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Synthesis and Redox Properties of Azino-Chalcogenoazafulvalenes: an Entry to Electroactive Azino Macrocyclic Compounds

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Dedicated to the memory of the late Prof. Dr. Valentin Koloini

Abstract

The synthesis of a series of dimers containing two redox active moieties, such as azino-chalcogenoazafulvalenes, connected through one or two non conjugated spacer group is reported. Various heterocycles have been used to build these donor molecules incorporating an azino spacer group between two thiazole moieties or a thiazole core and a selenazole one or two selenazole cores or a thiazole and a dithiole moiety. Cyclic voltammetry experiments have evidenced the influence of the nature of the heterocycle on the donating ability of these dimers. Moreover, sizable intramolecular interactions between the two electroactive moieties are observed depending on the length and the number of the non conjugated spacer group.

Keywords: π-electron donors, dimeric π-electron donors, azino-dithiadiazafulvalene, azino-diselenadiazafulvalene, azino-trithiaazafulvalene, crown-ether, macrocycles, redox behaviour

1. Introduction

Electron rich olefins, such as tetrathiafulvalenes and analogues have been extensively studied as precursors of molecular metals and superconductors.[1] In this research area it is well known that the physical properties are ascribed to the presence radical species in the solid state. For that purpose, most of the electron donor molecules used in this field exhibit three well defined oxidation states (neutral, cation radical and dication) with an easily accessible and stable cation radical state. The heterocyclic azines represent an interesting type of electron rich olefins as these derivatives present three redox states and a high thermodynamic stability of the cation radical species, some of the characteristics required to form conducting molecular materials.[2,3] Another important requirement in order to observe for instance conductivity is to form mixed valence species starting from electroactive molecule but this point is certainly less easy to control unless two electroactive units interact through space in a dimeric structure.[4] Indeed, electronic interaction between the two redox active cores would allow the removal of only one electron from the two electroactive cores and therefore the generation of mixed valence species. However, it is known that the through space interaction between two redox active cores within a molecule depends on the length of the spacer used as well as the number of linkers connecting the donors. Recently, we have demonstrated the potential of azino-dithiadiazafulvalenes (azino-DTDAF)[5,6] and azino-diselenadiazafulvalenes (azino-DSeDAF)[7] as precursors of molecular materials. Herein we decided to investigate the synthesis of symmetrical and unsymmetrical dimers where two donor cores are connected either through one or two linkers. We also modified the nature of the linker as we build the dimers linked by an ethyl or a bisethyleneglycol chain. In this paper, we will present also the electrochemical investigations carried out on these derivatives which allowed us to demonstrate the existence of intramolecular electronic interactions between the two donor cores. Furthermore, we studied the influence of alkali metal binding effect with the bis-oxaethyl chain on the redox behaviour of these dimers.

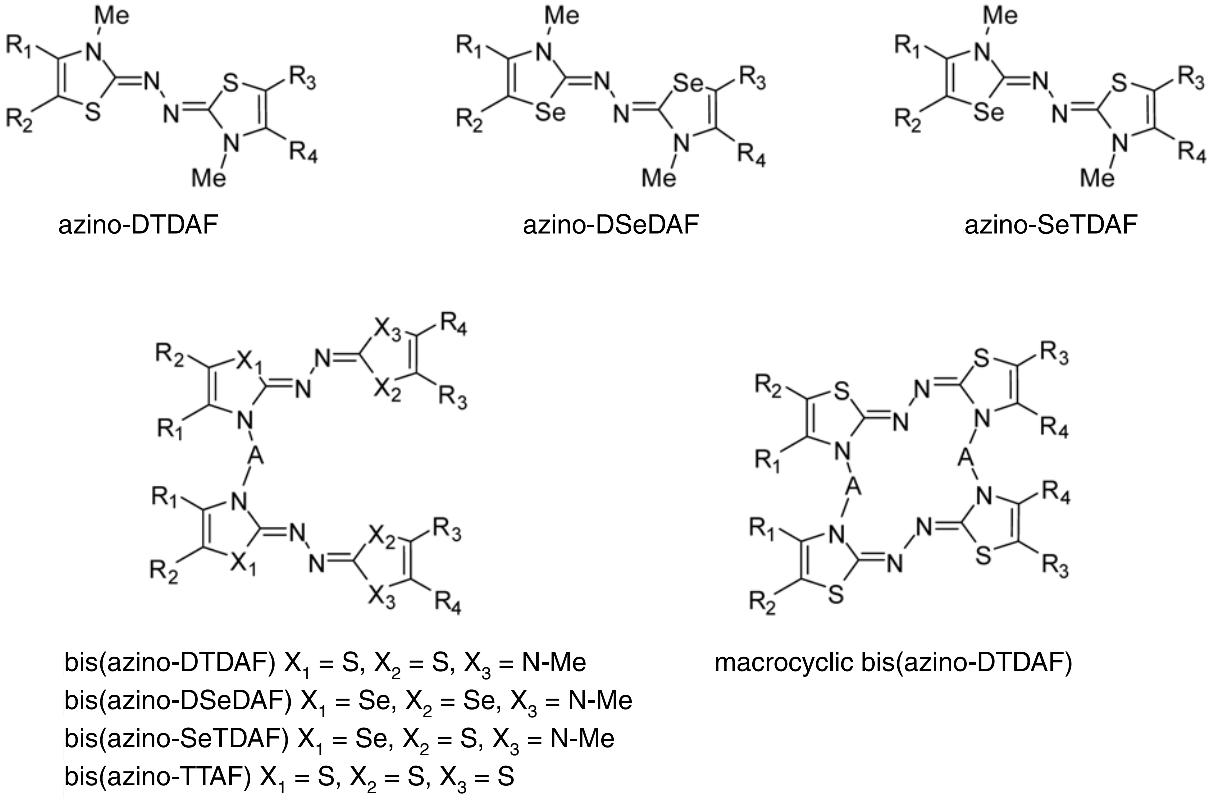


Figure 1. Structure of azino π-donors

2. Experimental

2. 1. Materials and Methods

Compounds **1**,[8] **4**,[9] **6**,[10] **8**,[11] **10**,[12] **15**,[13] **17**,[14] **23**[9] and **25**[10] were prepared according to the procedures described in the literature. All purchased reagents were used without further purification unless otherwise stated. All hydrazone and azine forming reactions were performed under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring and monitored by analytical thin layer chromatography (TLC) using Merck precoated silica gel plates with F254 indicator. Visualization on TLC was achieved by use of UV light (254 nm) and I_2. ^{1}H NMR spectra were recorded at 200 MHz and ^{13}C NMR spectra at 50 MHz. Chemical shift values (δ) are reported in parts per million relative to Me_4Si (δ 0.0 ppm). The proton spectra are reported as follows δ (multiplicity, number of protons, coupling constant *J*). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). ^{13}C NMR spectra were not recorded for dimeric donors due to the very low solubility of these compounds. Melting points were measured using a Kofler hot stage apparatus and are uncorrected. Elemental analyses were obtained from the Laboratoire Central de Microanalyse du CNRS (Lyon) and from the Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia. Mass spectra were carried out at Centre de Mesures Physiques de l'Ouest, Rennes, France and Mass Spectrometry Center, Jožef Stefan Institute, Ljubljana, Slovenia. Column chromatography was performed on silica gel 60 (0.040–0.063 mm). For the electrochemical determination of the redox potentials, CH_2Cl_2 was dried by refluxing over P_2O_5 followed by distillation. Cyclic voltammetry was carried out on a 10^{-3} M solution of metal complex derivative in CH_2Cl_2 containing 0.1 M $n\mathrm{Bu}_4\mathrm{NPF}_6$ as supporting electrolyte. Voltammograms were recorded at 0.1 Vs^{-1} on a platinum disk electrode (1 mm^2). Potentials were measured versus Saturated Calomel Electrode (SCE).

2. 2. Experimental Procedures

2-Methylthio-3,4,5-trimethyl-1,3-thiazolium hexafluorophosphate (2).

To a stirred solution of 4,5-dimethyl-2-methylthio-1,3-thiazole **1** (2.48 g, 15.57 mmol) in toluene (20 mL), dimethyl sulfate (2.06 g, 16.34 mmol) was added. The reaction mixture was stirred at reflux for 2 h. The mixture was cooled to room temperature. The solvent was evaporated and water (20 mL) was added to the brown residue. HPF_6 (60% solution in water) was added dropwise to a stirred solution as long as precipitation of a light brown solid was observed. The precipitate was recovered by filtration, washed with water and dried to afford a pale brown powder. The crude product was dissolved in minimum amount of acetone. Then, diethyl ether was added to the solution as long as precipitation of a white solid was observed. The precipitate was filtered, washed with diethyl ether and dried to give 4.22 g (85%) of 2-methylthio-3,4,5-trimethyl-1,3-thiazolium hexafluorophosphate **2** as a white powder, m.p. = 170 °C. ^{1}H NMR (200 MHz, acetone-d_6, 25 °C): δ = 2.33 (3H, s), 2.36 (3H, s), 2.85 (3H, s), 3.79 (3H, s) ppm. ^{13}C NMR (50 MHz, acetone-d_6, 25 °C): δ = 12.52, 12.64, 18.69, 38.66, 129.25, 144.35, 173.34 ppm. Anal. Calcd for $C_7H_{12}NS_2PF_6$: C, 26.33; H, 3.79; N, 4.39. Found: C, 26.03; H, 3.64; N, 4.27.

3,4,5-Trimethyl-3*H*-thiazol-2-one hydrazone (3).

To a stirred solution of 2-methylthio-3,4,5-trimethyl-1,3-thiazolium hexafluorophosphate 2 (0.80 g, 2.51 mmol) in acetonitrile (8 mL), hydrazine hydrate (1.25 g, 25.07 mmol) was added. The mixture was stirred under inert atmosphere at room temperature for 2.5 h. The solvent was removed under reduced pressure. The white solid residue was dissolved in CH_2Cl_2 (20 mL). The solution was washed with water (3 × 20 mL). After separation of layers, organic layer was dried with Na_2SO_4. Evaporation of the solvent afforded 0.38 g (97%) of 3,4,5-trimethyl-3*H*-thiazol-2-one hydrazone **3** as a light green powder, R_f (EtOH) = 0.18, m.p. = 99 °C. ^{1}H NMR (200 MHz, DMSO-d_6, 25 °C): δ = 1.97 (3H, s), 2.00 (3H, s), 3.11 (3H, s), 4.66 (2H, br s) ppm. ^{13}C NMR (50 MHz, DMSO-d_6, 25 °C): δ = 11.23, 12.38, 31.17, 101.00, 130.10, 158.75 ppm. MS (EI$^+$) m/z (%): 365 (M, 18), 311 (12), 185 (88), 143 (34), 93 (100). Anal. Calcd for $C_6H_{11}N_3S$: C, 45.83; H, 7.05; N, 26.72. Found: C, 45.83; H, 6.83; N, 26.38.

N,*N*'-Ethylene bis(1,3-benzothiazolyl-2-hydrazone) (5).

3,3'-Ethylenebis(2-ethylthiobenzothiazolium tetrafluoroborate) **4** (0.30 g, 0.51 mmol) was dissolved in 7 mL of acetonitrile. Separately, solution of triethylamine (0.10 g, 1.01 mmol) in 1 mL of acetonitrile, and solution of hydrazine hydrate (0.25 g, 5.07 mmol) in 1 mL of acetonitrile were prepared, and consecutively added to the solution of compound **4**. A yellow precipitate appeared immediately in the reaction mixture. It was further stirred under inert atmosphere at room temperature for 22.5 hours. Then, the precipitate was filtered off and dried at room temperature to give 0.12 g (67%) of hydrazone **5** as a yellow powder, m.p. = 238 °C (decomp.). ^{1}H NMR (200 MHz, DMSO-d_6, 25 °C): δ = 4.17 (s, 4H, NCH_2CH_2N), 5.15 (s, 4H, NH_2), 6.86 (ddd, 2H, Ar-H, ^3J = 7.6 Hz, 7.5 Hz, ^4J = 1.0 Hz), 6.90 (d, 2H, Ar-H, ^3J = 7.5 Hz), 7.13 (ddd, 2H, Ar-H, ^3J = 8.4 Hz, 8.4 Hz, ^4J = 1.3 Hz), 7.39 (dd, 2H, Ar-H, ^3J = 7.6 Hz, ^4J = 1.0 Hz) ppm. ^{13}C NMR (50 MHz, DMSO-d_6, 25 °C): δ = 46.47, 108.07, 120.48, 122.53, 122.76, 126.49, 141.35, 156.10 ppm. HRMS (EI) calcd. for $C_{16}H_{16}N_6S_2$ [M]: 356.0878, found: 356.0885.

N,*N*'-Ethylene bis(1,3-benzoselenazolyl-2-hydrazone) (7).

3,3'-Ethylenebis(2-ethylthiobenzoselenazolium tetrafluoroborate) **6** (0.40 g, 0.583 mmol) was dissolved in 6 mL of acetonitrile. Separately, solution of triethylamine (0.12 g, 1.16 mmol) in 1 mL of acetonitrile, and solution of hydrazine hydrate (0.29 g, 5.83 mmol) in 1 mL of acetonitrile were prepared, and consecutively added to the solution of compound **6**. A yellow-orange precipitate appeared immediately in the reaction mixture. It was further stirred under inert atmosphere at room temperature for 1 hour. Then, the precipitate was filtered off and washed with 10 mL of abs. ethanol. The product was dried at room temperature to give 0.25 g (96%) of hydrazone **7** as a yellow-orange powder, m.p. = 286 °C (decomp.). ^{1}H NMR (200 MHz, DMSO-d_6, 25 °C): δ = 4.20 (s, 4H, NCH_2CH_2N), 5.43 (s, 4H, NH_2), 6.86 (dd, 2H, Ar-H, ^3J = 7.8 Hz, 7.2 Hz), 7.01 (d, 2H, Ar-H, ^3J = 8.2 Hz), 7.18 (dd, 2H, Ar-H, ^3J = 7.4 Hz, 7.1 Hz), 7.52 (dd, 2H, Ar-H, ^3J = 7.5 Hz, ^4J = 0.5 Hz) ppm. ^{13}C NMR (50 MHz, DMSO-d_6, 25 °C): δ = 40.88, 109.48, 120.82, 121.18, 126.25, 126.81, 142.97, 158.14 ppm. MS (EI$^+$) m/z (%): 452 (M, 19), 404 (6), 239 (100), 223 (83), 179 (35). HRMS (EI) calcd. for $C_{16}H_{16}N_6Se_2$ [M]: 451.9767, found: 451.9775.

N,*N*'-Ethylene bis(4,5-dimethyl-1,3-thiazolyl-2-hydrazone) (9).

To the solution of *N*,*N*'-ethylene-bis(2-ethylthio-1,3-thiazolium tetraflouroborate) **8** (1.00 g, 1.82 mmol) in 20 mL of acetonitrile hydrazine hydrate was added (0.9 mL, 18 mmol). The reaction mixture was stirred at room temperature under inert atmosphere for 30 min. A white precipitate was formed. It was filtered off, washed with acetonitrile and dried at room temperature to give 0.48 g (85%) of hydrazone **9** as a white powder, m.p. = 210 °C. The product **9** was further used without additional purification. The product was stored in a refrigerator protected from air and light. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.76 (s, 6H, CH_3), 2.00 (s, 6H, CH_3), 3.88 (s, 4H, NCH_2CH_2N), 4.05 (s, 4H, NH_2) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 11.11, 12.75, 42.31, 102.90, 130.21, 160.92 ppm. Anal. Calcd for $C_{12}H_{20}N_6S_2$: C, 46.13; H, 6.45; N, 26.90; S, 20.52. Found: C, 45.80; H, 6.63; N, 26.18; S, 20.21.

N,*N*'-1,2-Diethoxyethylene-bis(4,5-dimethyl-1,3-thiazolyl -2-hydrazone) (11).

To the solution of *N*,*N*'-ethyleneoxy-bis(2-ethylthio-1,3-thiazolium tetraflouroborate) **10** (1.00 g, 1.6 mmol) in 20 mL of acetonitrile, hydrazine hydrate was added (0.8 mL, 16 mmol). The reaction mixture was stirred at room temperature under inert atmosphere for 30 min. Then, 3/4 of the solvent were evaporated and water was added for precipitation of hydrazone **11**. A white precipitate was filtered off, washed with water and dried at room temperature to give 0.44 g (70%) of hydrazone **11** as a white powder, m.p. < 60 °C. The product **11** was stored protected from air. It was immediately used in the next reaction step. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.99 (s, 6H, CH_3), 2.02 (s, 6H, CH_3), 3.47 (s, 4H, NH_2), 3.50 (s, 4H, OCH_2CH_2O), 3.61 (t, 4H, 2 × CH_2, ^3J = 5.2 Hz), 3.77 (t, 4H, 2 × CH_2, ^3J = 5.2 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 11.77, 12.72, 45.02, 68.59, 70.99, 102.82, 130.46, 161.53 ppm. Anal. Calcd for $C_6H_{11}N_3S$: C, 47.17; H, 6.79; N, 23.57. Found: C, 47.33; H, 6.83; N, 23.21.

N,N'-Ethylene bis(azino-trimethyl-benzoDTDAF) (12).

Compound **4** (0.28 g, 0.477 mmol) was dissolved in a mixture of abs. ethanol (5 mL) and acetonitrile (7 mL). Compound **3** (0.15 g, 0.954 mmol) was added to the solution. After addition of triethylamine (0.097 g, 0.954 mmmol) reaction took place and a brown suspension was formed immediately. The reaction mixture was further stirred under inert atmosphere at room temperature for 21 hours. During reaction a pale green precipitate was formed in the solution. It was filtered off and washed with 10 mL of abs. ethanol. The product was dried at room temperature to give 0.20 g (90%) of azine **12** as a pale green powder, m.p. > 260 °C, ^{1}H NMR (200 MHz, $CDCl_3/CF_3COOH$ = 10 : 1, 25 °C): δ = 2.24, 2.26 (2s, 12H, CH_3), 3.68 (s, 6H, CH_3), 4.83 (s, 4H, NCH_2CH_2N), 7.23 (dd, 2H, Ar-H, ^3J = 7.4 Hz), 7.34 (dd, 2H, Ar-H, ^3J = 7.3 Hz, 7.5 Hz), 7.44 (ddd, 2H, Ar-H, ^3J = 8.0 Hz, 7.4 Hz, ^4J = 1.5 Hz), 7.60 (dd, 2H, Ar-H, ^3J = 7.8 Hz, ^4J = 1.3 Hz) ppm. HRMS (EI) calcd. for $C_{28}H_{30}N_8S_4$ [M]: 606.1476, found: 606.1491.

N,N'-Ethylene bis(azino-trimethyl-benzoSeTDAF) (13).

Compound **6** (0.200 g, 0.29 mmol) and compound **3** (0.092 g, 0.583 mmol) were mixed together and then suspended in a mixture of acetonitrile : abs. ethanol (v/v = 1/1, 5 mL). Triethylamine (0.059 g, 0.583 mmol) was added to the reaction mixture and it was stirred under inert atmosphere at room temperature for 21 hours. During the reaction a yellow precipitate was formed. It was filtered off and washed with 25 mL of acetonitrile. The product was dried at room temperature to give 0.17 g (83%) of azine **13** as a yellow powder, m.p. > 260 °C. ^{1}H NMR (200 MHz, $CDCl_3/CF_3COOH$ = 10 : 1, 25 °C): δ = 2.22 (s, 12H, CH_3), 3.69 (s, 6H, CH_3), 4.54 (s, 4H, NCH_2CH_2N), 7.02–7.14 (m, 4H, Ar-H), 7.26 (m, 2H, Ar-H), 7.43 (dd, 2H, Ar-H, ^3J = 7.8 Hz, ^4J = 1.1 Hz) ppm. MS (EI^+) m/z (%): 702 (M, 36), 654 (10), 579 (7), 563 (4), 364 (100), 338 (28), 242 (45), 155 (64). HRMS (EI) calcd. for $C_{28}H_{30}N_8S_2Se_2$ [M]: 702.0365, found: 702.0364.

N,N'-Ethylene bis(azino-pentamethylDTDAF) (16).

To the solution of bis hydrazone **9** (0.310 g, 1 mmol) and 2-ethylthio-1,3-thiazolium tetrafluoroborate **15** (0.550 g, 2 mmol) in 20 mL of acetonitrile, triethylamine (0.56 mL, 4 mmol) was added. The reaction mixture was refluxed for 3 hours under inert atmosphere, and then stirred further for 12 hours at room temperature protected from light. A yellow precipitate was formed. It was filtered off, washed with acetonitrile and diethyl ether. The yellow powder was for analytical purposes further purified by silica gel column chromatography using solvent mixture CH_2Cl_2 : Et_2O = 80 : 20 (v/v) as eluent to give 0.18 g (32%) of azino-DTDAF **16** as a yellow powder, m.p. > 260 °C. The product is easily oxidized therefore it should be stored protected from air and light. ^{1}H NMR (200 MHz, $CDCl_3/CF_3COOH$ = 10 : 1, 25 °C): δ = 1.90–2.30 (m, 24H, CH_3), 3.65 (s, 6H, CH_3N), 4.16 (s, 4H, NCH_2CH_2N) ppm. HRMS (EI) calcd. for $C_{24}H_{34}N_8S_4$ [M]: 562.1789, found: 562.1781.

N,N'-Ethylene bis(azino-tetramethylTTAF) (18).

The solution of bis hydrazone **9** (0.310 g, 1 mmol) and 2-piperidino-1,3-dithiolum hexafluorophosphate **17** (0.720 g, 2 mmol) in 20 mL of acetonitrile was refluxed for 2 hours under inert atmosphere, and then stirred further for 12 hours at room temperature. A yellow precipitate was formed. It was filtered off, washed with acetonitrile and diethyl ether. The yellow powder was for analytical purposes further purified by silica gel column chromatography using solvent mixture CH_2Cl_2 : Et_2O = 80 : 20 as eluent to give 0.073 g (13%) of azino-DTDAF **18** as a yellow powder, m.p. > 260 °C. ^{1}H NMR (200 MHz, $CDCl_3/CD_3CN/CF_3COOH$ = 80 : 10 : 10, 25 °C): δ = 1.95–2.15 (m, 24H, CH_3), 4.52 (s, 4H, NCH_2CH_2N) ppm. HRMS (EI) calcd. for $C_{22}H_{28}N_6S_6$ [M]: 568.0700, found: 568.0704.

Cage bis(azino-tetramethylDTDAF) (19).

To the solution of bis hydrazone **11** (0.401 g, 1 mmol) and *N,N'*-1,2-diethoxyethylene-bis(2-ethylthio-1,3 thiazolium tetrafluoroborate) **10** (0.636 g, 1 mmol) in 20 mL of acetonitrile, triethylamine (0.404 g, 4 mmol) was added. The reaction mixture was refluxed for 3 hours under inert atmosphere, and then stirred further for 12 hours at room temperature protected from light. A yellow precipitate was formed. It was filtered off, washed with acetonitrile and diethyl ether. The product was purified by silica gel column chromatography using solvent mixture CH_2Cl_2 : Et_2O = 80 : 20 as eluent to give 0.096 g (13%) of cage azino-DTDAF **19** as a yellow powder, m.p. = 250 °C (decomp.). The product was stored under inert atmosphere protected from light. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.7–2.1 (m, 24H, CH_3), 3.55 (m, 8H, 4 × CH_2), 3.70 (m, 8H, 4 × CH_2), 3.81 (m, 8H, 4 × CH_2) ppm. HRMS (EI) calcd. for $C_{32}H_{48}N_8O_4S_4$ [M]: 736.2681, found: 736.2684.

N,*N*'-1,2-Diethoxyethylene-bis(azino-pentamethyl-DTDAF) (20).

To the solution of bis hydrazone **11** (0.401 g, 1 mmol) and 2-ethylthio-1,3-thiazolium tetrafluoroborate **15** (0.550 g, 2 mmol) in 20 mL of acetonitrile, triethylamine (0.404 g, 4 mmol) was added. The reaction mixture was refluxed for 3 hours under inert atmosphere, and then stirred further for 12 hours at room temperature protected from light. A yellow precipitate was formed. It was filtered off, washed with acetonitrile and diethyl ether. It was further purified by silica gel column chromatography using solvent mixture CH_2Cl_2 : THF = 50 : 50 as eluent to give 0.18 g (28%) of azino-DTDAF **20** as a yellow powder, m.p. = 140 °C. The product was stored under inert atmosphere protected from light. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.80$–2.30 (m, 24H, CH_3), 3.26 (s, 6H, CH_3N), 3.56 (s, 4H, OCH_2CH_2O), 3.75 (t, 4H, $2 \times CH_2$, $^3J = 4.2$ Hz), 3.80–4.10 (m, 4H, $2 \times CH_2$) ppm. HRMS (EI) calcd. for $C_{28}H_{42}N_8O_2S_4$ [M]: 650.2314, found: 650.2304.

N,*N*'-1,2-Diethoxyethylene-bis(azino-tetramethyl-TTAF) (21).

The solution of bis hydrazone **11** (0.401 g, 1 mmol) and 2-piperidino-1,3-dithiolum hexafluorophosphate **17** (0.719 g, 2 mmol) in 20 mL of acetonitrile was refluxed for 3 hours under inert atmosphere, and then stirred further for 12 hours at room temperature. A yellow precipitate was formed. It was filtered off, washed with acetonitrile and diethyl ether. The product was further purified by silica gel column chromatography using solvent mixture CH_2Cl_2 : Et_2O = 80 : 20 as eluent to give 0.053 g (8%) of azino-DTDAF **21** as a yellow powder, m.p. = 174–178 °C. The product was stored under inert atmosphere protected from light. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.05$ (s, 24H, CH_3), 3.59 (s, 4H, OCH_2CH_2O), 3.79 (m, 4H, $2 \times CH_2$), 3.93 (m, 4H, $2 \times CH_2$) ppm. HRMS (EI) calcd. for $C_{26}H_{36}N_6O_2S_6$ [M]: 656.1224, found: 656.1216.

Cage *N*,*N*'-ethylene bis(azino-dibenzoDTDAF) (22).

Compound **4** (0.228 g, 0.385 mmol) was dissolved in a mixture of acetonitrile : abs. ethanol (v/v = 1/1, 10 mL). After addition of compound **5** (0.137 g, 0.385 mmol) an orange suspension was obtained. Then, triethylamine (0.078 g, 0.771 mmol) was added to the mixture. The colour of the reaction mixture changed to light orange. The reaction mixture was stirred further under inert atmosphere at room temperature for 69 hours. Then, the orange precipitate was filtered off, washed with 10 mL of abs. ethanol and dried at room temperature to give 0.21 g (84%) of cage azine **22** as an orange powder, m.p. > 260 °C. ^1H NMR (200 MHz, $CDCl_3/CF_3COOH = 10:1$, 25 °C): $\delta = 4.18$ (s, 8H, NCH_2CH_2N), 6.49–7.20 (m, 16H, Ar-H) ppm. HRMS (EI) calcd. for $C_{32}H_{24}N_8S_4$ [M]: 648.1007, found: 648.0993.

N,*N*'-Ethylene bis(azino-methyl-dibenzoDTDAF) (24).

Compound **5** (0.10 g, 0.281 mmol) was suspended in a mixture of acetonitrile : abs. ethanol (v/v = 1/1, 10 mL). After addition of 2-ethylthio-1,3-benzothiazolium tetrafluoroborate **23** (0.17 g, 0.561 mmol) to the suspension a turbid orange solution was obtained. Then, triethylamine (0.06 g, 0.561 mmol) was added to the mixture. Colour of the reaction mixture turned to light yellow immediately and yellow precipitate was observed in the solution. The reaction mixture was stirred under inert atmosphere at room temperature for 63 hours. Then, the precipitate was filtered off and washed with abs. ethanol and dried at room temperature to give 0.12 g (67%) of azine **24** as a pale yellow powder, m.p. > 260 °C. ^1H NMR (200 MHz, $CDCl_3/CF_3COOH = 10:1$, 25 °C): $\delta = 3.94$ (s, 6H, CH_3), 4.71 (s, 4H, NCH_2CH_2N), 7.16–7.24 (m, 4H, Ar-H), 7.35–7.53 (m, 8H, Ar-H), 7.61–7.70 (m, 4H, Ar-H) ppm. HRMS (EI) calcd. for $C_{32}H_{26}N_8S_4$ [M]: 650.1163, found: 650.1180.

N,*N*'-Ethylene bis(azino-methyl-dibenzoSeTDAF) (26).

Compound **5** (0.100 g, 0.281 mmol) was suspended in a mixture of acetonitrile : abs. ethanol (v/v = 1/1, 10 mL). After addition of 2-ethylthio-1,3-benzoselenazolium tetrafluoroborate **25** (0.185 g, 0.561 mmol) to the suspension a turbid solution was obtained. Then, triethylamine (0.057 g, 0.561 mmol) was added to the mixture. Colour of the reaction mixture turned to light yellow immediately and a yellow precipitate was observed in the solution. The reaction mixture was stirred under inert atmosphere at room temperature for 64 hours. Then, the precipitate was filtered off and washed with 25 mL of acetonitrile. The product was dried at room temperature to give 0.160 g (76%) of azine **26** as a pale yellow powder, m.p. > 260 °C. ^1H NMR (200 MHz, $CDCl_3/CF_3COOH = 10:1$, 25 °C): $\delta = 3.90$ (s, 6H, CH_3), 4.67 (s, 4H, NCH_2CH_2N), 7.13–7.64 (m, 16H, Ar-H) ppm. MS (EI^+) m/z (%): 746 (M, 22), 698 (5), 591 (14) , 551 (6) , 536 (2), 386 (97), 175 (100), 149 (26). Anal. Calcd for $C_{32}H_{26}N_8S_2Se_2$: C, 51.75; H, 3.26; N, 15.09. Found: C, 51.53; H, 3.09; N, 14.92.

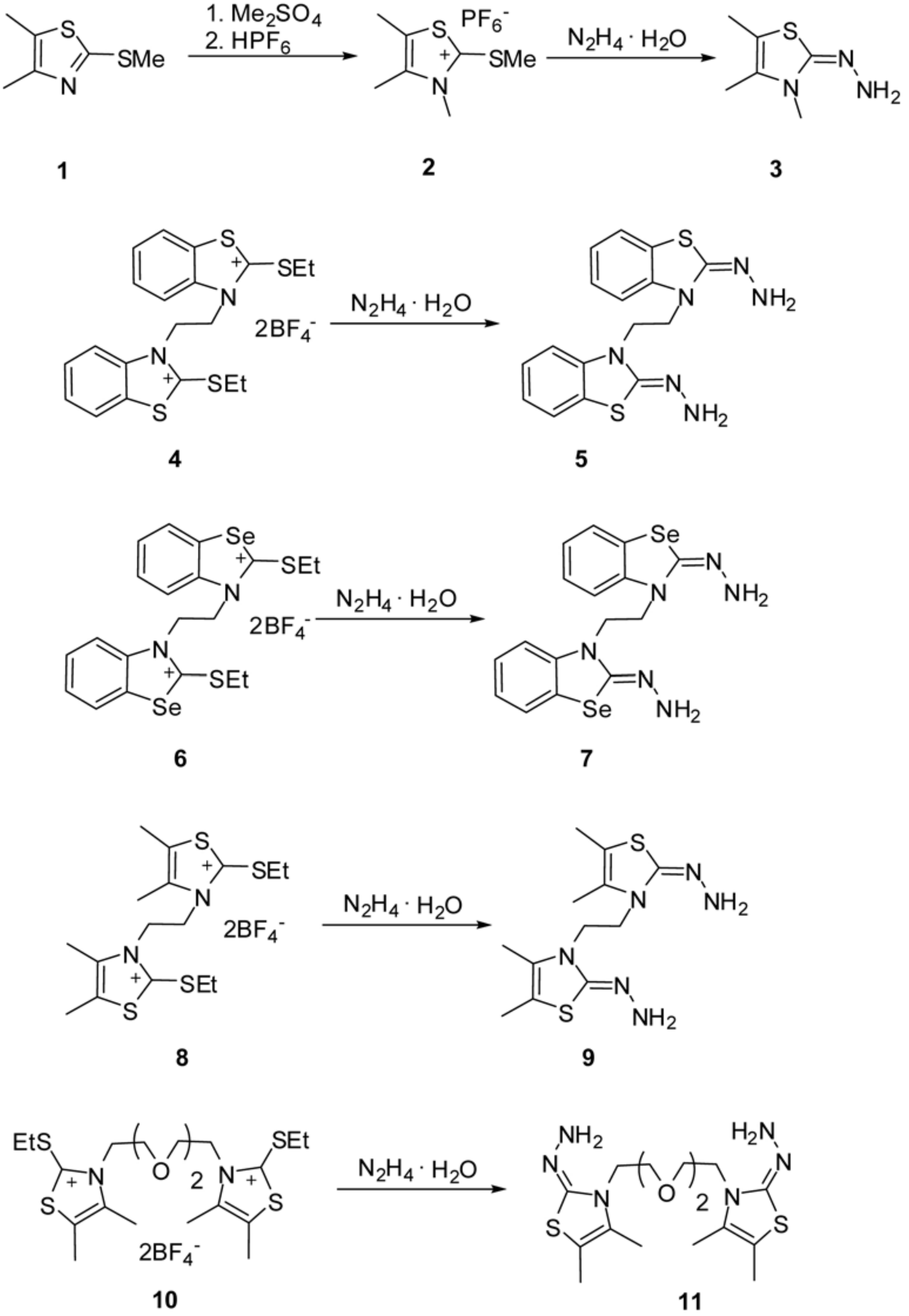
N,*N*'-Ethylene bis(azino-methyl-dibenzoDSeDAF) (27).

Compound **7** (0.100 g, 0.222 mol) was suspended in a mixture of acetonitrile : abs. ethanol (v/v = 1/1, 16 mL). After addition of 2-ethylthio-1,3-benzoselenazolium tetrafluoroborate **25** (0.147 g, 0.444 mmol) to the suspension a turbid solution was obtained. Then, triethylamine (0.045 g, 0.444 mmol) was added to the mixture. Colour of the reaction mixture turned to light yellow immediately and a yellow precipitate was observed in the solution. The reaction mixture was stirred under inert atmosphere at room temperature for 96 hours. Then, the precipitate was filtered off and washed with 25 mL of acetonitrile. The product was dried at room temperature to give 0.100 g (54%) of azine **27** as a pale yellow powder, m.p. > 260 °C. ^{1}H NMR (200 MHz, $CDCl_3/CF_3COOH$ = 10 : 1, 25 °C): δ = 3.94 (s, 6H, CH_3), 4.69 (s, 4H, NCH_2CH_2N), 7.18–7.69 (m, 16H, Ar-H) ppm. MS (EI$^+$) m/z (%): 840 (M, 18), 792 (5), 746 (6), 434 (70), 386 (38), 223 (100), 184 (46). Anal. Calcd for $C_{32}H_{26}N_8Se_4$: C, 45.84; H, 3.13; N, 13.36. Found: C, 45.80; H, 3.33; N, 13.53.

3. Results and Discussion

3. 1. Synthesis

For the preparation of bis(azino-chalcogenoazafulvalenes) two strategies could be applied, either reaction of heterocyclic hydrazone with bis(chalcogenoazolium salt) or reaction of bis(heterocyclic hydrazone) with chalcogenoazolium salt or dithiolium salt. Therefore, for applica-



Scheme 1. Synthesis of heterocyclic hydrazones

tion of both these strategies to bis-azino donors we firstly had to prepare corresponding heterocyclic hydrazones and bis(heterocyclic hydrazones).

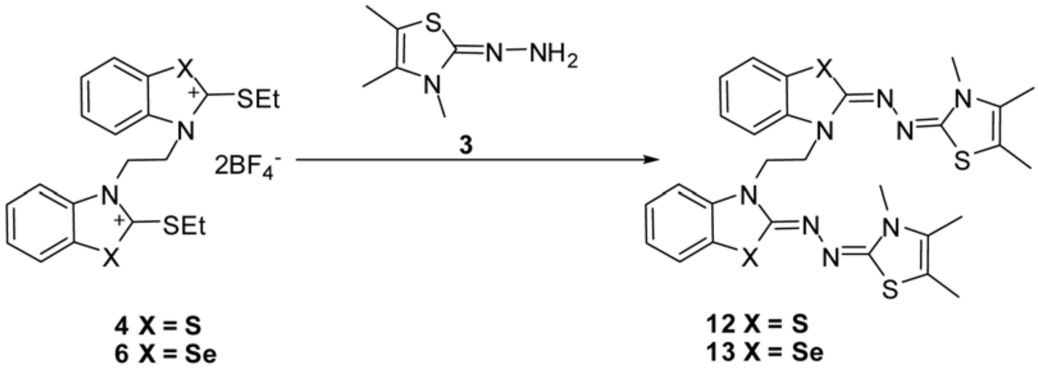
We started our synthetic approach with preparation of 2-methylthio-3,4,5-trimethyl-1,3-thiazolium hexafluorophosphate salt **2** from 4,5-dimethyl-2-methylthio-1,3-thiazole **1** by using a new one-pot transformation. The 4,5-dimethyl-2-methylthio-1,3-thiazole **1** was initially alkylated with dimethyl sulfate. This afforded oily sulfate salt which proved to be difficult to purify. To resolve this problem we found out that when aqueous solution of sulphate salt is treated with HPF_6, a water insoluble 2-methylthio-3,4,5-trimethyl-1,3-thiazolium hexafluorophosphate salt **2** precipitated. This method allows easy removal of an excess of the alkylating agent as well as the other water soluble impurities. Furthermore, hexafluorophosphate salt **2** was easily recrystallized from acetone/ether mixture to afford analytically pure salt **2** in 85% yield. When salt **2** was treated with 10 eq of hydrazine hydrate in the presence of triethylamine (2 eq) under inert atmosphere an air sensitive 3,4,5-trimethyl-3*H*-thiazol-2-one hydrazone **3** was isolated in 97% yield (Scheme 1).

For the preparation of bis(heterocyclic hydrazones), we reacted bis(chalcogenoazolium salts) with high excess (10 eq) of hydrazine hydrate. In these reactions hydrazine acts as a nucleophile and also as a base to promote the transformation. In some instances triethylamine (2 eq) was also added to facilitate the reaction. By applying this synthetic method bis-benzothiazolium salt **4** reacted with hydrazine hydrate (10 eq) in the presence of triethylamine (2 eq) under inert atmosphere to give bis-(benzothiazolyl hydrazone) **5** in 67%. When structuraly similar bis-benzoselenazolimum salt **6** was reacted under similar conditions bis-(benzoselenazolyl hydrazone) **7** was obtained in 96% yield. Treatment of bis-thiazolium salt **8** with hydrazine hydrate (10 eq) produced the corresponding bis(thiazolyl hydrazone) **9** in 85% yield. Finally, the polyether linked bis(thiazolium salt) **10** reacted with hydrazine hydrate (10 eq) under the same conditions and the corresponding polyether linked bis(thiazolyl hydrazone) **11** was isolated in 70% yield (Scheme 1).

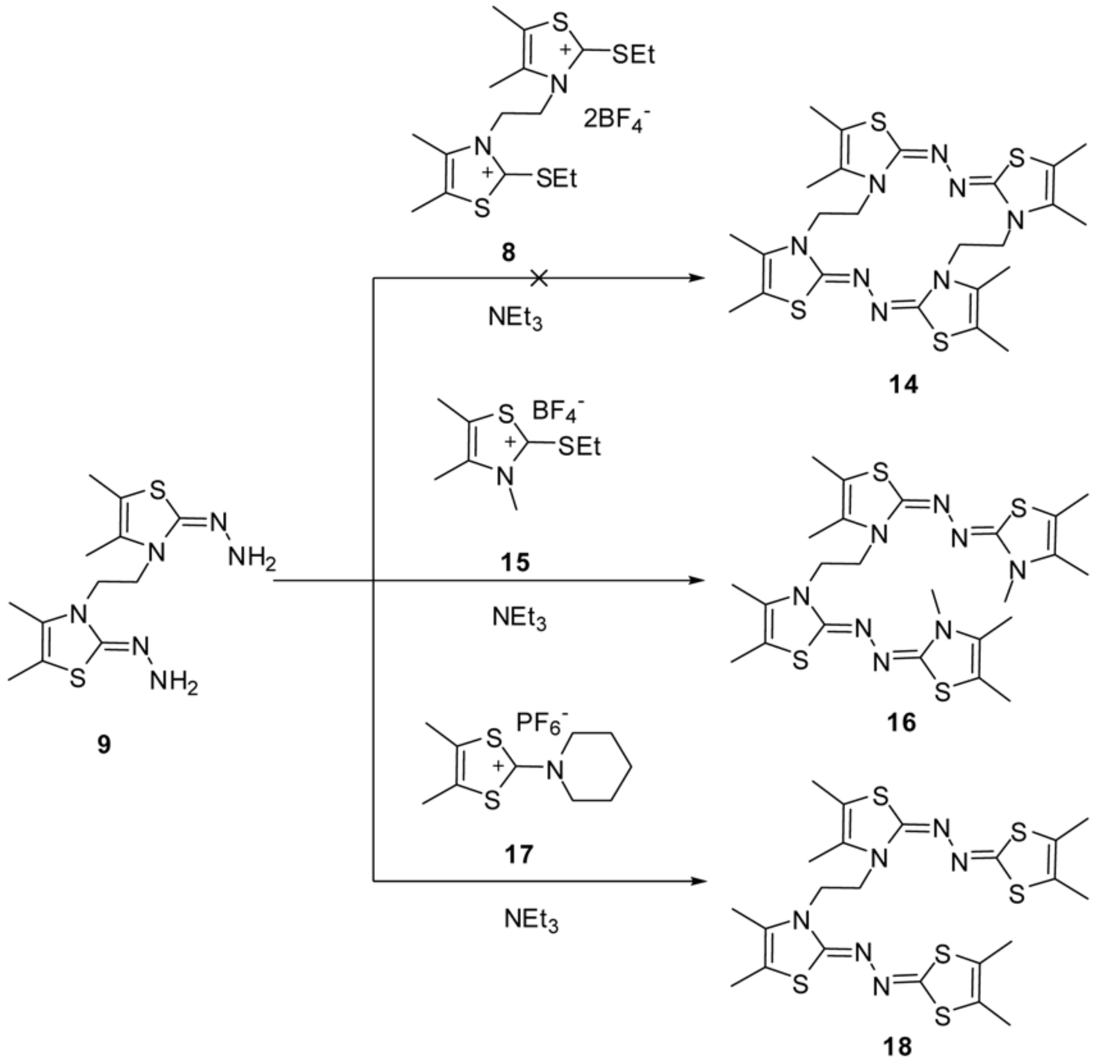
For the preparation of bis(azino-chalcogenoazafulvalenes) we extended our recently presented approach for the construction of unsymmetrical azino donors where heterocyclic hydrazones are coupled with chalcogenoazolium salt in the presence of a base to produce azines. Herein, we first applied this approach to the reaction of heterocyclic hydrazone with bis(chalcogenoazolium salt) to prepare bis(azino-dichalcogenodiazafulvalenes). Indeed, when bis-benzothiazolium salt **4** was treated with 2 eq azine **3** in the presence of triethylamine (2 eq) bis(azino-dithiadiazafulvalenes) **12** was obtained in 90% yield. Similarly, reaction of bis-benzoselenazolimum salt **6** with 2 eq azine **3** in the presence of triethylamine (2 eq) under the same conditions afforded bis(azino-selenathiadiazafulvalenes) **13** in 83% yield (Scheme 2).

After successfully completed couplings of heterocyclic hydrazone **3** with bis(chalcogenoazolium salts) we considered in the next part of our studies to conduct the coupling of bis(heterocyclic hydrazones) with chalcogenoazolium salts to extend the group of bis(azino-chalcogenoazafulvalenes). The first attempt to perform the coupling of bis(thiazolyl hydrazone) **9** with bis(chalcogenoazolium salts) in the presence of triethylamine (4 eq) did not allow us to isolate the symmetric caged azine **14**. This result could be ascribed to the sensitive nature of hydrazone **9** and consequently its azine **14** which is probably too sensitive to air to be isolated. Nevertheless, when bis(thiazolyl hydrazone) **9** was reacted with 2-ethylthio-1,3-thiazolium tetrafluoroborate **15** (2 eq) in the presence of triethylamine (4 eq) the desired bis(azino-dithiadiazafulvalenes) **16** was isolated in 32% after purification by silica gel column chromatography. Furthermore, when bis(thiazolyl hydrazone) **9** was reacted 2-piperidino-1,3-dithiolum hexafluorophosphate **17** (2 eq) a bis(azino-trithiaazafulvalene) **18** was isolated in 13% yield after purification by silica gel column chromatography (Scheme 3).

We extended the first group of bis(azino-chalcogenoazafulvalenes) with polyether linked analogues. For this purpose a polyether linked bis(thiazolyl hydrazone) **11** (1 eq) was reacted with polyether linked bis(thiazolium salt) **10** (1 eq) in the presence of triethylamine (4 eq) which af-



Scheme 2. Synthesis of benzo-fused bis-azines from bis(chalcogenobenzoazolium salts) **4** and **6**.



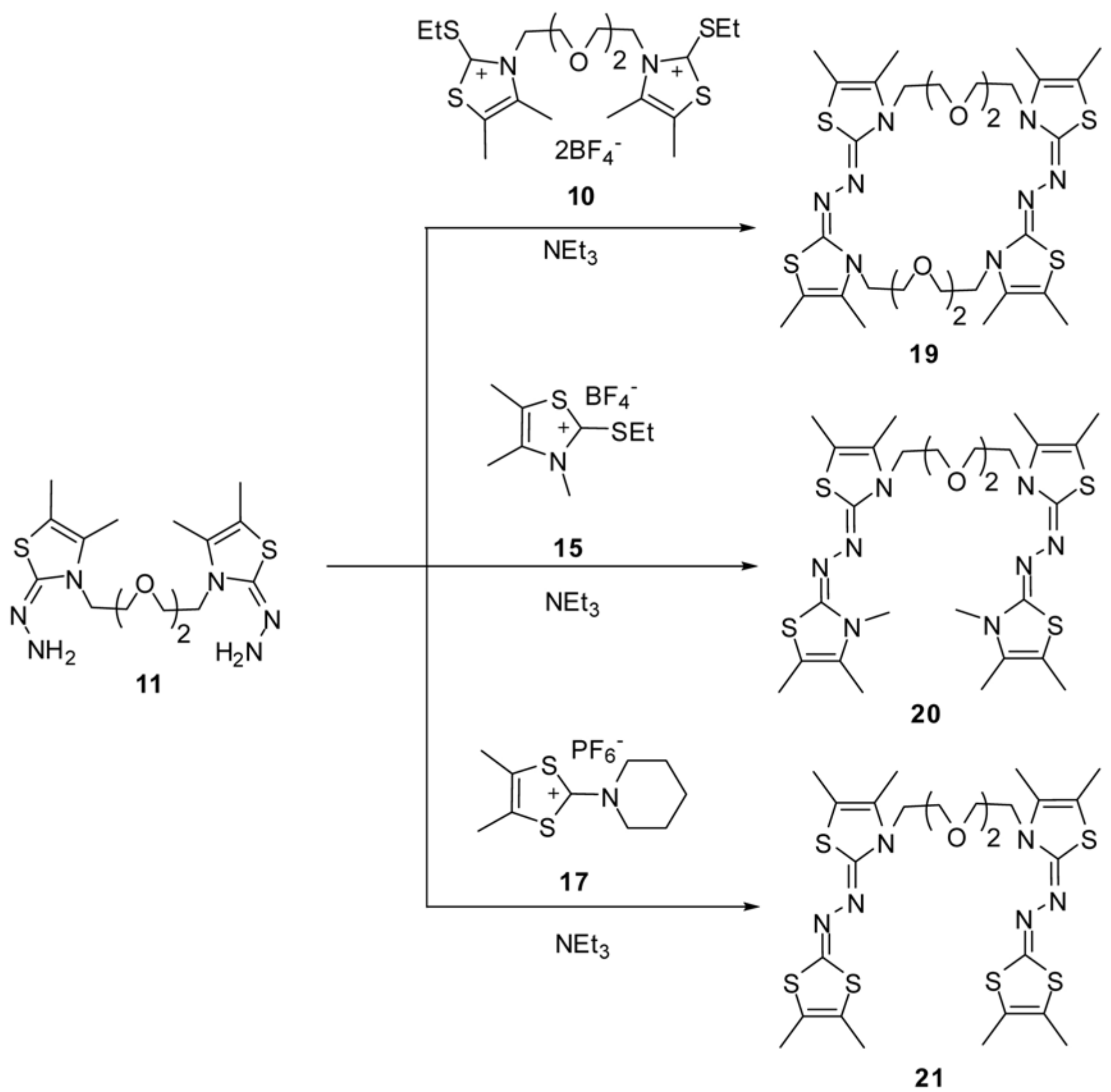
Scheme 3. Synthesis of methyl-substituted bis-azines from bis(thiazolyl hydrazone) **9**.

forded caged polyether linked bis(azino-dithiadiazafulvalene) **19** in 13% yield after purification by silica gel column chromatography. Similarly, reaction between bis(thiazolyl hydrazone) **11** and 2-ethylthio-1,3-thiazolium tetrafluoroborate **15** (2 eq) in the presence of triethylamine (4 eq) gave 28% of polyether linked bis(azino-dithiadiazafulvalene) **20** after silica gel column chromatography purification. In the last experiment of this group bis(thiazolyl hydrazone) **11** was reacted with 2-piperidino-1,3-dithiolum hexafluorophosphate **17** (2 eq) which afforded after chromatographic purification on silica gel polyether linked bis(azino-trithiaazafulvalene) **21** in 8% yield (Scheme 4).

In the last part of our studies we also explored the possibility of preparation of fully benzo-fused derivatives. In order to achieve this bis(benzothiazolyl hydrazone) **5** (1 eq) was reacted with 3,3'-ethylenebis(2-ethylthiobenzothiazolium tetrafluoroborate) **4** (1 eq) in the presence of triethylamine (2 eq) to give caged bis(azino-dibenzodithiadiazafulvalene) **22** in 84% yield. A reaction of bis(benzothiazolyl hydrazone) **5** (1 eq) with 2-ethylthio-1,3-benzothiazolium tetrafluoroborate **23** (2 eq) in the presence of triethylamine (2 eq) produced the bis(azino-dibenzodithiadiazafulvalene) **24** in 67% yield. To get the mixed sulfur/selenium donor bis(benzothiazolyl hydrazone) **5** was reacted with 2-ethylthio-1,3-benzoselenazolium tetrafluoroborate **25** (2 eq) in the presence of triethylamine (2 eq). In this instance bis(azino-dibenzodiselenadiazafulvalene) **26** was obtained in 76% yield**.** In order to prepare the fully selenium containing analogue we also conducted reaction of bis(benzoselenazolyl hydrazone) **7** with 2-ethylthio-1,3-benzoselenazolium tetrafluoroborate **25** (2 eq) in the presence of triethylamine (2 eq) which allowed us to isolate bis(azino-dibenzodiselenadiazafulvalene) **27** in 54% yield (Scheme 5).

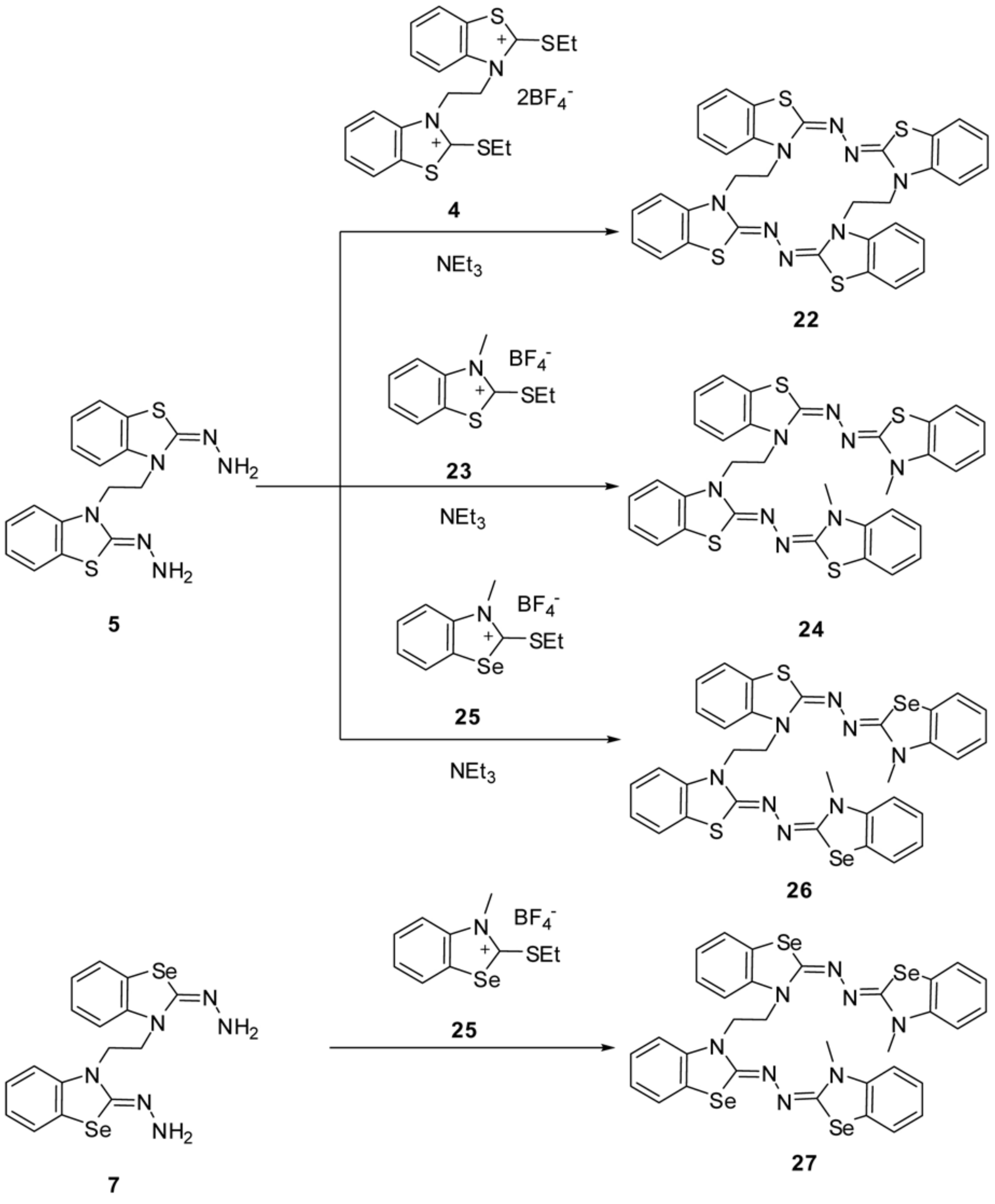
3. 2. Electrochemical Studies

The redox behaviour of the various bis(azino-chalcogenoazafulvalenes) described above was investigated



Scheme 4. Synthesis of polyether linked bis-azines from polyether linked bis(thiazolyl hydrazone) **11**.

by cyclic voltammetry either in $CHCl_2CH_2Cl$ or CH_2Cl_2 using tetrabutylammonium hexafluorophosphate as supporting electrolyte. The redox potentials of the donors are collected in Table 1 together with the data of the azinodibenzodiselenadiazafulvalene (azino-dibenzoDSeDAF) for comparison. All the donors exhibit two main bielectronic reversible systems, the first one in some cases being broader than the second one or even split into two peaks. Actually, all these molecules contain two electroactive cores which can either behave independently or can interact through space. Considering the dimers which exhibit only two reversible oxidation waves, (e.g. **12**, **13**, **16**, **20**, **21**) this behaviour indicates that the removal of one electron from the azino-chalchogenoazafulvalene core does not influence the removal of another electron from the second donor core. Therefore, the two donor cores are oxidized simultaneously and behave independently. On the contrary, the broadening or splitting of the first redox system (e. g. **18**, **24**-**27**), observed for the other dimers, indicates that the two donor cores in one molecule oxidize successively into cation radical species. This behaviour points to the existence of through space intramolecular electronic interactions as previously observed on dimeric TTFs.[4] It is noteworthy that these interactions are extremely variable and strongly dependent on the length of the spacer between two redox active cores and also on the number of linkers between the two TTFs. For instance, among the bis(azinochalcogenoazafulvalenes) where the two donors are linked by one spacer group, only those with an ethyl linker exhibit a broadening of the first redox systems. Otherwise, with a crown ether linkage the degree of freedom between the two donor core is too important to allow those intramolecular interactions. On the contrary, the two cage molecules (**19**, **22**) where the two azino derivatives are connected through two linkages exhibit a splitting of the first redox system as seen in Figure 2. In order to explain the splitting of only the first redox system the following hypothesis was ventured.



Scheme 5. Synthesis of bis-benzoazines from bis(benzo-fused heterocyclic hydrazones) **5** and **7**.

The two electroactive cores form a sandwich structure that contributes to the stabilization of the monoradical cation species. Removal of the second electron induces an opening out of the structure as a result of Coulombic repulsion between the two cation radical species. The two oxidized donors behave as two non interactive redox centers and the third and fourth electron are removed at the same potential.[15]

For all these dimers a difference between the two oxidation potentials larger than 480 mV ($\Delta E = E_2 - E_1$, K ~ 1.36 10^8, Table 1) is observed, which indicates a very high thermodynamic stability of the cation radical species. Comparison of the redox potentials between azino dibenzo-DSeDAF and azino dibenzo-DTDAF or the mixed derivatives show that substitution of one selenium atom with sulfur one, does not significantly modify the

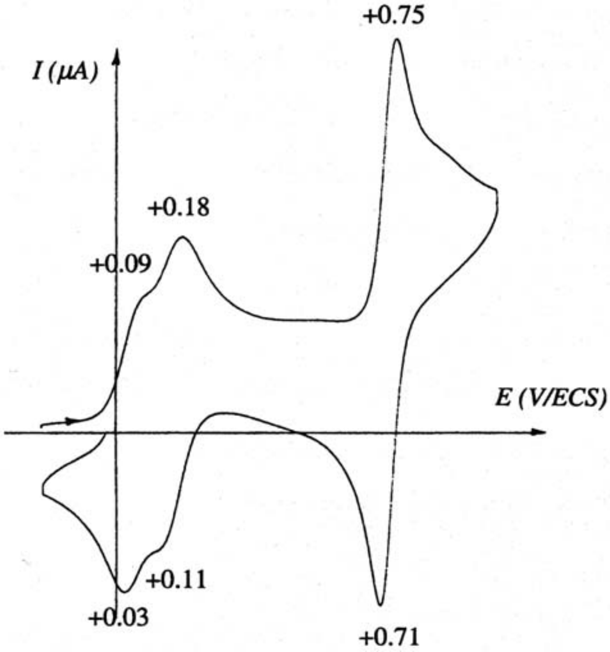


Figure 2. Cyclic voltammogram of the cage molecule **19** in CH_2Cl_2.

Table 1. Redox properties of bis(azinochalcogenoazafulvalenes) n-Bu_4NPF_6, 100 mV/s

Donor	E_1	E_2	$E_2 - E_1$ mV (K)
12[a]	0.31	0.97	660 ($1.53\ 10^{11}$)
13[a]	0.31	0.94	630 ($4.76\ 10^{10}$)
16[b]	0.11	0.79	680 ($3.35\ 10^{11}$)
18[b]	0.45 0.58	1.07	490 ($2.01\ 10^{8}$)
19[b]	0.06 0.14	0.73	590 ($1\ 10^{10}$)
20[b]	0.09	0.69	600 ($1.47\ 10^{10}$)
21[b]	0.52	1.00	480 ($1.36\ 10^{8}$)
22[a]	0.60 0.73	1.26	530 ($9.61\ 10^{8}$)
24[a]	0.57*	1.21	640 ($7.03\ 10^{10}$)
26[a]	0.56*	1.20	640 ($7.03\ 10^{10}$)
27[a]	0.62*	1.22	580 ($6.76\ 10^{9}$)
Azino dibenzo-DSeDAF[7]	0.53	1.07	540 ($1.42\ 10^{9}$)

* Broad redox system [a]$CHCl_2CH_2Cl$ [b]CH_2Cl_2

donor ability. On the contrary, substitution of one nitrogen atom with sulfur one induces a decrease of the overall donor ability of these dimers as the oxidation potentials are shifted anodically by at least 340 mV for **18** compared to **16** and 430 mV for **21** compared to **20**. Similarly, benzo-fused derivatives exhibit higher oxidation potentials than dimethyl derivatives which indicates that benzo-fusion decreases the donor ability.

We also studied the voltammetric response of the cage molecule **19** and the dimer **20** in the presence of various metal cations (Li^+, K^+) in order to detect a possible complexation of the metal to the ether chains. Indeed, the complexing ability of the two bis oxa ethyl chain could interfere in the redox properties of the donors due to electronic interactions between the electroactive system and the complexation site.[16] Therefore, the complexation should be observed by some modifications of the shape of the voltammograms.

Due to solubility problem of the alkali metal ions in CH_2Cl_2, we performed the complexation studies into a 50/50 solution of CH_2Cl_2/CH_3CN. First we investigated the redox behaviour of the cage **19** and the dimer **20** in this medium as the solvent might have a strong influence in the solvation of the various species and therefore on the redox properties. As observed in Figure 3a, the shape of the voltammogram in CH_2Cl_2/CH_3CN remains very similar to the one obtained in CH_2Cl_2. It is worth mentioning that there is no metal binding effect observed for **20** as when adding alkali metal ions, $LiBF_4$ or KPF_6, there is no

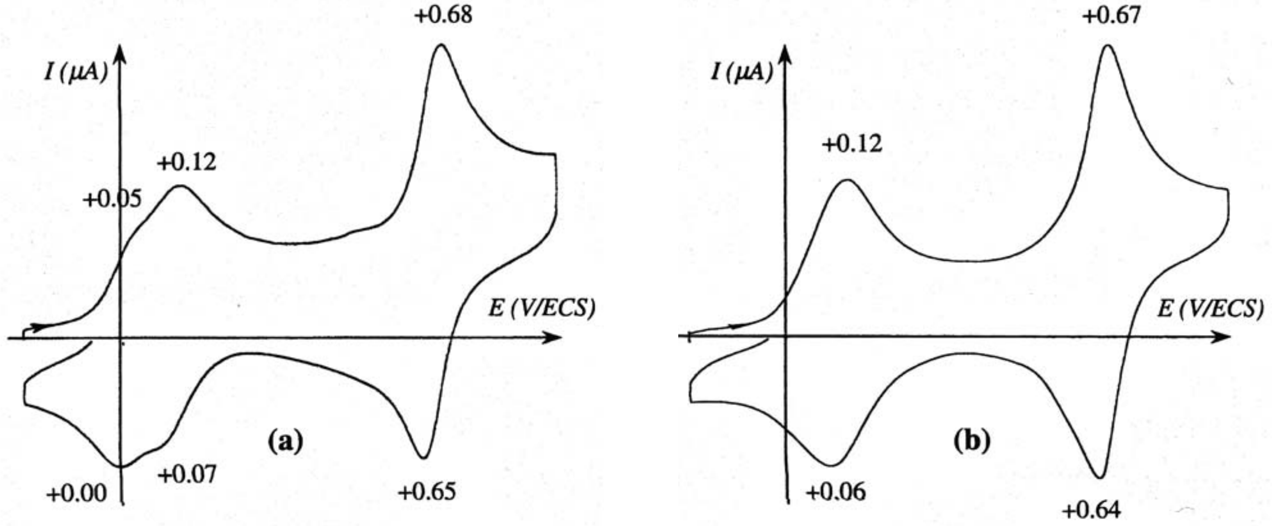


Figure 3. Cyclic voltammograms of azine **19**, (**a**) free and (**b**) complexed with K^+ (CH_2Cl_2/CH_3CN = 50:50, NBu_4PF_6, 1M, Pt, ESC).

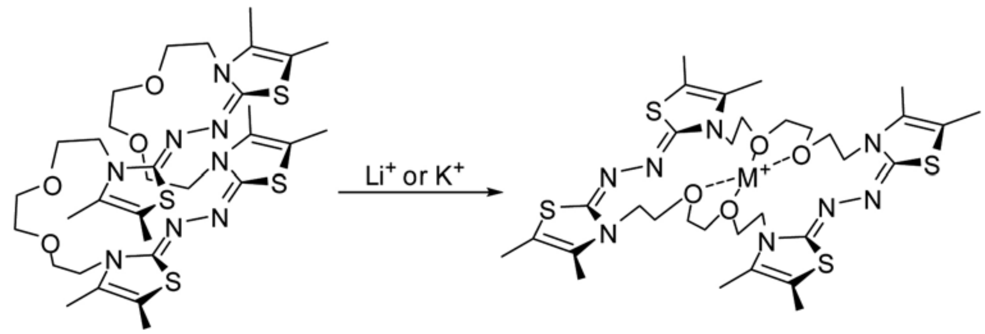


Figure 4. Schematic presentation of uncomplexed sandwich structure of **19** and complexed planar structure for **19.M$^+$** (M = Li or K).

modification on the shape and intensity of the redox systems for **20**, two bielectronic waves are still observed without any shift of the oxidation potentials. On the contrary, the progressive addition of LiBF4 or KPF_6 to **19** induces a coalescence of the two first oxidation processes while the third oxidation process remains unchanged (Figure 3b) and on the voltammogram two bielectronic reversible oxidation waves are now observed for the complex **19.M$^+$** (M = Li, K). This effect suggests that the metal ion is complexed with the ether chains of the cage structure in a way that both azino-donors are non interacting anymore as represented in Figure 4 and as such behave as two independent electroactive molecules.

4. Conclusion

We have prepared a series of bis(azino-chalcogenoazafulvalenes). Electrochemical investigations have evidenced intramolecular interactions between the two donor cores in regard to the length, the nature and the number of linkers used to connect the two azino-chalcogenoazafulvalene moieties. Moreover, these interactions allowed the formation of mixed valence species through the removal of only one electron per dimers. Preliminary complexation experiments show that the presence of alkali metal ions modifies these interactions due to different organization. Further investigations on these electroactive molecules will be devoted to the elaboration of molecular materials by electrocrystallization.

5. Acknowledgments

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Povzetek

Opisali smo sintezo serije dimernih π–donorskih spojin, ki vsebujejo dva redoks aktivna gradnika, kot npr. azino-halkogenoazafulvalena, povezana z eno ali dvema ne-konjugiranima povezovalnima skupinama. Za pripravo teh dimernih elektron-donorskih spojin, ki vsebujejo azinsko strukturno enoto smo uporabili vrsto heterocikličnih sistemov in sintetizirali dimerne π–donorske spojine, v katerih posamezni π–donorski gradnik vsebuje dve tiazolski ali tiazolsko in selenazolsko jedro ali dve selenazolski ali tiazolsko in ditiolsko jedro. Eksperimenti opravljeni s ciklično voltametrijo so nam omogočili zabeležiti vpliv lastnosti različnih heterocikličnih jeder na elektron-donorske lastnosti pripravljenih dimernih π–donorskih spojin. Nadalje, v določenih primerih smo opazili tudi znatne intramolekularne interakcije med dvema elektroaktivnima gradnikoma, ki so odvisne od dolžine in števila nekonjugiranih povezovalnih skupin.