neutral donor then become a real challenge. Actually, in order to form organic materials, isolation of the donor is not always a necessity. For example, we recently demonstrated that DTDAF can be generated *in situ* and trapped as a cation radical salt with polyoxometalate.[3] The first requirement in the search of new organic molecular complexes based on this donor is insight into its redox properties. Therefore, the choice of the acceptor will depend on the oxidation potentials of the donor.[4] The complementarity of chemical and electrochemical approaches might overcome the fact that DTDAFs are air-sensitive. Electroactive species such as DTDAF can be detected by cyclic voltammetry, either directly on the medium in which the donor was formed,[2,5] or by electroreduction of a chemically prepared diquaternary salt of 2,2′-bithiazole.[6] Another possibility is to realise an electrochemical synthesis of the DTDAF core, followed by direct *in-situ* detection of the donor formed.[3,7] Our synthetic pathway allows the formation of several DTDAF precursors which would lead to the formation of DTDAF, *N,N′*-phenyl-bridged DTDAF and dimers of DTDAF where the two donors are linked by a conjugated spacer group. In this paper we report the synthesis of these derivatives as well as the various strategies which have been developed in order to investigate the redox behavior of these donors.

Results and discussion

Chemical synthesis of DTDAF, followed by in-situ *electrochemical detection.* The synthesis of various substituted precursors of DTDAF was performed following the procedure outlined in Scheme 1.[8] Two chemical couplings of thiazolineselones in the presence of triethyl phosphite were studied, either an intermolecular coupling of **3** or an intramolecular coupling of *N,N′*-phenyl bridged bisthiazolineselone **6**. Under an inert atmosphere, a degassed solution of tetrabutylammonium hexafluorophosphate in CH_2Cl_2 was added to the reaction mixture. When there was a methyl group linked to the nitrogen, we were able to detect, by cyclic voltammetry, two main oxidation waves only in the case where $R^1=CH_3$, $R^2=CO_2Et$ (Fig. 1a). They are associated with the redox behavior of the DTDAF formed in the medium. In spite of the attachment of two electron-withdrawing groups, the oxidation potentials are very low ($E_1=-0.33$ and $E_2=-0.09$ V vs. SCE). This is in agreement with the results obtained by Thummel *et al.* on a similar donor $R^1=R^2=H$ ($E_1=-0.54$ and $E_2=-0.41$ V vs. SCE).[6] It is interesting to note the small potential difference

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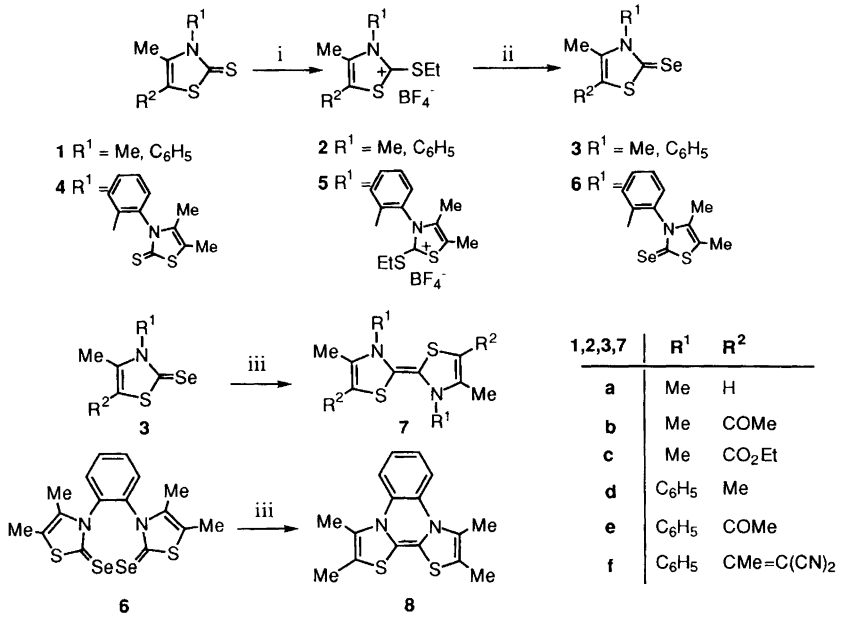


Scheme 1.

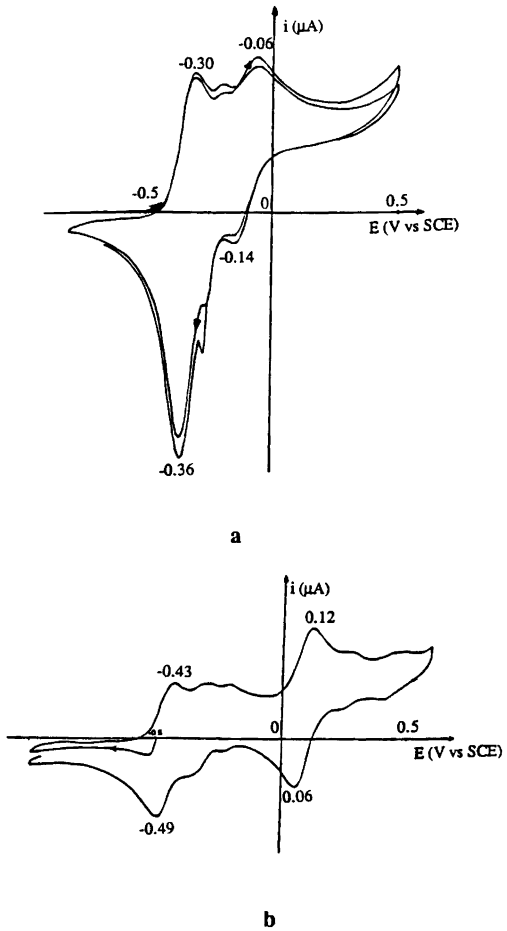
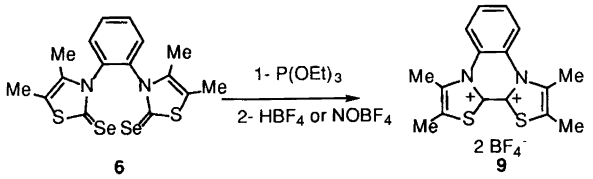


Fig. 1. Cyclic voltammogram of medium in which the DTDAF was formed by *in situ* addition of a solution of Bu_4NPF_6 (0.5 M) in CH_2Cl_2, platinum electrode, scanning rate 0.1 V s^{-1}, vs. SCE (a) starting from thiazoline selone **3c** and (b) starting from bisthiazolineselone **6**.

between the two oxidation states ($\Delta E = 0.24$ V). In fact, if we compare the potential difference reported in the literature for substrates substituted by a methyl group we notice a smaller ΔE than for the dithiadiazafulvalenes bearing an aromatic substituent at the nitrogen atom.[9] This smaller potential difference indicates the easier attainment of the dicationic state. The electrochemical behavior of *N,N'*-phenyl bridged DTDAF **8** analyzed under the same experimental conditions is in agreement with this observation ($E_1 = -0.46$ V $E_2 = 0.09$ V, $\Delta E = 0.55$ V, Fig. 1b). As can be seen in both cases, the complexity of these voltammograms might be due to the presence of other electroactive species, for instance oligomers in the case of **8**.

Chemical synthesis and electrochemical reduction of dicationic DTDAF. Another possibility for determining the redox properties of these π-donors lies in the preparation of the corresponding dicationic salt and then, in the redox behavior analyses of this salt by cyclic voltammetry. This way was used to investigate the case of the dication **9**, prepared by addition of either HBF_4 or $NOBF_4$ to the medium in which DTDAF **8** was formed (Scheme 2). It should be mentioned that tetrafluoroboric acid has been used to generate radical cation salts in the TTF family.[10] The same yellow powder was isolated using either HBF_4 or $NOBF_4$. Electrochemical reduction



Scheme 2.

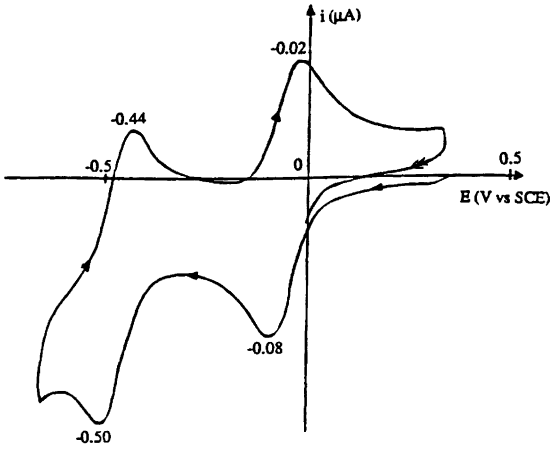
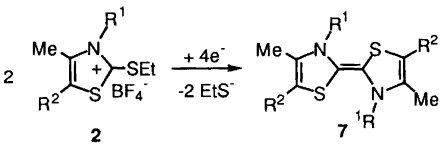


Fig. 2. Cyclic voltammogram of dication **9**, Bu_4NPF_6 (1 M), in CH_3CN, platinum electrode, scanning rate 0.1 V s^{-1}, vs. SCE.

Table 1. Cyclic voltammetry data of the thiazolium salts **2** and DTDAF **7** formed in the medium, E in V vs. SCE, Pt working electrode with 0.1 M n-Bu_4NPF_6 in CH_3CN, scanning rate 0.1 V s^{-1}.

			2	**7**		
	R^1	R^2	E_{red}	$E_{pa}{}^1$	$E_{pa}{}^2$	ΔE
b	Me	COMe	−1.1	−0.28	−0.03	0.25
c	Me	CO_2Et	−1.14	−0.30	−0.08	0.22
e	C_6H_5	COMe	−0.94	−0.20	0.24	0.44
f	C_6H_5	$CMe{=}C(NC)_2$	−0.8	−0.10	0.22	0.32



Scheme 4.

of dication **9** was studied by cyclic voltammetry in acetonitrile (Fig. 2). Two reversible waves were observed at very low potentials corresponding to two successive monoelectronic reductions $\Delta E_p = 0.06$ V ($E_1 = -0.47$ V and $E_2 = -0.05$ V vs. SCE). It should be recalled that the same voltammogram was obtained after reduction of bis(2-ethylthio-1,3-thiazolium salt) **5** at −1.0 V SCE.[3]

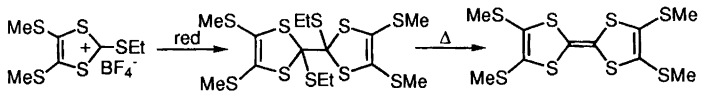
Electrochemical synthesis of DTDAF. Moses and Chambers have described the preparation of tetrathiomethyltetrathiafulvalene by electrochemical reduction of 2-ethylthio-1,3-dithiolium cation, followed by pyrolysis of the intermediate orthothiooxalate (Scheme 3).[11] Following the same strategy we attempted to prepare DTDAF from the corresponding thiazolium salts. When an electron-withdrawing substituent was linked to the thiazole ring, we were able, after electrochemical reduction of **2** in acetonitrile, to observe the formation of DTDAF **7** (Scheme 4).

During the reverse anodic scan, two oxidation peaks were detectable. Even when substituted by electron-withdrawing groups, DTDAF presents two reversible waves at very low potentials (Table 1). It seems that formation of DTDAF starting from thiazolium **2** is less than the quantitative yield observed from bisthiazolium **5**. In fact there is only a small amount of DTDAF **7** formed in the medium. As we have already reported, better results can be obtained from N,N'-phenyl bridged bisthiazolium salts **5**.[7] In all the cases the N,N'-phenyl-bridged DTDAF formed was observed on the voltammograms immediately after electrochemical reduction of the bis(2-ethylthio-1,3-thiazolium) salt. The formation of DTDAF from bisthiazolium salt probably occurs according to an ECE mechanism (Scheme 5).

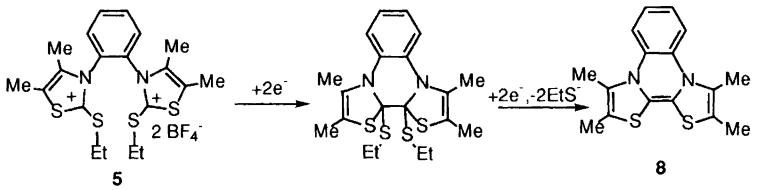
In the search for novel organic materials, conjugated systems containing two donor molecules have been synthesized which was expected would favor molecular assembly.[12] Following this idea we prepared the tetracation **12** including two precursors of DTDAF, linked together by a conjugated spacer group. A McMurry-type reaction on the bisthiazoline thione **10** successfully afforded the tetrathiazoline thione **11** by reductive dimerization of the aldehyde function into an alkene (Scheme 6). Treatment of the ethene tetra(thiazolinethione) **11** with boron trifluoride–diethyl ether and triethyl orthoformate afforded the tetrathiazolium salt **12** precursor of two quasi-planar dithiadiazafuvalenes linked by an ethenyl spacer group. Investigation on this salt was carried out by cyclic voltammetry in acetonitrile (Fig. 3).

During the first cathodic scan, two DTDAFs were formed by intramolecular coupling. On the reverse scan, two oxidation peaks were observed, the second cathodic scan showing the reversibility of the oxidation of bis-DTDAF **13**. Compared with the N,N'-phenyl-bridged DTDAF **8** or the dication **9**, the two oxidation steps occur at close potentials ($E_{pa_1} = -0.47$ V, $E_{pa_2} = 0.07$ V).

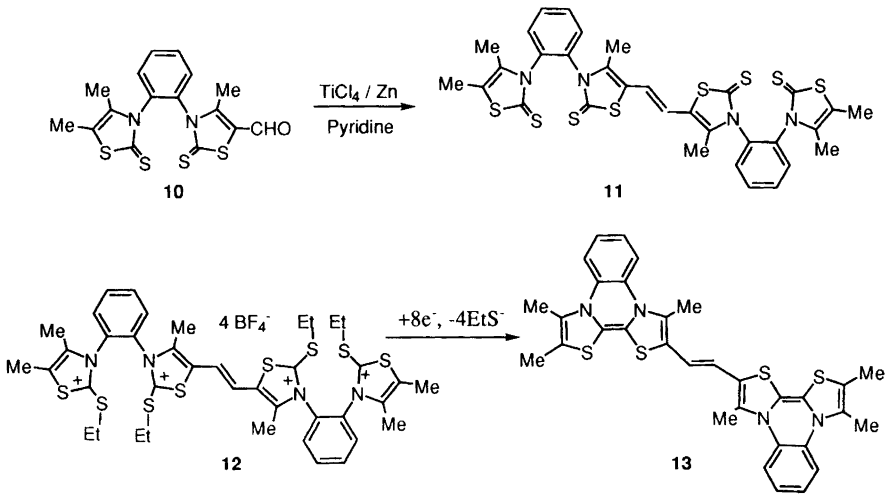
In conclusion we have investigated the redox properties of several DTDAFs, aza-analogues of tetrathiafulvalenes (TTF). The fact that these donors are oxygen-sensitive, due to their redox properties, imposes a different approach than the one used for TTFs. Detection of DTDAF was possible by a combination of chemistry and electrochemistry. We also prepared a DTDAF dimer in order to obtain charge transfer salts with improved control of the organis-



Scheme 3.



Scheme 5.



Scheme 6.

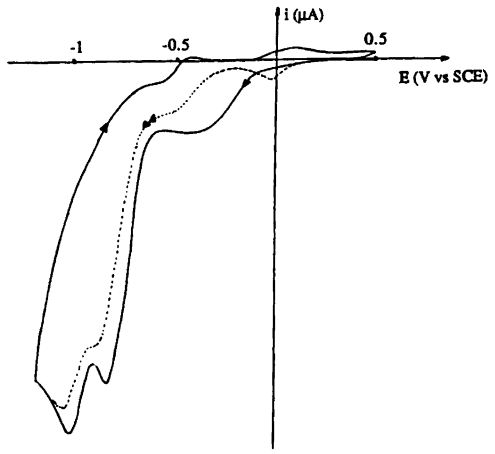


Fig. 3. Cyclic voltammogram of tetracation **12**, Bu_4NPF_6 (1 M), in CH_3CN, scanning rate, platinum electrode, 0.1 V s^{-1} vs. SCE.

ation of the molecules compared with *N,N'*-phenyl-bridged DTDAF.[3] As the physical properties of organic materials are closely associated with molecular assembly it would be of interest to see whether or not intramolecular or intermolecular interactions would be enhanced with these dimeric DTDAFs.

Experimental

^1H NMR spectra were recorded on 200 and 300 MHz spectrometers. ^{13}C NMR spectrometry was carried out at 50 and 75 MHz. Chemical shifts are reported in ppm referenced to tetramethylsilane. Mass spectra were determined with a Varian Mat 311 spectrometer (Centre de Mesures Physiques de l'Ouest). Melting points were measured using a Kofler hot stage apparatus and are uncorrected. Column chromatography was carried out on silica gel Merck 60 (70–260 mesh). Elemental analyses were performed at the Laboratoire Central de Microanalyse du CNRS (Lyon).

The different α-halogenated ketones used for the synthesis of thiazolinethione **1** were chloroacetone, 3-chlorobutanone and chloropentanedione. The syntheses of bisthiazolinethiones **4**, **10**, thiazolium salt **5** and bisthiazolineselone **6** and *N,N'*-bridged DTDAF **8** are described in Ref. 8. Thiazolinethiones **1** were prepared according to the experimental procedure described above.

Dithiocarbamate salt. To a solution of primary amine [32 mmol, methylamine: 20 ml of a 40% solution in water extracted with Et_2O (3 × 50 ml) dried over $MgSO_4$: aniline 29 ml] in 60 ml of carbon disulfide was added triethylamine (6.7 ml, 48 mmol). The reaction mixture was stirred for 2 h at room temperature. The precipitate was filtered off, washed with Et_2O, dried under vacuum and used without further purification. $R^1=CH_3$: white powder, yield 82% (5.5 g). m.p. 115 °C. ^1H NMR (D_2O): δ 1.17 (t, 9 H), 2.89 (s, 3 H), 3.10 (q, 6 H). ^{13}C NMR (D_2O): δ 11.06, 37.12, 49.38, 213.58; $R^1=C_6H_5$, white powder, yield 93% (8.0 g), m.p. 95–100 °C. ^1H NMR

(CD_3CN): δ 0.97 (t, 9 H), 2.61 (q, 6 H), 6.40–7.95 (m, 5 H).

1,3-Thiazoline-2-thione **1**. The dithiocarbamate salt (26 mmol) was dissolved in 100 ml of acetonitrile and the α-halogenated ketone $MeCOCHXR^2$ (26 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 5 h. CH_3CN was removed under vacuum and sulfuric acid 98% (2.5 ml) was slowly added under stirring to the resulting oil. After 15 min, water (50 ml) was added and the reaction mixture was extracted with CH_2Cl_2 (2 × 100 ml). The organic phase was washed with water (3 × 100 ml), dried over $MgSO_4$ and evaporated. The precipitate was recrystallized from 95% EtOH to give thiazoline thione **1**.

1a: $R^1=CH_3$, $R^2=H$, white powder, yield 80%, m.p. 112 °C. ^1H NMR ($CDCl_3$): δ 2.21 (s, 3 H), 3.55 (s, 3 H), 6.23 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ 16.15, 34.63, 106.40, 140.37, 188.29. Anal. Calcd. for $C_5H_7NS_2$: C, 41.35; H, 4.86; N, 9.64; S, 44.15. Found C, 41.52; H, 4.79; N, 9.69; S, 44.19.

1b: $R^1=CH_3$, $R^2=COCH_3$, white powder, yield 90%, m.p. 123 °C. ^1H NMR ($CDCl_3$): δ 2.31 (s, 3 H), 2.61 (s, 3 H), 3.62 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 16.28, 30.84, 35.00, 120.73, 147.56, 188.19, 188.62. Anal. Calcd. for C_7H_9NOS: C, 44.90; H, 4.84; N, 7.48; S, 34.24. Found C, 44.93; H, 4.78; N, 7.46; S, 34.10.

1d: $R^1=C_6H_5$, $R^2=CH_3$, white powder, yield 76%, m.p. 98 °C. ^1H NMR ($CDCl_3$): δ 1.84 (s, 3 H), 2.19 (s, 3 H), 7.22–7.55 (m,5 H). ^{13}C NMR ($CDCl_3$): δ 12.26, 14.20, 118.33, 128.59, 129.97, 130.33, 135.51, 139.08, 188.19.

1e: $R^1=C_6H_5$, $R^2=COCH_3$, white powder, yield 59%, m.p. 173 °C. ^1H NMR ($CDCl_3$): δ 2.33 (s, 3 H), 2.43 (s, 3 H), 7.21–7.60 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 16.70, 30.75, 121.79, 128.57, 130.62, 130.64, 137.55, 147.76, 188.63, 189.82.

1,3-thiazoline-2-thione **1c**. To a solution of the 1,3-thiazoline-2-thione **1a** (2.0 g, 9.2 mmol) in dry THF (100 ml) was added *n*-BuLi (4 ml, from a 2.5 M solution in hexane) at −80 °C under an atmosphere of argon. The reaction was stirred for 0.5 h, after which ethyl chloroformate (1 ml, 10.75 mmol) was added and the solution was stirred for an additional 0.5 h at −80 °C. The temperature was slowly allowed to reach r.t. and the mixture was left to stir for 5 h. The solvent was evaporated off and CH_2Cl_2 (60 ml) was added to the residue. The organic phase was washed several times with water (3 × 100 ml), dried over Na_2SO_4 and the solvent was evaporated off. The residue was chromatographed on silica gel column with CH_2Cl_2 as the eluent and afforded **1c** as a yellow powder, yield 83%, m.p. 73–74 °C. ^1H NMR ($CDCl_3$): δ 1.27 (t, 3 H), 2.60 (s, 3 H), 3.61 (s, 3 H),4.22 (q, 2 H). ^{13}C NMR ($CDCl_3$): δ 14.71, 14.98, 35.02, 62.04, 112.17, 148.55, 160.49, 189.14. Anal. Calcd. for $C_8H_{11}NO_2S_2$: C, 44.22; H, 5.10; N, 6.45; S, 29.51. Found C, 44.21; H, 5.13; N, 6.41; S, 29.67.

1,3-thiazoline-2-thione **1f**. To a suspension of 1,3-thiazoline-2-thione **1e** (2.0 g, 8 mmol) in 15 ml of anhydrous CH_3CN was added malononitrile (1.0 g, 15 mmol), glacial acetic acid (4 ml) and piperidine (1 ml). The reaction mixture was refluxed for 3 h. The solvent was evaporated off and CH_2Cl_2 (70 ml) was added to the residue. The organic phase was washed several times with water (3 × 100 ml), dried over $MgSO_4$ and the solvent was evaporated off. The residue was chromatographed on silica gel column with CH_2Cl_2 as the eluent and recrystallised from 95% EtOH to afford thiazoline thione **1f** as an orange powder, yield 44%, m.p. 214 °C. ^1H NMR ($CDCl_3$): δ 1.97 (s, 3 H), 2.47 (s, 3 H), 7.17–7.53 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 18.68, 25.51, 87.17, 112.66, 113.18, 118.85, 128.57, 131.01, 131.11, 137.79, 143.02, 164.16, 190.00. Anal. Calcd. for $C_{15}H_{11}N_3S_2$: C, 60.58; H, 3.73; N, 14.13; S, 21.56. Found C, 60.69; H, 3.81; N, 14.29; S, 21.75.

General synthesis of 1,3-Thiazoline-2-selone **3**. To a solution of 1,3-thiazolinethione **1** (3 mmol) in $CHCl_3$ (30 ml) was added $HC(OEt)_3$ (2 ml) and $Et_2O \cdot BF_3$ (2 ml). The reaction mixture was refluxed for 30 min and stirred at room temperature for 12 h. Dry ether (25 ml) was added to the solution, and the resulting oil was washed several times with Et_2O. The thiazolium salt **2** was precipitated by addition of ethanol, and then dried under vacuum. It was characterised by ^1H NMR spectroscopy and used without further purification.

2a: $R^1=CH_3$, $R^2=H$, yield 71%, colorless oil. ^1H NMR (CD_3CN): δ 1.54 (t, 3 H), 2.48 (s, 3 H), 3.45 (q, 2 H), 3.78 (s, 3 H), 7.54 (s, 1 H).

2b: $R^1=CH_3$, $R^2=COCH_3$, quantitative yield, red oil. ^1H NMR (CD_3CN): δ 1.58 (t, 3 H), 2.64 (s, 3 H), 2.76 (s, 3 H), 3.52 (q, 2 H), 3.81 (s, 3 H).

2c: $R^1=CH_3$, $R^2=CO_2Et$, quantitative yield, red oil. ^1H NMR (CD_3CN): δ 1.28 (t, 3 H), 1.46 (t, 3 H), 2.67 (s, 3 H), 3.40 (q, 2H), 3.69 (s, 3 H), 4.32 (q, 2 H).

2d: $R^1=Ph$, $R^2=CH_3$, white powder, yield 92%, m.p. 119 °C. ^1H NMR (CD_3CN): δ 1.44 (t, 3 H), 2.05 (s, 3 H), 2.50 (s, 3 H), 3.32 (q, 2 H), 7.46–7.75 (m, 5 H).

2e: $R^1=Ph$, $R^2=COCH_3$, quantitative yield, red oil. ^1H NMR (CD_3CN): δ 1.59 (t, 3 H), 2.56 (s, 3 H), 2.77 (s, 3 H), 3.54 (q, 2 H), 7.68–7.91 (m, 5 H).

2f: $R^1=Ph$, $R^2=CH_2=C(CN)_2$, yield quantitative, orange oil. ^1H NMR (CD_3CN): δ 1.53 (t, 3 H), 2.24 (s, 3 H), 2.70 (s, 3 H), 3.45 (q, 2 H), 7.60–7.82 (m, 5 H).

A solution of thiazolium salt **2** (2 mmol) in dry CH_3CN (20 ml) was slowly added to a mixture of $NaBH_4$ (4.4 mmol) and selenium powder (4 mmol) in degassed absolute ethanol (50 ml). After being stirred for 30 min at room temperature, the reaction mixture was pourred into 2% acetic acid solution. The red precipitate was filtered off, washed with CH_2Cl_2 several times. The aqueous layer was separated from the filtrate and extracted with CH_2Cl_2. The combined organic phases were washed with water, dried over $MgSO_4$ and the solvent was evaporated off. The residue was chroma-

tographed on a silica gel column with CH_2Cl_2 as the eluent, after which recrystallization from 95% EtOH afforded the thiazolineselone **3**.

3a: $R^1=CH_3$, $R^2=H$, white powder, yield 65%, m.p. 127 °C. ^1H NMR ($CDCl_3$): δ 2.34 (d, 3 H), 3.74 (s, 3 H), 6.53 (q, 1 H). ^{13}C NMR ($CDCl_3$): δ 16.14, 37.19, 111.03, 142.48, 180.91. Anal. Calcd. for C_5H_7NSSe: C, 31.26; H, 3.67; N, 7.29. Found C, 31.14; H, 3.68; N, 7.24.

3b: $R^1=CH_3$, $R^2=COCH_3$, orange powder, yield 43%, m.p. 107 °C. ^1H NMR ($CDCl_3$): δ 2.36 (s, 3 H), 2.71 (s, 3 H), 3.76 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 15.67, 30.86, 37.64, 125.03, 148.61, 182.83, 188.34. Anal. Calcd. for C_7H_9NOSSe: C, 35.90; H, 3.87; N, 5.98. Found C, 36.10; H, 3.92; N, 5.94.

3c: $R^1=CH_3$, $R^2=CO_2Et$, orange powder, yield 88%, m.p. 103–104 °C. ^1H NMR ($CDCl_3$): δ 1.31 (s, 3 H), 2.70 (s, 3 H), 3.75 (s, 3 H), 4.26 (q, 2 H). ^{13}C NMR ($CDCl_3$): δ 14.71, 15.13, 37.71, 62.27, 116.87, 149.73, 160.25, 184.01. Anal. Calcd. for $C_8H_{11}NO_2SSe$: C, 36.37; H, 4.20; N, 5.30; S, 12.13. Found C, 36.51; H, 4.14; N, 5.31; S; 12.12.

3d: $R^1=C_6H_5$, $R^2=CH_3$, white powder, yield 84%, m.p. 119 °C. ^1H NMR ($CDCl_3$): δ 1.86 (s, 3 H, CH_3), 2.15 (s, 3 H, CH_3), 7.18–7.52 (m, 5 H, Ar). ^{13}C NMR ($CDCl_3$): δ 12.26, 14.30, 122.80, 128.21, 129.95, 130.14, 137.91, 139.95, 180.40.

3e: $R^1=Ph$, $R^2=COCH_3$, orange powder, yield 87%, m.p. 153 °C. ^1H NMR ($CDCl_3$): δ 2.42 (s, 3 H), 2.47 (s, 3 H), 7.25–7.64 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 16.89, 30.90, 125.90, 128.59, 130.81, 130.92, 138.90, 149.34, 185.09, 188.51. Anal. Calcd. for $C_{12}H_{11}NOSSe$: C, 48.64; H, 3.74; N, 4.72; S, 10.82. Found C, 48.90; H, 3.78; N, 4.51; S, 11.10.

General procedure for the synthesis of DTDAF **7**. A suspension of 1,3-thiazoline-2-selone **3** (0.2 mmol) in degassed toluene (2 ml) and $P(OEt)_3$ (34 µl, 0.2 mmol), freshly distilled, was heated to 110 °C under Ar for 30 min. The reaction was then cooled to room temperature, after which a degassed solution of tetrabutylammonium hexafluorophosphate in CH_2Cl_2, was added to the reaction mixture for electrochemical investigations.

Dicationic DTDAF **9**. A suspension of 1,3-thiazoline-2-selone **3** (0.1 mmol) in degassed toluene (2 ml) and $P(OEt)_3$ (34 µl, 0.2 mmol), freshly distilled, was heated to 110 °C under Ar for 30 min. The solution of DTDAF generated in the medium was cooled to room temperature, then treated with $NOBF_4$ (14 mg) under Ar. The solution was stirred vigorously for 5 min and the dication **9** precipitated as a yellow powder. The precipitate was rapidly filtered off, washed with anhydrous ether and analysed by ^1H NMR spectroscopy. ^1H NMR (CD_3CN): δ 2.70 (s, 6 H), 3.00 (s, 6 H), 8.03–8.81 (m, 4 H).

Tetrathiazoline-2-thione **11**. To a stirred mixture of Zn powder (2.0 g, 30 mmol) in dry THF (200 ml) was added $TiCl_4$ (15 ml, 15 mmol of a solution 1 M in CH_2Cl_2) under N_2 at room temperature. The mixture was stirred under reflux for 1 h. A solution of aldehyde **10** (1 g, 2.6 mmol) in anhydrous THF (100 ml) and 2 ml of pyridine were added and the mixture was refluxed for 12 h. A quenching solution of 10% K_2CO_3 was added to the cooled mixture and the resulting solution was stirred for 15 min. The mixture was filtered and the precipitate was washed with CH_2Cl_2. The organic phase was washed with water and dried over Na_2SO_4. After evaporation of the solvent the residue was chromatographed on a silica gel column with CH_2Cl_2 as the eluent and afforded **11** as a yellow powder, yield 42%, m.p. > 260 °C. ^1H NMR ($CDCl_3$): δ 2.07 (s, 3 H), 2.09 (s, 3 H), 2.15 (s, 3 H), 2.18 (s, 6 H), 2.26 (s, 3 H), 6.33 (s, 2 H), 7.32–7.71 (m, 8 H). HRMS. Calcd. for $C_{32}H_{28}N_4S_8$. 724.0080, found 724.0083.

Tetrathiazolium salt **12**. To a solution of 1,3-thiazolinethione **11** (500 mg, 6.4×10^{-1} mmol) in $CHCl_3$ (50 ml) was added $HC(OEt)_3$ (2 ml) and $Et_2O\cdot BF_3$ (2 ml). The reaction mixture was refluxed for 30 min and stirred at room temperature for 12 h. Dry ether (25 ml) was added to the solution and the resulting oil was washed several times with Et_2O. Tetrathiazolium salt **12** was isolated as an colorless oil characterised by ^1H NMR spectroscopy and used without further purification, quantitative yield. ^1H NMR (CD_3CN): δ 1.43 (m, 12 H, CH_3), 2.26 (s, 6 H, CH_3), 2.37 (s, 3 H, CH_3), 2.47 (s, 3 H, CH_3), 2.51 (s, 6 H, CH_3), 3.44 (m, 8H, CH_2), 7.26 (s, 2 H, =CH), 7.92–8.20 (m, 8 H, Ar).

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