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Crown-ether annelated dithiadiazafulvalenes

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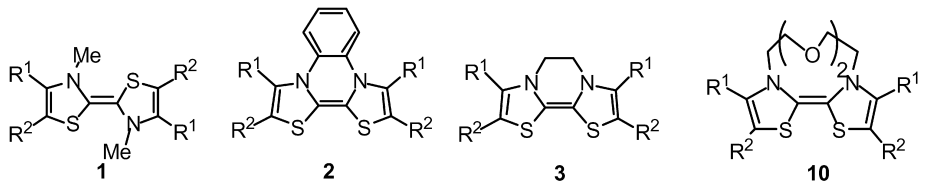
Abstract—The synthetic approaches towards crown-ether annelated dithiadiazafulvalenes (DTDAF) are described. As evidenced by electrochemistry, the reaction of *N*,*N*′-bridged-bisthiazolium salts in basic medium favors the formation of the DTDAF via an intramolecular coupling while the reaction of *N*,*N*′-bridged-bisthiazoline selone with trivalent phosphorus derivative leads to the donor core via an intermolecular coupling. The complexation of various metal cations on these crown-ether annelated DTDAF is investigated by electrochemistry.

1. Introduction

Organic π-donor molecules such as dithiadiazafulvalenes (DTDAF) (**1**) with their excellent donor properties are interesting candidates for the preparation of conducting charge transfer salts.[1] These compounds (**1**), almost planar in the neutral state,[2] undergo pronounced conformational changes upon oxidation such as a marked twist between the two thiazole rings of the donor core.[3] Contrariwise, when a phenylene group bridges the two thiazole rings, e.g. **2**, no structural modification occurs upon oxidation.[4] This can be observed not only by crystallographic studies but also by electrochemical investigations. For example, non bridged DTDAF (**1**) exhibit a smaller potential difference (ΔE) between the two oxidation potentials (E_1: DTDAF/DTDAF$^{+\cdot}$ E_2: DTDAF$^{+\cdot}$/DTDAF^{2+}) than their bridged analogues (**2**, **3**), as the distortion allows reduced coulombic interactions in the dicationic form.[1–6] Similarly, Thummel et al. studied the effect of the *N*,*N*′-bridge length—from two to four carbons—and found that ΔE decreases when the length increases.[6] Therefore, it seemed of interest to introduce a bis oxa ethyl chain to bridge the two thiazole cores. Indeed, the complexing ability of crown ether of the linking bridge could interfere in the modulation of the redox properties of DTDAF. In this paper, we report the first synthesis of crown annelated DTDAF as well as the electrochemical investigations of alkali metal binding effect on their redox behavior (Scheme 1).

2. Results and discussion

The two main chemical approaches for the synthesis of DTDAF are: (i) the coupling of thiazoline-2-selones in the presence of trivalent phosphorus derivatives or (ii) the coupling of thiazolium salts in basic medium.[1–5] The synthetic methodology used to reach bisthiazoline-2-selones **6** and bisthiazolium salts **7**, starting from (2,2′-(ethylenedioxy)bis(ethylamine), is summarized in Scheme 2. Following this general strategy, we prepared first the bis dithiocarbamate salt **4** and the bisthiazoline-2-thiones **5** where the two thiazole cores are linked together with a bis oxa ethyl chain. Bisthiazoline-2-thiones **5** were quantitatively alkylated on the exocyclic sulfur with diethoxycarbonium tetrafluoroborate formed in situ from $BF_3{\cdot}Et_2O$ and triethyl orthoformate. Subsequent treatment with sodium hydrogen selenide leads to bisthiazoline-2-selones **6** in good yields.[4] Recently, we showed that *N*,*N*′-ethylene-bridged bis-(1,3-thiazoline-2-thiones) treated with tetrafluoroboric acid and hydrogen peroxide followed by the addition of $Ba(OH)_2{\cdot}8H_2O$, gave the corresponding bisthiazolium salts.[5] Herein we simplified this strategy using only



Keywords: dithiadiazafulvalene; crown-ether; complexation; redox behavior.

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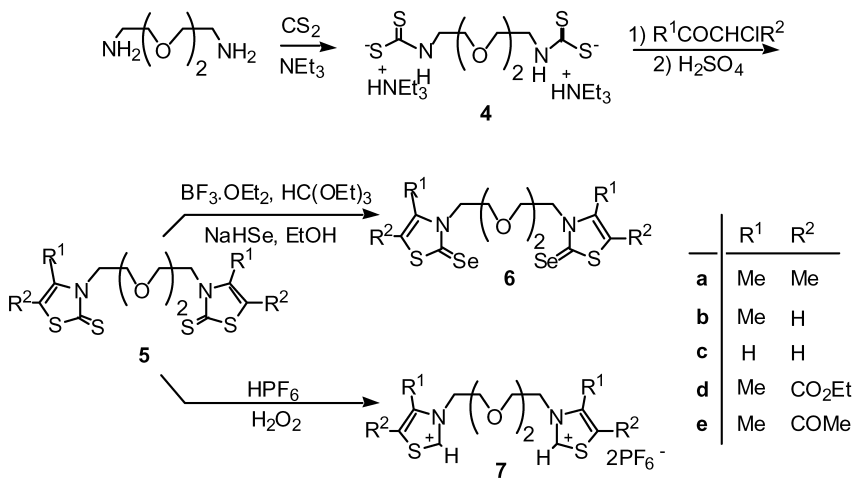
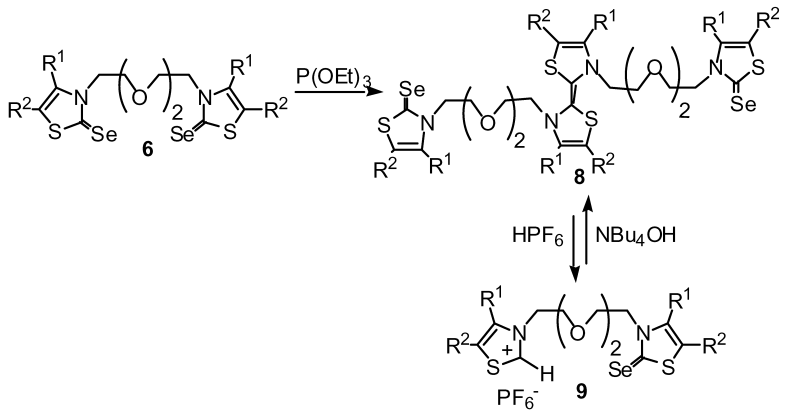


Scheme 1.



Scheme 2.

hexafluorophosphoric acid and hydrogen peroxide and bisthiazolium salts **7** are obtained.

DTDAFs are highly oxygen-sensitive. For example, on exposure to air, oxidative rearrangement of benzo-DTDAF has been observed into the spiro amide derivative or into a ten membered ring compound.[7] Therefore, we performed the analysis of the redox behavior, by cyclic voltammetry, directly on the medium where the donor was formed.[4,5] This can be realized just after the chemical coupling by adding under inert atmosphere the supporting electrolyte in the medium. We studied first the coupling of bisthiazoline-2-selone **6** in the presence of $P(OEt)_3$. Only one fully reversible bielectronic oxidation wave is observed indicating the formation of an electroactive compound in the medium (Fig. 1(a)). Contrariwise, electrochemical investigations

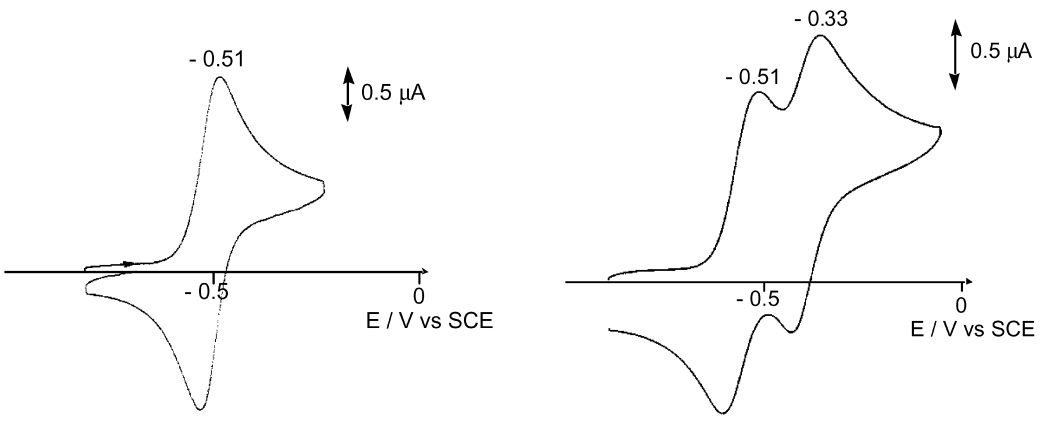


Figure 1. Cyclic voltammetry performed in the medium (a) where the bisthiazoline-2-selone **6a** was treated with $P(OEt)_3$, (b) where the bisthiazolium salt **7c** was treated with NBu_4OH.

Table 1. Oxidation peak potentials of the donors formed in the medium after the chemical coupling, *E* in V vs SCE, Pt working electrode with 0.1 M NBu_4NPF_6 scanning rate 0.1 V/s in CH_3CN

		Coupling of **6** with $P(OEt)_3$ DTDAF **8**	Coupling of **7** with NBu_4OH DTDAF **10**			DTDAF **3**[5]		
R^1	R^2		Epa^1	Epa^2	ΔEp	Epa^1	Epa^2	ΔEp
A Me	Me	−0.51	−0.59	−0.48	110	−0.69	−0.22	470
B Me	H		−0.53	−0.34	190	−0.66	−0.12	540
C H	H		−0.51	−0.33	180	−0.65	−0.10	550
D Me	CO_2Et	−0.14	−0.21	0.02	230	−0.27	0.28	550
E Me	COMe	−0.11	−0.19	0.00	190	−0.24	0.19	430
1 Me	COMe	Epa^1 −0.30, Epa^2 −0.06	−0.26	−0.07	190			

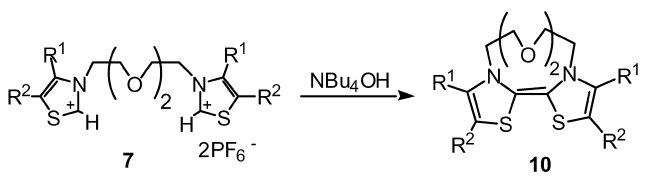
performed just after the coupling in basic medium of bisthiazolium salts **7** gives rise to a voltammogram exhibiting two monoelectronic processes (Fig. 1(b)).

The oxidation peak potentials of the donors formed in the medium using either the phosphite or the basic coupling are collected in Table 1 together with the data of *N*,*N*′-ethylene bridged DTDAF **3** formed in basic medium from the corresponding bisthiazolium salts.[5] For comparison, we also added in Table 1 the oxidation peak potentials of DTDAF **1** (R^1=Me, and R^2=COMe) formed using the phosphite coupling and the basic one. One can observed that in this case no significant difference are noted on the voltammograms as two reversible monoelectronic waves are observed in both cases. The differences observed, from the coupling of bisthiazoline selone **6** compared to bisthiazolium salt **7**, suggest here that the electroactive species formed in the two different chemical approaches are not the same.

Metzger et al. demonstrated that *N*,*N*′-dimethyl bisbenzo-DTDAF treated with acid yielded the corresponding *N*-methyl benzothiazolium salt.[8] This reaction can be used to decompose a given DTDAF into the two corresponding thiazolium moieties and has been applied here after the phosphite coupling of **6a**. Therefore, we treated the medium where the donor was formed with an excess of hexafluorophosphoric acid (Scheme 2). After work up of the reaction mixture we isolated the monothiazolium salt **9a** as an orange powder, which can only result from the reaction of DTDAF **8a** with hexafluorophosphoric acid. Reversibly, this thiazolium salt **9a** (R^1=R^2=Me) treated with NBu_4OH yields the DTDAF **8a** affording the same reversible oxidation wave as previously observed after the phosphite coupling.

Therefore, the coupling of bisthiazoline-2-selones **6** in the presence of $P(OEt)_3$ affords the DTDAF **8** resulting from an intermolecular coupling rather than an intramolecular coupling as in the case of bisthiazolium salt **7** in basic medium where **10** is obtained (Scheme 3).

Interestingly, if we compare the oxidation potentials of **1** (R^1=Me, and R^2=COMe) with **10e**, bearing the same substituents R^1 and R^2, we can observe only a small shift on both oxidation processes due to the presence of the *N*,*N*′-bis oxa ethyl chain instead of the methyl group. Otherwise, the difference between the two oxidation potentials (ΔE= Epa_2-Epa_1=190 mV) is similar in both cases. It has been shown that large molecular movements are associated with the electron transfer for *N*,*N*′-dimethyl DTDAF **1**.[3] In the neutral state, this DTDAF is almost planar[2] while in the oxidized species, the two thiazole rings are twisted around the central C–C bond by a large dihedral angle (76.6°). The second electron is then easier to remove due to reduced coulombic interactions. Herein, for **1** and **10e** the similar ΔE indicates that the side chain is long enough for allowing similar modifications. Indeed, with shorter bridging chain such as an ethylene[5] **3** (see Table 1) or phenylene one **2**[4] the two thiazole cores are forced to remain coplanar and the ΔE value is larger and close to 500 mV.



Scheme 3.

Contrariwise, the presence of bulky substituents on the thiazole rings, such as in DTDAF **8**, modifies the redox behavior as only a single wave is observed. Thummel et al. reported similar observation and assigned this behavior to the fact that such DTDAF would be less planar and hence less stabilized by resonance delocalisation.[6]

We also studied the voltammetric response of these DTDAFs in presence of alkali metal ions (Li^+, Na^+, K^+). In order to detect a possible interaction of the metal and the donor core we first studied DTDAF **1** (R^1=Me, and R^2=COMe) whose exocyclic acetyl substituents could eventually interfere with the different metal ions. After the addition of the metal salts in the medium no displacement of the oxidation peak potentials was observed showing that the ion has no influence on the redox DTDAF core of **1**. Similarly, we studied DTDAFs **8**, resulting from the intermolecular coupling of **6**, in the presence of alkali metal ions and there again no modification was detected. The effect of adding the metal ions was then studied on crown-ether annelated DTDAF **10e**. The largest anodic shift was observed for **10e**–Li^+. The metal binding effect is only observed for the smallest one, certainly due to the correlation between the hole size of the cavity and the radius of Li^+. The progressive addition of $LiBF_4$ shows that the first oxidation process was only shifted by 15 mV while on the second oxidation process the shift was more pronounced (45 mV). The magnitude of the shift remained constant after the addition of 1 equiv. of $LiBF_4$ (Fig. 2), showing that the complexation equilibrium is strongly displaced toward the formation of the 1:1 complex **10e**:Li^+.

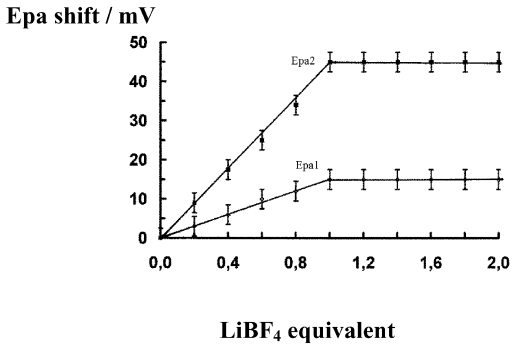


Figure 2. Shift of Epa_1 and Epa_2 in the CV of **10e** with added equivalent of $LiBF_4$ in CH_3CN.

This effect on Epa_1 and also Epa_2 is due to electrostatic repulsion with the bound metal cation and this strongly suggests that the metal is still complexed with the crown annelated DTDAF **10e** during the two processes. It is noteworthy that no shift has been observed on the reduction waves (Epc_1 and Epc_2), indicating that the metal ion has been expelled of the cavity only after the second oxidation process. This behavior is markedly different from what was observed with crown-ether annelated TTF in the presence of alkali metal ions where the first oxidation is usually shifted anodically whereas the second oxidation remained unchanged indicating that the metal ion is expelled upon oxidation to the cation radical.[9] Furthermore, the resulting ΔE of **10e**–Li^+ (220 mV) is larger than for **10e** itself (190 mV) presumably due to conformational modifications restrictions. Therefore, the presence of Li^+ could account for the stabilization of the cation radical specie by complexing the side chain and maintaining the thiazole cores in the same plane. Further work is underway to increase the nature and the size of the complexing side chain in order to take advantage of the original behavior demonstrated here for this crown annelated DTDAF upon complexation.

3. Experimental

^1H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz with tetramethylsilane as internal reference. Mass spectra were carried out at Centre de Mesures Physiques de l'Ouest, Rennes. Melting points were measured using a Kofler hot stage apparatus and are uncorrected. Elemental analysis results were obtained from the Laboratoire Central de Microanalyse du CNRS (Lyon).

Synthesis of dithiocarbamate salt **4**. A solution of carbon disulfide (50 mL), triethylamine (50 mL) and acetonitrile (50 mL) was stirred at 0°C and 2,2′-(ethylenedioxy)bisethylamine (10 g, 67.4 mmol) was added dropwise. The reaction mixture was then stirred at room temperature for 0.5 h. To this solution Et_2O was added (75 mL) and the precipitate was filtered, washed with Et_2O and dried. Bis dithiocarbamate salt **4** was obtained as a white powder; (33.1 g, 97%); mp (dec) 85°C and used without further purification. ^1H NMR (D_2O): δ 0.93 (t, 18H, CH_3), 2.86 (q, 12H, CH_2), 3.36 (s, 4H, OCH_2CH_2O), 3.38 (s, 8H, OCH_2CH_2N).

3.1. General procedure for the synthesis of 5(a–e)

To a solution of **4** (8 g, 16 mmol) in CH_3CN (100 mL), α-halogenated carbonyl derivative $R^1COCHXR^2$ (32 mmol) was added. The reaction mixture was refluxed for 5 h. Then the solvent was removed in vacuo and sulfuric acid 98% (1.6 mL, 32 mmol) was added to the cooled medium (0°C). After 15 min stirring, water (50 mL) was added. The mixture was extracted with CH_2Cl_2 (2×50 mL) and the organic phase was washed with water (3×50 mL), dried over Na_2SO_4 and evaporated. Column chromatography of the residue on silica gel column with CH_2Cl_2–Et_2O 80:20 as eluent afforded **5**. Bis thiazoline thiones **5** were recrystallized from EtOH.

3.1.1. 3,3′-[Ethane-1,2-diylbis(oxyethane-2,1-diyl)]-bis(4,5-dimethyl-1,3-thiazole-2(3*H*)-thione) 5a. White powder; yield: 82%; mp 131°C; ^1H NMR ($CDCl_3$): δ 2.16 (s, 6H, CH_3), 2.22 (s, 6H, CH_3), 3.51 (s, 4H, OCH_2CH_2O), 3.80 (t, 4H, OCH_2CH_2N, ^3J=5.3 Hz), 4.32 (t, 4H, OCH_2CH_2N, ^3J=5.3 Hz); ^{13}C NMR ($CDCl_3$): δ 12.19, 13.33, 48.39, 68.27, 71.10, 117.36, 136.25, 185.79; Anal. calcd for $C_{16}H_{24}N_2O_2S_4$: C, 47.50; H, 5.98; N, 6.92; S, 31.69. Found: C, 47.37; H, 6.02; N, 6.73; S, 31.37.

3.1.2. 3,3′-[Ethane-1,2-diylbis(oxyethane-2,1-diyl)]bis(4-methyl-1,3-thiazole-2(3*H*)-thione) 5b. White powder; yield: 75%; mp 83°C; ^1H NMR ($CDCl_3$): δ 2.29 (s, 6H, CH_3), 3.46 (s, 4H, OCH_2CH_2O), 3.77 (t, 4H, OCH_2CH_2N, ^3J=5.1 Hz), 4.30 (t, 4H, OCH_2CH_2N, ^3J=5.1 Hz), 6.22 (s, 2H, =CH); ^{13}C NMR ($CDCl_3$): δ 16.16, 47.89, 68.07, 71.05, 106.17, 141.70, 188.17; Anal. calcd for $C_{14}H_{20}N_2O_2S_4$: C, 44.65; H, 5.35; N, 7.44; S, 34.06. Found: C, 44.46; H, 5.39; N, 7.25; S, 33.83.

3.1.3. 3,3′-[Ethane-1,2-diylbis(oxyethane-2,1-diyl)]-bis(1,3-thiazole-2(3*H*)-thione) 5c. White powder; yield: 66%; mp 79°C; ^1H NMR ($CDCl_3$): δ 3.53 (s, 4H, OCH_2CH_2O), 3.77 (t, 4H, OCH_2CH_2N, ^3J=4.9 Hz), 4.34 (t, 4H, OCH_2CH_2N, ^3J=4.9 Hz), 6.57 (d, 2H, =CH, ^3J=4.6 Hz), 7.17 (d, 2H, =CH, ^3J=4.6 Hz); ^{13}C NMR ($CDCl_3$): δ 50.05, 68.45, 70.75, 110.72, 133.57, 187.50; Anal. calcd for $C_{12}H_{16}N_2O_2S_4$: C, 41.36; H, 4.63; N, 8.04; S, 36.80. Found: C, 41.58; H, 4.68; N, 8.08; S, 35.53.

3.1.4. Diethyl 3,3′-[ethane-1,2-diylbis(oxyethane-2,1-diyl)]bis(4-methyl-2-thioxo-2,3-dihydro-1,3-thiazole-5-carboxylate) 5d. White powder; yield: 75%; mp 121°C; ^1H NMR ($CDCl_3$): δ 1.34 (t, 6H, CH_3, ^3J=7.1 Hz), 2.70 (s, 6H, CH_3), 3.48 (s, 4H, OCH_2CH_2O), 3.80 (t, 4H, OCH_2CH_2N, ^3J=5.1 Hz), 4.29 (q, 4H, CH_2, ^3J=7.1 Hz), 4.37 (t, 4H, OCH_2CH_2N, ^3J=5.1 Hz); ^{13}C NMR ($CDCl_3$): δ 14.84, 14.71, 48.02, 61.92, 67.90, 70.87, 111.83, 149.91, 160.42, 188.90; Anal. calcd for $C_{20}H_{28}N_2O_6S_4$: C, 46.13; H, 5.42; N, 5.38; S, 24.63. Found: C, 46.24; H, 5.60; N, 5.45; S, 24.47.

3.1.5. 1,1′-{Ethane-1,2-diylbis[oxyethane-2,1-diyl(4-methyl-2-thioxo-1,3-thiazole-3,5-diyl)]}diethanone 5e. Yellow powder; yield: 82%; mp 158°C; ^1H NMR ($CDCl_3$): δ 2.39 (s, 6H, CH_3), 2.71 (s, 6H, CH_3), 3.50 (s, 4H, OCH_2CH_2O), 3.80 (t, 4H, OCH_2CH_2N, ^3J=5.1 Hz), 4.34 (t, 4H, OCH_2CH_2N, ^3J=5.1 Hz); ^{13}C NMR ($CDCl_3$): δ

15.31, 30.86, 47.94, 67.95, 70.97, 120.55, 148.80, 188.02, 188.64; Anal. calcd for $C_{18}H_{24}N_2O_4S_4$: C, 46.93; H, 5.25; N, 6.08; S, 27.84. Found: C, 46.51; H, 5.29; N, 6.10; S, 27.12.

3.2. General procedure for the synthesis of 6(a–e)

To a solution of bis (1,3-thiazoline-2-thione) **5** (4 mmol) in $CHCl_3$ (100 mL), $CH(OEt)_3$ (30.8 mmol, 5 mL) and $BF_3{\cdot}Et_2O$ (38.5 mmol, 5 mL) were added. After stirring at reflux for 30 min, the reaction mixture was allowed to reach room temperature and diethyl ether was added. The resulting oil was washed several times with diethyl ether and dried under vacuum. Then, selenium powder (790 mg, 10 mmol) was added into a solution of $NaBH_4$ (415 mg, 11 mmol) in absolute EtOH (50 mL) under flux of nitrogen. The reaction mixture was stirred, under nitrogen, until the formation of a turbid colorless solution of NaHSe. To this solution, the oil dissolved in MeCN (30 mL), was slowly added. The reaction mixture was stirred under nitrogen for 30 min. Water (100 mL) was added into the reaction mixture and extracted with CH_2Cl_2 (2×50 mL). The combined organic layers were dried over Na_2SO_4. After evaporation of the solvent under reduced pressure the residue was chromatographied over silica gel (CH_2Cl_2–Et_2O 80/20). Bis thiazoline-2-selones **6** were recrystallized in absolute ethanol.

3.2.1. 3,3′-[Ethane-1,2-diylbis(oxyethane-2,1-diyl)]-bis(4,5-dimethyl-1,3-thiazole-2(3*H*)-selone) 6a. Yellow powder; yield: 83%; mp 144°C; ^{1}H NMR ($CDCl_3$): δ 2.12 (s, 6H, CH_3), 2.24 (s, 6H, CH_3), 3.46 (s, 4H, OCH_2CH_2O), 3.81 (t, 4H, OCH_2CH_2N, ^3J=5.2 Hz), 4.38 (t, 4H, OCH_2CH_2N, ^3J=5.2 Hz); ^{13}C NMR ($CDCl_3$): δ 12.41, 13.53, 50.70, 68.67, 71.12, 122.10, 138.67, 177.75; Anal. calcd for $C_{16}H_{24}N_2O_2S_2Se_2C$, 38.56; H, 4.85; N, 5.62; S, 12.86. Found: C, 38.31; H, 4.73; N, 5.32; S, 12.67.

3.2.2. 3,3′-[Ethane-1,2-diylbis(oxyethane-2,1-diyl)]bis(4-methyl-1,3-thiazole-2(3*H*)-selone) 6b. Yellow powder; yield: 80%; mp 107°C; ^{1}H NMR ($CDCl_3$): δ 2.37 (s, 6H, CH_3), 3.46 (s, 4H, OCH_2CH_2O), 3.83 (t, 4H, OCH_2CH_2N, ^3J=5.1 Hz), 4.41 (t, 4H, OCH_2CH_2N, ^3J=5.1 Hz), 6.49 (s, 2H, =CH); ^{13}C NMR ($CDCl_3$): δ 16.09, 50.12, 68.49, 71.07, 110.92, 144.03, 180.47.

3.2.3. 3,3′-[Ethane-1,2-diylbis(oxyethane-2,1-diyl)]-bis(1,3-thiazole-2(3*H*)-selone) 6c. Yellow powder; yield: 82%; mp 102°C; ^{1}H NMR ($CDCl_3$): δ 3.54 (s, 4H, OCH_2CH_2O), 3.83 (t, 4H, OCH_2CH_2N, ^3J=4.9 Hz), 4.47 (t, 4H, OCH_2CH_2N, ^3J=4.9 Hz), 6.84 (d, 2H, =CH, ^3J=4.4 Hz), 7.34 (d, 2H, =CH, ^3J=4.4 Hz); ^{13}C NMR ($CDCl_3$): δ 52.63, 68.69, 70.99, 115.39, 135.71, 180.02.

3.2.4. Diethyl 3,3′-[ethane-1,2-diylbis(oxyethane-2,1-diyl)]bis(4-methyl-2-selenoxo-2,3-dihydro-1,3-thiazole-5-carboxylate) 6d. Yellow powder; yield: 70%; mp 110°C; ^{1}H NMR ($CDCl_3$): δ 1.31 (t, 6H, CH_3, ^3J=7.1 Hz), 2.74 (s, 6H, CH_3), 3.45 (s, 4H, OCH_2CH_2O), 3.83 (t, 4H, OCH_2CH_2N, ^3J=4.8 Hz), 4.27 (q, 4H, CH_2, ^3J=7.1 Hz); ^{13}C NMR ($CDCl_3$): δ 14.22, 14.37, 49.94, 61.75, 67.93, 70.48, 116.13, 150.81, 159.80, 183.13.

3.2.5. 1,1′-{Ethane-1,2-diylbis[oxyethane-2,1-diyl(4-methyl-2-selenoxo-1,3-thiazole-3,5-diyl)]}diethanone 6e. Orange powder; yield: 33%; mp 122°C; ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 6H, CH_3), 2.78 (s, 6H, CH_3CO), 3.50 (s, 4H, OCH_2CH_2O), 3.87 (t, 4H, OCH_2CH_2N, ^3J=5.1 Hz), 4.51 (t, 4H, OCH_2CH_2N, ^3J=5.1 Hz); ^{13}C NMR ($CDCl_3$): δ 15.35, 30.90, 50.22, 68.28, 70.93, 124.92, 150.04, 182.51, 188.41; Anal. calcd for $C_{18}H_{24}N_2O_4S_2Se_2$ C, 38.99; H, 4.36; N, 5.05; S, 11.56. Found: C, 39.08; H, 4.29; N, 5.04; S, 11.83.

3.3. General procedure for the synthesis of 7(a–e)

To a suspension of bis thiazoline thione **5** (2.5 mmol) in 10 mL of acetone under stirring at 0°C was added HPF_6 (1.2 g, 5 mmol, 60% solution in water) and H_2O_2 (1.7 mL, 20 mmol, 35% solution in water). The reaction mixture was stirred at 0°C for 0.5 h until the formation of an homogeneous solution. The solution was concentrated under vacuo and water was added to the resulting oil. The precipitate was filtered, washed several times with water and then recrystallized with THF/acetone 80:20.

3.3.1. 3,3′-[Ethane-1,2-diylbis(oxyethane-2,1-diyl)]-bis(4,5-dimethyl-1,3-thiazol-3-ium) dihexafluorophosphate 7a. White crystals; yield: 58 %; mp 118°C; ^{1}H NMR ($(CD_3)_2CO$): δ 2.50 (s, 6H, CH_3), 2.53 (s, 6H, CH_3), 3.57 (s, 4H, OCH_2CH_2O), 3.91 (t, 4H, OCH_2CH_2N, ^3J=4.8 Hz), 4.69 (t, 4H, OCH_2CH_2N, ^3J=4.8 Hz), 9.72 (s, 2H, =CH); ^{13}C NMR ($(CD_3)_2CO$): δ 12.09, 12.76, 54.65, 69.12, 71.47, 134.31, 143.97, 156.47; Anal. calcd for $C_{16}H_{26}N_2O_2S_2P_2F_{12}$: C, 30.39; H, 4.14; N, 4.43; S, 10.14. Found: C, 30.38; H, 4.11; N, 4.39; S, 10.52.

3.3.2. 3,3′-[Ethane-1,2-diylbis(oxyethane-2,1-diyl)]bis(4-methyl-1,3-thiazol-3-ium) dihexafluorophosphate 7b. White crystals; yield: 53%; mp 126°C; ^{1}H NMR ($(CD_3)_2CO$): δ 2.79 (s, 6H, CH_3), 3.75 (s, 4H, OCH_2CH_2O), 4.11 (t, 4H, OCH_2CH_2N, ^3J=4.8 Hz), 4.90 (t, 4H, OCH_2CH_2N, ^3J=4.8 Hz), 8.12 (d, 2H, =CH), 10.09 (s, 2H, =CH); ^{13}C NMR ($(CD_3)_2CO$): δ 13.97, 54.12, 69.29, 71.46, 122.05, 148.60, 160.28; Anal. calcd for $C_{14}H_{22}N_2O_2S_2P_2F_{12}$: C, 27.82; H, 3.67; N, 4.63; S, 10.61. Found: C, 27.93; H, 3.67; N, 4.68; S, 10.49.

3.3.3. 3,3′-[Ethane-1,2-diylbis(oxyethane-2,1-diyl)]-bis(1,3-thiazol-3-ium) dihexafluoro-phosphate 7c. White crystals; yield: 62%; mp 96°C; ^{1}H NMR ($(CD_3)_2CO$): δ 3.69 (s, 4H, OCH_2CH_2O), 4.03 (t, 4H, OCH_2CH_2N, ^3J=4.6 Hz), 4.93 (t, 4H, OCH_2CH_2N, ^3J=4.6 Hz), 8.37 (d, 2H, =CH, ^3J=2.2 Hz), 8.52 (d, 2H, =CH, ^3J=2.2 Hz), 10.08 (s, 2H, =CH); ^{13}C NMR ($(CD_3)_2CO$): δ 56.65, 69.54, 71.42, 127.02, 139.14, 160.24; Anal. calcd for $C_{12}H_{18}N_2O_2S_2P_2F_{12}$: C, 25.01; H, 3.15; N, 4.86; S, 11.13. Found: C, 25.26; H, 3.14; N, 4.89; S, 11.45.

3.3.4. 3,3′-[Ethane-1,2-diylbis(oxyethane-2,1-diyl)]bis[5-(ethoxycarbonyl)-4-methyl-1,3-thiazol-3-ium) dihexafluorophosphate 7d. White powder; yield: 59%; mp 104°C; ^{1}H NMR (CD_3CN): δ 1.46 (t, 6H, CH_3, ^3J=7.1 Hz), 2.88 (s, 6H, CH_3), 3.64 (s, 4H, OCH_2CH_2O), 3.92 (t, 4H, OCH_2CH_2N, ^3J=4.7 Hz), 4.51 (q, 4H, CH_2, ^3J=7.1 Hz), 4.64 (t, 4H, OCH_2CH_2N, ^3J=4.7 Hz), 9.71 (s, 2H, =CH); ^{13}C NMR ($(CD_3)_2CO$): δ 13.62, 14.73, 54.84,

64.44, 68.81, 71.47, 128.01, 153.71, 160.15, 162.01; Anal. calcd for $C_{20}H_{30}N_2O_6S_2P_2F_{12}$: C, 32.09; H, 4.04; N, 3.74; S, 8.57. Found: C, 32.52; H, 4.17; N, 3.65; S, 8.78.

3.3.5. 3,3′-[Ethane-1,2-diylbis(oxyethane-2,1-diyl)]bis(5-acetyl-4-methyl-1,3-thiazol-3-ium) dihexafluorophosphate 7e. White powder; yield: 59%; mp 128°C; ^{1}H NMR ($(CD_3)_2CO$): δ 2.74 (s, 6H, CH_3), 2.94 (s, 6H, CH_3CO), 3.65 (s, 4H, OCH_2CH_2O), 4.01 (t, 4H, OCH_2-CH_2N, ^3J=4.4 Hz), 4.86 (t, 4H, OCH_2CH_2N, ^3J=4.4 Hz), 10.06 (s, 2H, =CH); ^{13}C NMR ($(CD_3)_2CO$): δ 14.21, 30.63, 54.88, 68.80, 71.49, 137.13, 151.39, 161.58, 190.45; Anal. calcd for $C_{18}H_{26}N_2O_4S_2P_2F_{12}$: C, 31.40; H, 3.81; N, 4.07; S, 9.31. Found: C, 31.59; H, 3.82; N, 4.13; S, 9.56.

3.3.6. General procedure for the preparation of DTDAF 8 and in situ electrochemical investigations. A solution of **6** (0.05 mmol) in freshly distilled toluene (2 mL) was heated to 80°C under nitrogen and freshly distilled triethylphosphite (20 μL, 0.1 mmol) was added. The reaction mixture was stirred for 5 min at 80°C and then cooled down to the room temperature. The solution was then transferred into an electrochemical cell under nitrogen to a degassed solution 1 M of tetrabutylammonium hexafluorophosphate in CH_3CN and the CV of the solution was recorded.

Monothiazolium salt **9a**: a solution of **6a** (50 mg, 0.1 mmol) in freshly distilled toluene (5 mL) was heated to 80°C under nitrogen and freshly distilled triethylphosphite (40 μL, 0.2 mmol) was added. The reaction mixture was stirred for 5 min at 80°C and then cooled down to the room temperature. HPF_6 (0.2 mL) is then added to the reaction mixture which is further stirred for 15 min. The orange precipitate formed in the solution is filtered off, washed with water and dried. ^{1}H NMR ($(CD_3)_2CO$): δ 2.04 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 3.58 (m, 2H, OCH_2CH_2O), 3.61 (m, 2H, OCH_2CH_2O), 3.85 (t, 2H OCH_2CH_2N, ^3J=5.5 Hz), 3.99 (m, 2H OCH_2CH_2-N),4.45 (t, 2H, OCH_2CH_2N, ^3J=5.5 Hz), 9.87 (s, 1H, =CH). HRMS calcd for $C_{16}H_{25}N_2O_2S_2Se$: 421.0522. Found: 421.0523.

3.4. General procedure for the preparation of DTDAF 10 and in situ electrochemical investigations

To a solution 1 M of tetrabutylammonium hexafluorophosphate in 20 mL of CH_3CN bisthiazolium salt **7** (0.05 mmol) was added. The reaction mixture was degassed and NBu_4OH (65 μL, 0.1 mmol, 40% solution in water) was added under nitrogen. The solution turned immediately to red indicating the formation of the donor in the medium. The CV of the solution was then recorded.

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