PERKIN 1

Synthesis of diselenadiazafulvalenes and influence of steric strain on their anodic behavior

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A novel family of π-donor molecules, the diselenadiazafulvalenes (DSeDAFs), is presented. The synthetic approach to these donors, from *o*-nitroaniline, allows the formation of *N,N′*-dimethyldibenzoDSeDAF and *N,N′*-ethylene-dibenzoDSeDAF. Comparative electrochemical study of these π-donor molecules demonstrates their excellent donor ability and the stabilizing effect of the ethylene bridge on the cation radical species.

Several heterocyclic systems have been used as precursors of organic materials, mainly built on the fulvalene framework including heteroatoms such as sulfur or selenium.[1] In order to tune the electronic properties of the donor, substitution of one or more heteroatoms within the fulvalene skeleton has been performed.[2] For example, the diselenadiazafulvalene **1** (DSeDAF), an aza analogue of tetraselenafulvalene (TSF), exhibits high electron-donating properties.[3] Therefore, **1** is oxygen-sensitive, as evidenced by the spiroamide derivative obtained after oxidation of a DSeDAF.[3] An interesting feature is the fact that for **1** the cation radical species detected by cyclic voltammetry (CV) is stable within a narrow potential window, and a dicationic diamagnetic salt is easily obtained. Nevertheless, most of the physical properties (conductivity, magnetism, *etc.*) in organic materials are ascribed to the presence of radical species. It has been shown in the case of the *N,N′*-dimethyldithiadiazafulvalene **2** (DTDAF) that this narrow potential window is due to reduced Coulombic interactions associated with conformational modifications upon electron transfer.[4] Consequently the introduction of an N,N′-bridge between the two heterocyclic rings hinders such structural changes and increases the electrochemical domain of stability of cation radicals.[5] The same effect is therefore expected in DSeDAFs with the introduction of a N,N′-bridge between the two selenazole rings. In a preliminary communication we reported a route towards *N,N′*-dimethyldibenzoDSeDAF **1**.[3] Therefore, it was of interest to investigate the possibility of extending this route to *N,N′*-ethylene-bridged dibenzo-DSeDAF **3** (Chart 1). In this article we report full experimental details of the synthesis of both *N,N′*-dimethyl- and *N,N′*-ethylene-bridged dibenzo-DSeDAF and the analysis of their electron-donating properties.

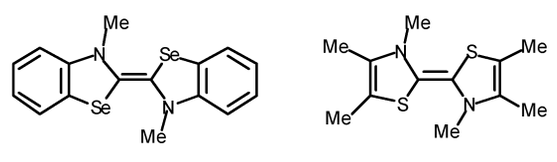
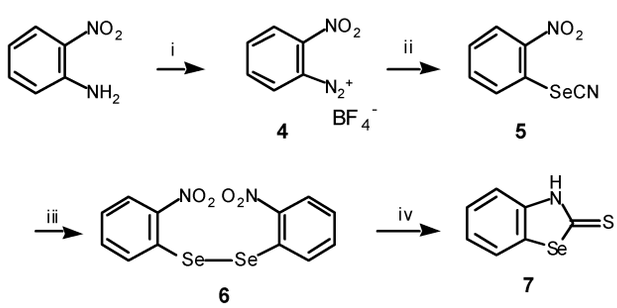


Chart 1

Results and discussion

The common approach to the synthesis of *N,N′*-dimethyl- or *N,N′*-bridged dibenzo-DSeDAF consists first in the preparation of bis(*o*-nitrophenyl) diselenide and then formation of the 1,3-selenazole core (Scheme 1). The synthesis of benzoselenazole-2-thione **7**, starting from *o*-nitroaniline, was described some decades ago.[6] The chemistry of benzo-1,3-selenazole has been scarcely studied recently. Therefore, we decided to improve the chemical pathway to benzoselenazole-2-thione **7** with regard to the yields, quantity (multi-gram scale) and simplicity.



Scheme 1 *Reagents and conditions*: i, $BF_3{\cdot}Et_2O$, *t*-BuONO, CH_2Cl_2, −15 °C; ii, KSeCN, H_2O, 0 °C; iii, Na, EtOH; iv, NaSH, CS_2, HCl.

Our key material is bis(*o*-nitrophenyl) diselenide **6** which is smoothly prepared from *o*-nitroaniline in high overall yield (71%) *via* an isolable arenediazonium salt **4**.[7] Reaction of potassium selenocyanate with **4** gave **5**. Treatment of **5** with sodium in ethanol induces the formation of sodium *o*-nitrobenzene selenolate, which couples to afford **6**.[8]

The key to the short synthesis of 3*H*-benzoselenazole-2-thione **7** is the *in situ* reduction of **6** into the presumable intermediate *o*-aminobenzeneselenolate with sodium hydrosulfide, followed by cyclization with carbon disulfide in basic medium, and then acidic treatment. This route becomes simpler compared with those described earlier.[6,9]

The next step involves the reaction of alkyl halides with benzoselenazole-2-thione. Alkylation in the presence of base is

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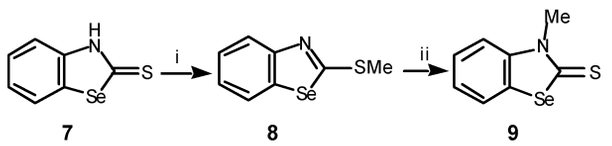
not in favor of direct N-alkylation but rather affords S-alkylation. Using methyl iodide in the presence of triethylamine, 2-(methylsulfanyl)benzoselenazole **8** was isolated (Scheme 2).[3] Interestingly, 2-(methylsulfanyl)benzoselenazole **8**, as its benzo-



7 8 9

Scheme 2 *Reagents and conditions*: i, MeI, NEt_3, CH_2Cl_2; rt, ii, I_2, 200–220 °C.

thiazole analog,[10,11] undergoes thermal rearrangement in the presence of iodine, and we found that *N*-methylbenzoselenazole-2-thione **9** is obtained in good yield upon identical treatment of compound **8**.

For the synthesis of the *N,N′*-ethylene-bridged derivatives we needed to link two benzoselenazole rings by an ethylene bridge system and therefore we used ethylene dibromide as the alkylating agent. Addition of half an equivalent of ethylene dibromide to benzoselenazole-2-thione **7** in the presence of potassium carbonate afforded the product **10** resulting from *S,S*-intermolecular alkylation (66%), together with a minor amount of the *N,S*-intermolecular dialkylated derivative **11** (7%) (Scheme 3). The structure of compound **10** was confirmed by an X-ray diffraction study.† Compound **10** crystallizes with three molecules in the asymmetric unit as can be seen in Fig. 1. These three molecules have different conformational arrangements essentially due to the ethylene link. Partial direct *N*-alkylation (*e.g.* **11**) is possible but we never

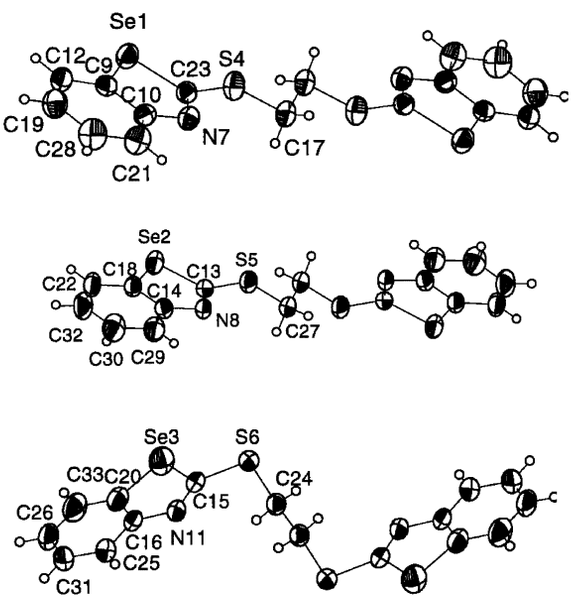


Fig. 1 View of the molecular structure of 2,2′-(ethylenedisulfanyl)-bis(benzoselenazole) **10**. The three crystallographically independent molecules, each of them located on an inversion center, are shown.

† CCDC reference number(s) 183223–183224. See http://www.rsc.org/suppdata/p1/b2/b203317h/ for crystallographic files in .cif or other electronic format.

isolated the *N,N′*-di alkylated derivative (**12**; see below) using this procedure.

Since *N*-methylbenzoselenazole-2-thiones such as **9** can be conveniently prepared from 2-(methylsulfanylbenzoselenazoles such as **8** by thermal rearrangement in the presence of iodine, we investigated the possibility of forming *N,N′*-ethylene-bisbenzoselenazole-2-thione by applying the same strategy to 2,2′-(ethylenedisulfanyl)bis(benzoselenazole) **10**. Treatment of **10** with iodine at a temperature up to 250 °C led to **12** in moderate yield (28%) (Scheme 4). Crystal structure of compound **12** was determined by an X-ray diffraction study (Fig. 2)†.

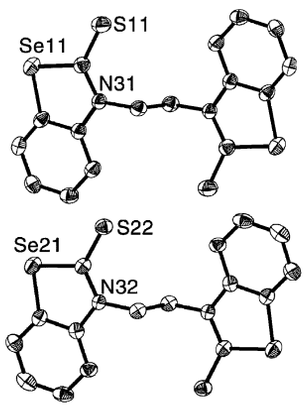
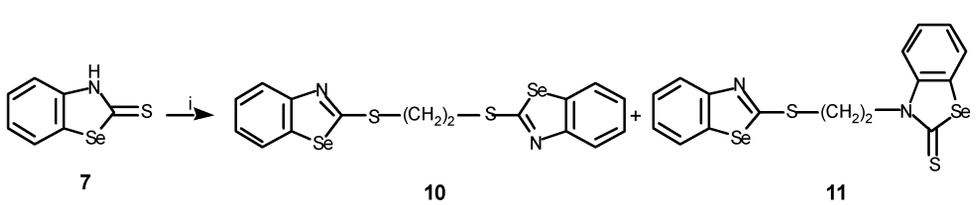


Fig. 2 View of the molecular structure of 3,3′-ethylenebis(benzoselenazole-2-thione) **12**. The two crystallographically independent molecules, each of them located on an inversion center, are shown.

The final step towards DSeDAF does not involve the coupling reaction of **9** or **12** to form the central double bond of the donor molecules. As *N*-alkylbenzoselenazole-2-thiones do not (in our hands) undergo inter- (for **9**) or intramolecular (for **12**) coupling by treatment with trivalent phosphorus derivatives they were converted into the corresponding selones, as shown in Scheme 5. First, **9** and **12** were quantitatively alkylated on the exocyclic sulfur with a strong alkylating agent such as diethoxycarbonium tetrafluoroborate,[12] which was formed *in situ* from $BF_3{\cdot}Et_2O$ and triethyl orthoformate. Due to the low solubility of the bisbenzoselenazole-2-thione **12**, alkylation did not occur in refluxing chloroform as for **9**, but 3,3-ethylenebis-[2-(ethylsulfanyl)benzoselenazolium tetrafluoroborate] **15** was obtained in excellent yield in boiling toluene. Treatment of the salts **13** and **15** with sodium hydrogen selenide led, respectively, to the benzoselenazole-2-selone **14** and the bisbenzoselenazole-2-selone **16** in excellent yields (Scheme 5).

Finally, intermolecular coupling of the benzoselenazole-2-selone **14** in the presence of triethyl phosphite in refluxing toluene under inert atmosphere afforded the dibenzo-DSeDAF **1**, while bisbenzoselenazole-2-selone derivative **16** underwent intramolecular coupling give to *N,N′*-ethylene-bridged donor **3** (Scheme 6). Due to air-sentivity, these donors are difficult to isolate without undergoing further oxidation with oxygen.[3] Therefore, in order to get informations on their redox properties we undertook electrochemical investigations directly on the medium where the donors were formed by adding the reaction mixture, under inert atmosphere, to a degassed solution of tetrabutylammonium hexafluorophosphate in CH_2Cl_2. The oxidation potentials of dibenzo-DSeDAFs obtained by CV are



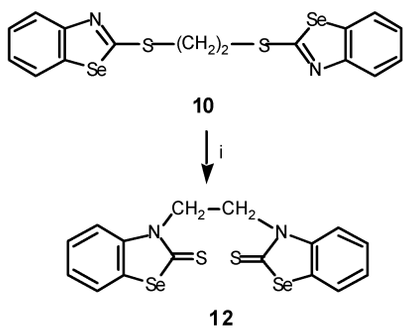
7 10 11

Scheme 3 *Reagents and conditions*: i, $BrCH_2CH_2Br$, K_2CO_3, EtOH.

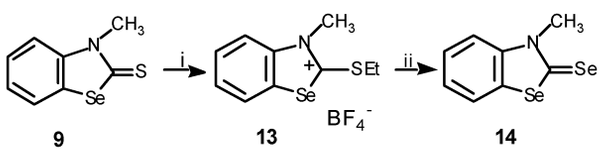
Table 1 Oxidation potentials (V) *vs* SCE obtained after chemical coupling of benzoazoleselone derivatives[a]

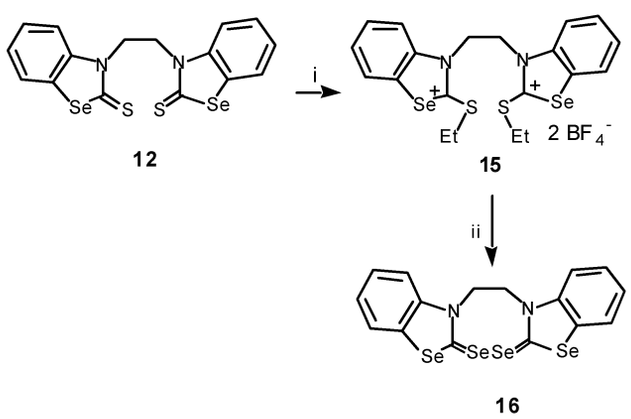
	E_{pa^1}/V	E_{pa^2}/V	ΔE/mV
DSeDAF **1**	−0.07	+0.09	160
N,N′-dimethyldibenzo-DTDAF[13]	−0.17	−0.02	150
DSeDAF **3**	−0.18	+0.36	540
N,N′-ethylenedibenzo-DTDAF[13]	−0.23	+0.26	490

[a] Pt working electrode with 0.1 M n-Bu_4NPF_6; scanning rate 0.1 V s^{-1}.

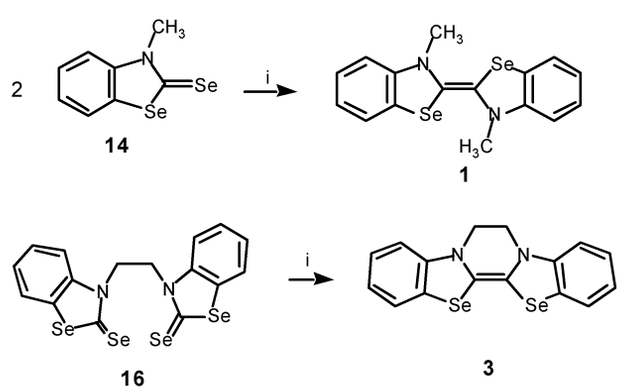


Scheme 4 *Reagents and conditions*: i, I_2, 250 °C.





Scheme 5 *Reagents and conditions*: i, $BF_3{\cdot}Et_2O$, $CH(OEt)_3$, reflux; ii, NaSeH, EtOH, rt.



Scheme 6 *Reagents and conditions*: i, $P(OEt)_3$, toluene, reflux.

listed in Table 1 together with the redox potentials of the *N,N′*-dimethyl- and *N,N′*-ethylene-bridged dibenzo-DTDAFs prepared by Hünig[13,14] *et al.* for comparison. After either intermolecular or intramolecular coupling two main oxidation

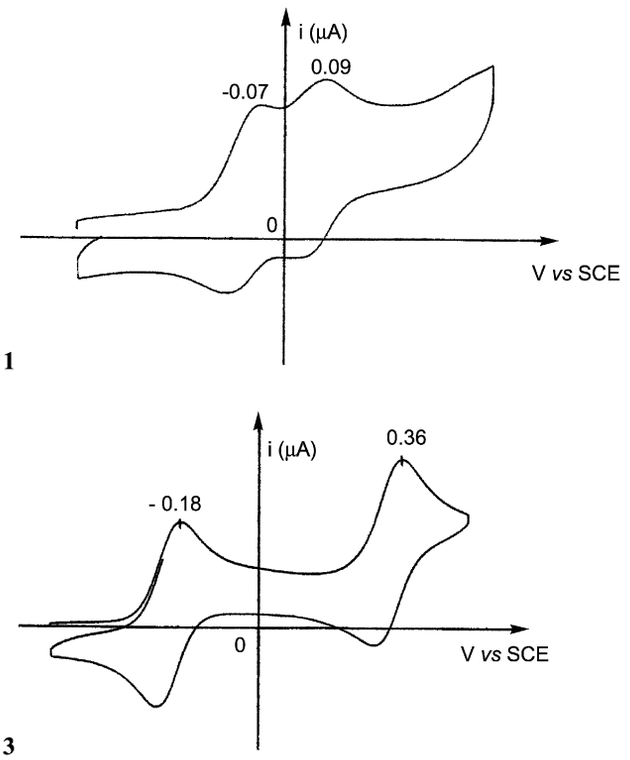


Fig. 3 Cyclic voltammograms performed on the medium where the DSeDAFs **1** and **3** were formed, Bu_4NPF_6 (0.5 M), CH_2Cl_2, platinum electrode; scanning rate 0.1 V s^{-1}, *vs* SCE.

waves, associated with the redox behavior of the donors, were observed at low potentials (Fig. 3). The introduction of selenium atoms instead of the sulfur ones only slightly decreased the donor ability. Furthermore, the potential difference observed between the two oxidation states ($\Delta E = E_{pa^2} - E_{pa^1}$) for *N*-methyl-substituted donors is smaller than in the case of *N,N′*-ethylene-bridged donors. Indeed, the presence of a bridge between the two heterocyclic rings hinders conformational modification upon oxidation and therefore due to Coulombic interactions the removal of the second electron is more difficult in the case of **3** than for **1**.

In summary we have developed a strategy that allowed us to reach DSeDAFs *via* alkylation of benzoselenazole rings. For that purpose an improved synthesis of benzoselenazole-2-thione has been performed. The key step of this strategy involves the thermal rearrangement of a 2-(alkylsulfanyl)-benzoselenazole into the *N*-alkylbenzoselenazole-2-thione. We show also that the general procedure can be successfully applied to the synthesis of either *N,N′*-dimethyldibenzo-DSeDAF or the hitherto unknown *N,N′*-ethylene-bridged dibenzo-DSeDAF. Both molecules are excellent donors and exhibit close redox properties but the presence of an ethylene bridge increases the potential domain of stability of the cation radical species.

Experimental

^1H NMR spectra were recorded in $CDCl_3$, unless otherwise indicated, at 200 and 300 MHz, and ^{13}C NMR spectra at 50 and 75 MHz. Chemical shifts are reported in ppm referenced to TMS. 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. Column chromatography was performed on silica gel 60 (0.040–0.063 mm). CH_2Cl_2 was dried by refluxing over P_2O_5 followed by distillation, and toluene was dried by refluxing over

NaH followed by distillation. Petroleum ether refers to the fractions boiling in the range 40–65 °C.

2-Nitrobenzenediazonium tetrafluoroborate 4

To a solution of $BF_3{\cdot}Et_2O$ (35.97 g, 0.253 mol), cooled at −15 °C, was added a solution of *o*-nitroaniline (23.32 g, 0.168 mol) in 250 mL of dry CH_2Cl_2. The suspension was stirred at −15 °C for 15 min. Then a solution of *tert*-butyl nitrite (23.25 g 0.203 mol) in 100 mL of dry CH_2Cl_2 was added dropwise to the vigorously stirred reaction mixture. After complete addition of the reactant, this mixture was stirred at −15 °C for 30 min and then at 0 °C for 30 min. Cold pentane (200 mL) was added to the suspension and the precipitate was filtered off and washed with cold dry diethyl ether (200 mL). Diazonium salt **4** was obtained in quantitative yield as a pale brown powder, and used without further purification. Mp 94 °C (dec.); ^{1}H NMR (acetone-d_6) δ 9.43–9.26 (1H, dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz), 9.16–8.95 (1H, dd, ^3J = 8.3 Hz, ^4J = 1.3 Hz), 8.93–8.74 (1H, td, ^3J = 8.3 Hz, ^4J = 1.3 Hz), 8.73–8.51 (1H, td, ^3J = 8.1 Hz, ^4J = 1.3 Hz); ^{13}C NMR (acetone-d_6) δ 146.50, 144.30, 138.54, 138.12, 129.64, 111.89.

o-Nitrophenyl selenocyanate 5

The amount of 2-nitrobenzenediazonium tetrafluoroborate **4** obtained above was divided into four equal portions and treated as follows. To a solution of 2-nitrobenzenediazonium tetrafluoroborate **4** (10.00 g, 42.10 mmol) in cold water (200 mL) was added a solution of KSeCN (6.14 g, 42.62 mmol) in 50 mL of water dropwise (5 min) at 0 °C. After complete addition of KSeCN, the suspension was stirred at 0 °C for 10 min and the precipitate was filtered off. The crude product obtained in the four similar experiments was fused and used in the next step without further purification. In order to obtain analytically pure compound a small sample was subjected to flash chromatography over silica gel using methylene dichloride as eluant. The yellow solution was dried over Na_2SO_4 and the solvent was evaporated. The yellow powder was then recrystallized from EtOH and gave title compound **5** as yellow needles, R_f (CH_2Cl_2) 0.79; mp 142 °C (lit.,[8] 142 °C); ^{1}H NMR δ 8.55–8.39 (1H, dd, ^3J = 8.3 Hz, ^4J = 1.5 Hz), 8.31–8.13 (1H, dd, ^3J = 8.1 Hz, ^4J = 1 Hz), 7.86–7.71 (1H, td, ^3J = 8.1 Hz, ^4J = 1.5 Hz), 7.70–7.54 (1H, td, ^3J = 8.3 Hz, ^4J = 1 Hz); ^{13}C NMR δ 144.96, 136.57, 131.47, 129.44, 127.01, 126.25, 104.88. Calc. for $C_7H_4N_2O_2Se$: C, 37.03; H, 1.78; N, 12.34. Found: C, 36.85; H, 1.72; N, 12.19%.

Bis(*o*-nitrophenyl) diselenide 6

To a suspension of *o*-nitrophenyl selenocyanate **5** in 600 mL of absolute EtOH was slowly added sodium (4.00 g, 173.91 mmol), cut into small pieces, over a 10-min period. After complete addition of sodium the reaction mixture was stirred for 1 h at room temperature. The green precipitate was filtered off and washed with 1200 mL of EtOH to give 36.59 g of a green powder. The crude product was suspended in 370 mL of toluene and the suspension was heated to boiling. The hot suspension was filtered to remove toluene-insoluble side-products. Upon cooling, bis(*o*-nitrophenyl) diselenide **6** precipitated. Filtration afforded 24.20 g of compound **6** as yellow plates (71%, calculated on starting *o*-nitroaniline), mp 215 °C (lit.,[8] 209 °C); R_f (CH_2Cl_2) 0.84; ^{1}H NMR δ 8.42–8.24 (2H, dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz), 7.94–7.78 (2H, dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz), 7.57–7.28 (4H, m); ^{13}C NMR δ 146.96, 135.21, 132.03, 129.19, 128.06, 126.83. Calc. for $C_{12}H_8N_2O_4Se_2$: C, 35.84; H, 2.01; N, 6.97. Found: C, 36.31; H, 1.97; N, 6.83%.

3*H*-Benzoselenazole-2-thione 7

Bis-(2-nitrophenyl) diselenide **6** (9.88 g, 24.57 mmol), well-powdered $NaSH{\cdot}H_2O$ (32.65 g, 440.78 mmol) and NaOH (24.72 g, 617.92 mmol) were placed in a 1 L flask fitted with a condenser, and 200 mL of water was added. The suspension was stirred at room temperature until the formation of a red–brown solution. Then CS_2 (64 mL) was added and the reaction mixture was heated at reflux for 2 h and then stirred at room temperature for 14 h. The red solution was concentrated to approximately 100 mL by evaporation of unchanged CS_2 and partial evaporation of water. Excess of NaSH was eliminated from the solution by slow addition of 130 mL of 26% aq. HCl **Caution**! For trapping the highly toxic H_2S gas formed during the addition of acid the flask was hermetically closed with a septum and connected in series to three traps, each containing 250 mL of saturated aq. NaOH. The alkaline solution of NaSH obtained in the traps was subsequently oxidized with aq. NaOCl and neutralized with dilute H_2SO_4 (both operations were performed on an ice–acetone-bath in a well-ventilated hood). After complete addition of acid the pH of the solution was brought to 1 and a yellow–green precipitate was obtained. Then the pH of solution was adjusted to 10 by addition of saturated aq. NaOH and the suspension was heated to reflux and stirred at reflux until the formation of a red solution. The reaction mixture was cooled to room temperature and dilute HCl was added until pH = 1. The green precipitate was filtered off and dried. The resulting green powder was suspended in acetone (300 mL) and acetone-insoluble side-product (sulfur) was filtered off. The orange filtrate was evaporated under reduced pressure to give 10.27 g (98%) of crude product as an orange crystalline powder, which was recrystallized from 130 mL of MeOH–H_2O (2.25 : 1 v/v) mixture to give 9.46 g (90%) of benzoselenazole-2-thione **7** as yellow needles, mp 159 °C (lit.,[6] 159 °C); R_f (CH_2Cl_2) 0.45; ^{1}H NMR δ 11.86 (1H, br s), 7.60–7.47 (1H, dd, ^3J = 7.8 Hz, ^4J = 1 Hz), 7.43–7.15 (3H, m); ^{13}C NMR δ 194.46, 141.97, 130.74, 127.61, 125.42, 125.33, 113.92. Calc. for C_7H_5NSSe: C, 39.26; H, 2.35; N, 6.54. Found: C, 38.97; H, 2.06; N, 6.24%.

2-(Methylsulfanyl)benzoselenazole 8

To a suspension of **7** (5.50 g, 25.68 mmol) in CH_2Cl_2 (30 mL) were added a solution of iodomethane (5.47 g, 38.52 mmol) in CH_2Cl_2 (10 mL) and a solution of trimethylamine (5.21 g, 51.37 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 10 min and then extracted with water (5 × 30 mL). The organic phase was dried over Na_2SO_4. Evaporation of the solvent afforded a dark orange oil, which was distilled twice. (Kugelrohr, 0.04 mbar,‡ 115 °C) to give 5.45 g (93%) of compound **8** as a yellow oil, R_f (CH_2Cl_2) 0.70; ^{1}H NMR δ 7.94–7.80 (1H, dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz), 7.78–7.66 (1H, dd, ^3J = 7.8 Hz, ^4J = 1.3 Hz), 7.45–7.29 (1H, td, ^3J = 7.3 Hz, ^4J = 1.3 Hz), 7.22–7.09 (1H, td, ^3J = 7.3 Hz, ^4J = 1.3 Hz), 2.71 (3H, s); ^{13}C NMR δ 170.15, 155.30, 138.56, 126.65, 124.75, 124.64, 123.28, 17.22. Calc. for C_8H_7NSSe: C, 42.11; H, 3.09; N, 6.14. Found: C, 42.63; H, 3.01; N, 6.13.%

N-Methyl-3*H*-benzoselenazole-2-thione 9

A 25 mL round-bottom flask containing 2-(methylsulfanyl)-benzoselenazole **8** (4.99 g, 21.87 mmol) and 0.21 g of iodine was placed in a metallic bath. The temperature of the bath was maintained between 206 and 220 °C while the reaction mixture was stirred for 8 h. Upon cooling to room temperature the reaction mixture solidified and a brown solid was obtained. The solid was dissolved in CH_2Cl_2 and the dark brown solution was extracted with 5% aq. Na_2SO_3 (30 mL). The organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography over silica gel (CH_2Cl_2) to afford a yellow solid 4.89 g (98%). Recrystallization from EtOH gave 3.36 g (67%) of *N*-methylbenzoselenazole-2-thione **9** as a pale

‡ 1 bar = 10^5 Pa.

yellow powder, mp 80 °C (lit.,[6] 80 °C); R_f (CH_2Cl_2) 0.79; ^{1}H NMR δ 7.65–7.10 (4H, m), 3.85 (3H, s); ^{13}C NMR δ 192.89, 143.88, 127.90, 127.52, 125.65, 125.36, 114.49, 34.50. Calc. for C_8H_7NSSe: C, 42.11; H, 3.09; N, 6.14. Found: C, 42.45; H, 3.03; N, 5.90%.

2,2′-(Ethylenedisulfanyl)bis(benzoselenazole) 10

3*H*-Benzoselenazole-2-thione **7** (15.00 g, 70.04 mmol) and K_2CO_3 (9.68 g, 70.04 mmol) were suspended in EtOH (50 mL). The suspension was heated to reflux and ethylene dibromide (6.58 g, 35.02 mmol), as a solution in 10 mL of EtOH, was added in one portion. Immediately a white precipitate began to form from the yellow turbid reaction mixture. The reaction mixture was vigorously stirred at reflux for 30 min, then was cooled to room temperature. The precipitate was filtered off and dried to give pale brown powder, which was suspended in CH_2Cl_2 (250 mL). The suspension was stirred at room temperature for 1 h. Undissolved inorganic salts (white precipitate) were filtered off. The brown filtrate was evaporated under reduced pressure to give 13.22 g of crude product as a pale brown powder. The crude product was suspended in 60 mL of acetone and the suspension was heated to boiling. The hot suspension was filtered to remove the slightly acetone-soluble **10**. After drying, compound **10** was obtained as a white crystalline powder. The filtrate was evaporated and the brown residue was chromatographed over silica gel (CH_2Cl_2–petroleum ether 1 : 1) to afford the remaining quantity of **10**, and the isomer **11** as a major side-product of the reaction.

2,2′-(Ethylenedisulfanyl)bis(benzoselenazole) **10**, R_f (CH_2Cl_2–petroleum ether 1 : 1) 0.29, white cristals, yield 10.51 g (66%); mp 154 °C; ^{1}H NMR δ 7.81 (2H, d, J = 8.3 Hz), 7.73 (2H, d, J = 7.8 Hz), 7.42–7.27 (2H, td, ^3J = 7.8 Hz, ^4J = 1.3 Hz), 7.25–7.09 (2H, td, ^3J = 7.8 Hz, ^4J = 1.3 Hz), 3.76 (4H, s); ^{13}C NMR δ 167.31, 154.96, 138.84, 126.62, 124.91, 124.79, 123.50, 33.88. Calc. for $C_{16}H_{12}N_2S_2Se_2$: C, 42.30; H, 2.66; N, 6.17. Found: C, 42.19; H, 2.65; N, 6.24%.

3-[2-(benzoselenazol-2-ylsulfanyl)ethyl]benzoselenazole-2-thione **11**, R_f (CH_2Cl_2–petroleum ether 1 : 1) 0.40, white needles, yield 1.08 g (7%); mp 140 °C; ^{1}H NMR δ 8.08 (1H, d, J = 8.3 Hz), 8.03–7.91 (1H, dd, ^3J = 8.1 Hz, ^4J = 0.8 Hz), 7.89–7.77 (1H, dd, ^3J = 7.8 Hz, ^4J = 0.8 Hz), 7.61–7.42 (3H, m), 7.40–7.21 (2H, m), 4.91 (2H, m), 3.67 (2H, m); ^{13}C NMR δ 192.71, 167.49, 154.69, 143.45, 138.97, 128.06, 127.56, 126.77, 125.69, 125.40, 125.13, 125.08, 123.05, 115.49, 46.46, 29.16. Calc. for $C_{16}H_{12}N_2S_2Se_2$: C, 42.30; H, 2.66; N, 6.17. Found: C, 42.53; H, 2.57; N, 6.18%.

3,3′-Ethylenebis(benzoselenazole-2-thione) 12

A 50 mL round-bottom flask containing 2,2′-(ethylenedidisulfanyl)bis(benzoselenazole) **9** (7.25 g, 15.96 mmol) and iodine (0.32 g) was placed in a metallic bath with a starting temperature of 212 °C. In 3 min a purple liquid was obtained and the reaction mixture was stirred for 1 h while the temperature of the bath was maintained between 212 and 221 °C. Then, the temperature of the bath was raised and the mixture was stirred further for 2 h while the temperature of the bath was kept between 220 and 250 °C. Upon cooling to room temperature the reaction mixture solidified and a dark brown solid was obtained. It was partially solubilized in CH_2Cl_2 (300 mL). The insoluble dark brown crystalline solid was filtered off and the filtrate was extracted with 5% aq. Na_2SO_3 (30 mL) in order to remove residual iodine. The organic layer was dried over Na_2SO_4, and evaporation of the solvent gave a dark brown semi-solid. Flash chromatography, over silica gel (CH_2Cl_2), of both the crystalline powder and the semi-solid afforded in each case an orange–brown powder. The combined crude products were recrystallised from 60 mL of pyridine and upon cooling a yellow crystalline precipitate was obtained. Filtration afforded dimer **12** as yellow needles. TLC of the filtrate showed the presence of some **12**. The filtrate was evaporated under reduced pressure to give a brown semi-solid, which was flash chromatographed over silica gel (CH_2Cl_2). Fractions which contained **12** were collected, combined, and dried (Na_2SO_4). Evaporation of CH_2Cl_2 and recrystallization in 10 mL of pyridine afforded the remaining quantity of **12** as yellow needles, yield 1.99 g (28%), R_f (CH_2Cl_2) 0.79; mp 286–288 °C (dec.); ^{1}H NMR (DMSO-d_6) δ 7.87–7.77 (2H, dd, ^3J = 7.8 Hz, ^4J = 1 Hz), 7.57–7.23 (6H, m), 4.89 (4H, s); ^{13}C NMR (DMSO-d_6) δ 193.64, 142.69, 127.14, 126.90, 125.64, 125.09, 113.83, 42.70. Calc. for $C_{16}H_{12}N_2S_2Se_2$: C, 42.30; H, 2.66; N, 6.17. Found: C, 42.20; H, 2.63; N, 6.13%.

2-(Ethylthiosulfanyl)-1,3-benzoselenazolium tetrafluoroborate 13

To a solution of *N*-methyl-3*H*-benzoselenazole-2-thione **9** (0.78 g, 3.41 mmol) in $CHCl_3$ (30 mL) were added solutions of $CH(OEt)_3$ (2.03 g, 13.7 mmol) in 10 mL of $CHCl_3$, and BF_3·Et_2O (2.58 g, 18.2 mmol) in 10 mL of $CHCl_3$. The reaction mixture was stirred at reflux for 1 h, then was allowed to reach room temperature and approximately 3/4 of the solvent was removed under reduced pressure. Diethyl ether was added to the reaction mixture and a light brown solid precipitated out. The precipitate was filtered off, washed with diethyl ether, and dried to give 1.10 g (93%) of salt **13** as a light brown powder, mp 178 °C; ^{1}H NMR (CD_3CN) δ 8.46–8.35 (1H, dd, ^3J = 8.1 Hz, ^4J = 0.8 Hz), 8.20–8.08 (1H, dd, ^3J = 8.3 Hz, ^4J = 0.8 Hz), 8.05–7.91 (1H, m), 7.90–7.75 (1H, m), 4.21 (3H, s), 3.75 (2H, q, J = 7.6 Hz), 1.80 (3H, t, J = 7.3 Hz); ^{13}C NMR (CD_3CN) δ 187.60, 143.44, 129.50, 128.78, 127.04, 125.95, 116.70, 37.70, 32.74, 12.17. Calc. for $C_{10}H_{12}NSSeBF_4$: C, 34.91; H, 3.52; N, 4.07. Found: C, 35.01; H, 3.32; N, 4.03%.

N-Methylbenzoselenazole-2-selone 14

$NaBH_4$ (0.36 g, 9.53 mmol) was dissolved in absolute EtOH (50 mL) and a stream of nitrogen was bubbled for 15 min into the solution. Selenium powder (0.68 g, 8.66 mmol) was added to the solution under flux of nitrogen and the reaction mixture was stirred, under nitrogen, until the formation of a turbid, colorless solution of NaSeH. To this solution was slowly added a solution of 2-(ethylsulfanyl)-1,3-benzoselenazolium tetrafluoroborate **13** (1.49 g, 4.33 mmol) in MeCN (25 mL). The reaction mixture was stirred under nitrogen for 30 min. Water (50 mL) was added to the reaction mixture, which was then extracted with CH_2Cl_2 (5 × 50 mL). The combined organic layers were dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave an orange crystalline solid. The residue was flash chromatographed over silica gel (CH_2Cl_2) twice in order to eliminate residual red selenium. The eluate was dried (Na_2SO_4) and evaporated under reduced pressure to furnish 1.13 g (95%) of benzoselenazole-2-selone **14** as yellow crystals, mp 100 °C, R_f (CH_2Cl_2) 0.73; ^{1}H NMR δ 7.69–7.28 (4H, m), 3.97 (3H, s); ^{13}C NMR δ 188.87, 144.89, 130.82, 127.71, 126.02, 125.26, 115.12, 37.09. Calc. for $C_8H_7NSe_2$: C, 34.93; H, 2.57; N, 5.09. Found: C, 35.08; H, 2.55; N, 4.72%.

3,3′-Ethylenebis[2-(ethylsulfanyl)benzoselenazolium tetrafluoroborate] 15

To a suspension of 3,3′-ethylenebis(benzoselenazole-2-thione) **12** (0.44 g, 0.97 mmol) in toluene (50 mL) were added, in turn, solutions of $CH(OEt)_3$ (1.15 g, 7.75 mmol) in 5 mL of toluene, and BF_3·Et_2O (1.47 g, 10.32 mmol) in 5 mL of toluene. The reaction mixture was heated to reflux for 2 hours, cooled to room temperature, and diethyl ether (30 mL) was added. The precipitate was filtered off, washed with diethyl ether, and dried to give salt **15** as a pale brown powder, yield 0.63 g (96%) mp 232 °C (dec.); ^{1}H NMR (DMSO-d_6) δ 8.55 (2H, d, J = 7.3 Hz), 8.15 (2H, d, J = 7.3 Hz), 8.01–7.73 (4H, m), 5.33 (4H, s), 3.67

(4H, q, J = 7.3 Hz), 1.44 (6H, t, J = 7.3 Hz); ^{13}C NMR (DMSO-d_6) δ 191.19, 142.88, 130.56, 129.57, 127.84, 127.67, 116.75, 48.41, 32.94, 13.10. Calc. for $C_{20}H_{22}N_2S_2Se_2B_2F_8$: C, 35.01; H, 3.23; N, 4.08. Found: C, 34.74; H, 3.27; N, 3.96%.

3,3′-Ethylenebis(benzoselenazole-2-selone) 16

$NaBH_4$ (120 mg, 3.21 mmol) was dissolved in absolute EtOH (30 mL) and a stream of nitrogen was bubbled for 15 min into the solution. Selenium powder (230 mg, 2.92 mmol) was added to the solution under flux of nitrogen and the mixture was stirred at room temperature for 15 min. Then a solution of 3,3′-ethylenebis[2-(ethylsulfanyl)benzoselenazolium tetrafluoroborate] **15** (500 mg, 0.73 mmol) in MeCN (20 mL) was slowly added. The reaction mixture was stirred at room temperature under nitrogen for 40 min. Water (50 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (3 × 100 mL). Combined organic layers were evaporated under reduced pressure. The orange–yellow residue was dissolved in hot pyridine (20 mL) in order to eliminate red selenium by filtration. Evaporation of the filtrate and recrystallization of the residue in 25 mL of pyridine afforded dimer **16** as green–yellow needles, R_f (CH_2Cl_2) 0.83, yield 0.35 g (88%), mp 288–289 °C (dec.); ^{1}H NMR (DMSO-d_6) δ 7.92–7.84 (2H, dd, ^3J = 7.3 Hz, ^4J = 1.3 Hz), 7.75–7.65 (2H, dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz), 7.49–7.29 (4H, m), 5.05 (4H, s); ^{13}C NMR (DMSO-d_6) δ 190.08, 143.79, 129.92, 127.24, 125.59, 125.42, 114.58, 45.27. Calc. for $C_{16}H_{12}N_4Se_4$: C, 35.06; H, 2.21; N, 5.11. Found: C, 35.25; H, 1.98; N, 5.30%.

N,N′-Dimethyldibenzo-DSeDAF 1

A solution of 3-methylbenzoselenazole-2-selone **14** (20.0 mg, 0.073 mmol) in freshly distilled toluene (2 mL) was heated to reflux under nitrogen and freshly distilled triethyl phosphite (20.6 μL, 0.12 mmol) was added dropwise. The reaction mixture was stirred at reflux for 30 min, giving a clear, orange clear solution. The reaction mixture was cooled to the room temperature and the solution was then transferred into an electrochemical cell under nitrogen containing a degassed solution of tetrabutylammonium hexafluorophosphate in CH_2Cl_2. The CV of the solution was recorded after the addition of aluminium oxide (activated, basic, 150 mesh).

N,N′-Ethylenedibenzo-DSeDAF 3

The same procedure that decribed above for the synthesis of **1**, using 3,3′-ethylenebis(benzoselenazole-2-selone) **16** (20.0 mg, 0.037 mmol) in freshly distilled toluene (7 mL) and triethyl phosphite (20 μL, 0.117 mmol), afforded the title pentacycle **3**, which was also subjected to electrochemical analysis.

Crystal-structure determination of isomeric dimers 10 and 12†

Crystal data for 10. $C_{16}H_{12}N_2S_2Se_2$, M = 454.32, triclinic, space group P-1, a = 9.8982(3), b = 10.0070(3), c = 13.9470(3) Å, α = 102.747(3), β = 104.027(3), γ = 103.336(3)°, V = 1246.92(6) Å^3, Z = 3, T = 293(2) K, μ(Mo-Kα) = 4.695 mm^{-1}, 9637 reflections measured, 5628 unique (R_{int} = 0.0227) of which 4728 with $I > 2\sigma(I)$. The final reliability factors are $wR_2(F_0^2)$ = 0.1243 (all data) and R_1 = 0.0475 [$F_0 > 4\sigma(F_0)$].

Crystal data for 12. $C_{16}H_{12}N_2S_2Se_2$, M = 454.32, monoclinic, space group $P2_1/n$, a = 16.3534(4), b = 5.3820(2), c = 19.3559(6) Å, β = 110.5239(14), V = 1595.46(9) Å^3, Z = 4, T = 200(2) K, μ(Mo-Kα) = 4.893 mm^{-1}, 5500 reflections measured, 2922 unique (R_{int} = 0.0335) of which 2259 with $I > 2\sigma(I)$. The final reliability factors are $wR_2(F_0^2)$ = 0.0785 (all data) and R_1 = 0.0345 [$F_0 > 4\sigma(F_0)$].

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