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# Selenium-Containing Tetrachalcogenins and Pentachalcogenepins Fused to Aromatic Systems

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Various ring-sized cyclic polychalcogenides fused to aromatic systems were synthesized, and the structures were sufficiently characterized. Stabilities of the rings were examined in terms of the existence of selenium atoms. Benzopolychalcogenides are unstable molecules. However, benzo[1,2,3,4,5]-tetrathiaselenepins with an isopropyl group or two methoxy groups on the ring were found to be stable. Similarly, the novel benzo[2,3,4,1,5]trithiadiselenepin ring was also stabilized by two methoxy groups. Benzo[1,2,3,4]trithiaselenin and benzo[2,3,1,4]dithiadiselenin were also synthesized by a controlled reaction with $S_2Cl_2$ at –78 °C. The ring systems were sensitive to air, moisture, light, and polar solvents. Extended π-systems such as naphthalene and phenanthrene showed remarkable thermodynamic stability toward unstable rings. The unprecedented stabilities possessed by the polyaromatics are yet unclear. Phenanthro[9,10-*d*][1,2,3]dithiaselenole was also successfully isolated as a novel molecule. It is the first isolated trichalcogenole having one selenium atom, which is stabilized by an extended π system. Phenanthro[9,10-*f*][1,2,3,4,5]tetrathiaselenepin is stable in the solid state. The use of polar solvents under ambient conditions resulted in the extrusion of selenium from the ring to generate more stable trithiole rings. The structures of the five-, six-, and seven-membered cyclic polychalcogenides were extensively established in this report.

## Introduction

Multilinked sulfur bonds on cyclic polysulfides such as benzopentathiepin (BPT) and benzotrithiole (BTT) have generated significant interest in organosulfur chemistry for their exciting physical, chemical, and biological properties.[1,2] The synthetic usefulness of benzopolysulfides was initiated in 1971 from the pioneering research of Fehér and Langer.[3] Relative to the syntheses and reactions of linear or cyclic polysulfides, only a few examples of cyclic polychalcogenides containing selenium have been reported. Cyclic polychalcogenides containing selenium often exhibited significant unfamiliar properties such as skeletal rearrangements, unusual structures, and transfer of sulfur or selenium atoms to acceptors.[4] Selenium is more polarizable than sulfur, and therefore, the synthesis of stable compounds having Se–Se and/or Se–S linkages in a cyclic manner are attractive in application to material sciences.[5] Moreover, the thermal and photochemical labilities of the Se–Se/S–Se bond have resulted in a variety of interesting findings involving selenium-rich polychalcogenides.

BPT is the most stable polysulfur system, whereas BTT and benzotetrathiin (BTTT) are unstable species. Both BTT and BTTT appear to be very labile because of their lower torsional angles (50 to 55°, respectively) for the C–S–S–S bonds relative to that of BPT (88.6°). However, these unstable ring systems have been successfully isolated by using kinetic stabilization units attached to the aromatic rings.[6] Greer at al. made a relationship between the stability of the cyclic polysulfide and the ring size by computational methods, and he proposed that ring systems bearing an odd number of sulfur atoms in $o$-$C_6H_4S_x$ ($x$ = 3, 5, and 7) have higher stability than their even-numbered counterparts.[7] Five- and seven-membered rings were found to be very stable relative to other ring systems. In the cyclic multichalcogen array of different ring sizes, a favorable lone pair–lone pair repulsion of different nonbonding p orbitals stabilizes the ring system. Furthermore, comparative bond energies for the Ch–Ch (Ch = chalcogen) bonds play a vital role in stabilization. Although there is a lot of theoretical and experimental evidence and many reports on the stabilization of cyclic benzopolysulfides ($o$-$C_6H_4S_x$, where $x$ = 2–8),[8] only a few reports deal with the analogous six- and seven-membered benzopolychalcogenides containing selenium.[1]

Five-membered benzotrichalcogenoles showed well-defined chemical and electrochemical redox behaviors and all compounds were extensively studied.[9] In other words, seven-membered rings are of great interest owing to their diversity in nature and cytotoxic activity.[8] Seven-mem-

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bered multichalcogen compounds are also intriguing due to the rich chalcogen chemistry associated with the flexible Se–S bond and intramolecular ring rearrangement through selenium extrusion – these compounds are important for their inherent stability.[4,10] Although there is only one report about the formation of BTTT,[6a] the similar six-membered benzopolychalcogenide containing selenium has never been reported. It is well known that the C–Se bond is stronger than the S–Se or Se–Se bonds.[10] Therefore, the syntheses of cyclic benzopolychalcogenides **1**–**4** (Figure 1) were attempted with the intention to build upon the aromatic systems to develop compounds that contain one or more selenium atoms directly bonded to the aromatic carbon atoms. The intrinsic and extrinsic nature of these cyclic polychalcogenides as influenced by the fused aromatic rings still remains to be studied. Here, we wish to report evidence of the lability of cyclic benzotetrachalcogenins and pentachalcogenepins having one or two selenium atoms in their rings.

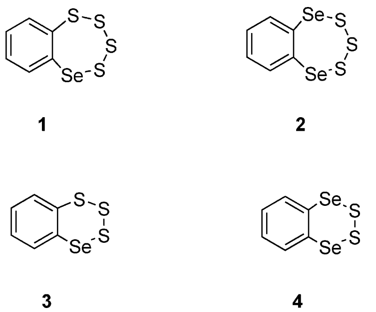
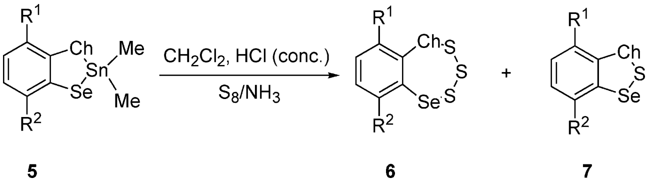


Figure 1. Cyclic benzopolychalcogenides.

## Results and Discussion

### Synthesis of Benzo[1,2,3,4,5]tetrathiaselenepins and Benzo[2,3,4,1,5]trithiadiselenepin

Benzodicalcogenastannoles served as ideal starting materials for the synthesis of cyclic polychalcogenides fused to aromatic systems.[9a] The precursors, benzo[1,3,2]thiaselenastannoles (**5a**–**d**) and benzo[1,3,2]diselenastannoles (**5e**–**g**) were prepared according to the reported procedures (Scheme 1, Table 1).[9f,9i] Benzodichalcogenastannoles such as **5a** and **5e** were treated with concentrated HCl in $CH_2Cl_2$ at a volume ratio of 1:1 for 7 h at room temperature to generate benzodichalcogenols. The unstable benzodichalcogenols were immediately extracted with $CH_2Cl_2$, dried with anhydrous $MgSO_4$, and allowed to react with $S_8/NH_3$ in a flask in $CH_2Cl_2$ in air. The outcome of the experiments did not, however, afford any stable product. During isolation, the products converted into insoluble pasty oligomers along with some red elemental selenium. Many authors also experienced similar results concerning the handling of labile selenium compounds.[10] Several attempts by other methods also did not give either target product **1** or **2** (Figure 1). The sulfur source was also changed from $S_8$ to $S_2Cl_2$ in the presence or absence of a Lewis acid catalyst at low temperature, but stable products were still not isolated. Simple benzopolychalcogenides were expected to be labile under the usual reaction conditions.



Scheme 1. Synthesis of cyclic polychalcogenides from benzodichalcogenastannole **5**.

Table 1. Synthesis of cyclic polychalcogenides.

| Entry | **5** | $R^1$ | $R^2$ | Ch | **6**, Yield [%] | **7**, Yield [%] |
|---|---|---|---|---|---|---|
| 1 | **5a** | H | H | S | | |
| 2 | **5b** | *i*Pr | H | S | **6b**, 54 | **7b**, 6 |
| 3 | **5c** | OMe | OMe | S | **6c**, 45 | **7c**, 30 |
| 4 | **5d** | *i*Pr | *i*Pr | S | | **7d**, 70 |
| 5 | **5e** | H | H | Se | | |
| 6 | **5f** | OMe | OMe | Se | **6f**, 46 | **7f**, 29 |
| 7 | **5g** | *i*Pr | *i*Pr | Se | | **7g**, 72 |

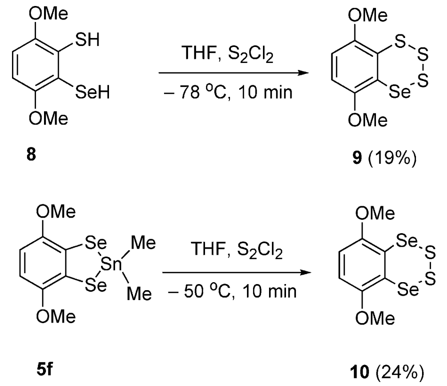
Therefore, an isopropyl group was placed in proximity to the polychalcogen ring (Table 1, Entry 2) and surprisingly the reaction afforded both five- and seven-membered rings as air-stable products. Gel permeation liquid chromatography (GPLC) and mass spectra perfectly reflected the size of the rings. Previously, the methoxy group also proved to be effective for kinetic or thermodynamic stabilization of unstable five-membered trichalcogenoles.[9] The substrate having two methoxy groups (**5c**) gave two stable products, **6c** (45%) and **7c** (30%). By the similar reaction, **6f** and **7f** were also obtained in 46 and 29% yields, respectively. The experimental findings (Table 1) clearly implied that [1,2,3,4,5]tetrathiaselenepin and [2,3,4,1,5]trithiadiselenepin rings were unstable on benzo-fused derivatives, but benzene derivatives substituted at the neighboring positions of the chalcogen ring prevented the rings from usual degradation.

The effect of ring size was observed for substrates **5d** and **5g**, which both contained two isopropyl groups. In those cases, only five-membered rings were isolated in excellent yields. The strong steric repulsion between the bulky isopropyl groups and the large size of the polychalcogen ring did not allow bigger-sized rings to be generated. The isopropyl groups may also force the extrusion of two sulfur atoms from **6d** and **6g** (not isolated) to generate kinetically more relaxed trichalcogenoles **7d** and **7g** (isolated). In all studied pentachalcogenepins, fragmentation resulted in the appearance of peaks corresponding to $[M - S/Se]^+$, $[M - 2S]^+$, and $[M - 3S]^+$ in the mass spectrum, which reflects the weakness of the Se–S/S–S bonds and the readiness of these compounds to lose sulfur. The behavior is also common for other cyclic benzopolysulfides.[8]

## Synthesis of Benzo[1,2,3,4]trithiaselenin and Benzo[2,3,1,4]dithiadiselenin

The ring strain in the tetrathiin ring in BTTT makes the ring unstable, whereas the conventional chair/boat conformation of the pentathiepin ring provides extra stability. The tetrathiin ring was also previously stabilized by protection with methoxy groups.[6] According to Scheme 1, the reactions of **5c** and **5f** in $CH_2Cl_2$ with $S_8/NH_3$ afforded both five- and seven-membered rings, but no six-membered polychalcogenide was isolated. One might be able to postulate that the Lewis basicity of the solvent, such as THF, suppresses $S_2Cl_2$ from further attack on the generated polychalcogen ring. Therefore, a controlled reaction of a suitable substrate with $S_2Cl_2$ in THF would be able to stabilize the tetrachalcogenins.

For instance, a reaction of 3,6-dimethoxy-2-mercaptobenzeneselenol (**8**) at –78 °C with $S_2Cl_2$ (1.0 equiv.) in dry THF and subsequent purification afforded a stable product (Scheme 2). $^1H$, $^{13}C$, and $^{77}Se$ NMR spectra of the compound were completely different from its corresponding **6c** or **7c** analogue. Mass spectra and microanalysis data also suggested the generation of 5,8-dimethoxybenzo[1,2,3,4]trithiaselenin (**9**). In contrast, the corresponding diselenol analogue of **8** was difficult to obtain in pure form due to its prompt oxidation behavior. Therefore, a solution of **5f** in THF at –50 °C was treated with $S_2Cl_2$ and surprisingly the reaction also afforded 5,8-dimethoxybenzo[2,3,1,4]dithiadiselenin (**10**) in 24% yield as orange needles. Both the $^1H$ and $^{13}C$ NMR spectra of compound **10** provided one set of signals, which assigned a high level of symmetry to the molecule, but these spectra were completely different from those of **6f** or **7f**. The five- and seven-membered polychalcogenides of Table 1 served as authentic samples for the structural elucidation of their six-membered analogue by spectroscopy.

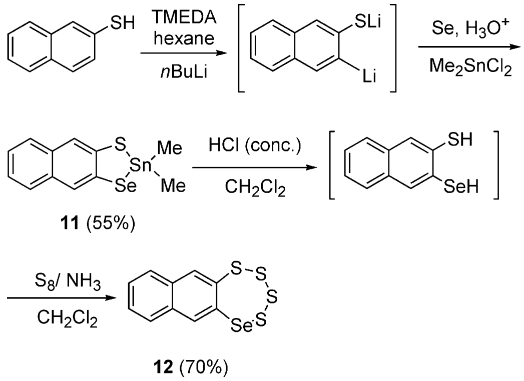


Scheme 2. Synthesis of 5,8-dimethoxybenzochalcogenin **9** and **10**.

Once purified, six-membered polychalcogenides **9** and **10** were quite unstable, and the solid was unchanged in the refrigerator. Polar solvent, such as $CHCl_3$, $CH_3OH$, and DMSO were also shown to be very sensitive to rings. During storage on the bench, these compounds decomposed after several hours.

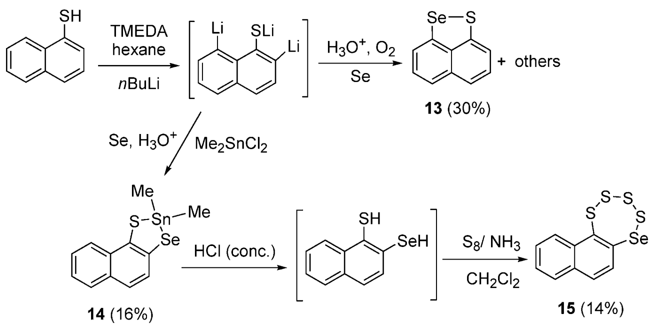
## Synthesis of Naphtho[1,2,3,4,5]tetrathiaselenepins

Extended π-conjugated systems are able to stabilize unstable cyclic polysulfides. Naphthalene is the most simple, planar, as well as readily available π-conjugated system. Recently, we obtained very impressive results by using a naphthalene moiety as a stabilization unit for unstable polychalcogen rings.[6b,11,17] Therefore, we wished to explore unstable cyclic polychalcogenides at the $C^2$–$C^3$ position. 2-Naphthalenethiol was used to synthesize the target ring system according to Scheme 3; it was converted into 2,2-dimethylnaphtho[2,3-*b*][1,3,2]thiaselenastannole (**11**) by a sequential chemical process, such as lithiation with *n*BuLi (4 equiv.), selenation with elemental selenium, and protection with $Me_2SnCl_2$. The yield of **11** was low due to the selectivity of *ortho* lithiation of 2-naphthalenethiol.[12] *ortho* Lithiation occurred in both the $C^1$ and $C^3$ positions. Another isomer of **11**, which was fused at the $C^1$–$C^2$ position, was also generated in a little amount. However, almost pure **11** was obtained after recrystallization. Compound **11** was also treated with $S_8/NH_3$ according to the conditions of Scheme 1, and naphtho[2,3-*f*][1,2,3,4,5]tetrathiaselenepin (**12**) was isolated in 70% yield as a pale yellow powder. Here, neither the five-membered ring nor any other isomer was isolated. Surprisingly, the solid product was found to be stable in air for several months. On standing in an NMR tube in $CDCl_3$, compound **12** also remained unchanged. In the EI mass fragmentation spectrum, it gave both $[M]^+$ and $[M - 2S]^+$ molecular ion peaks in high intensities.



Scheme 3. Synthesis of naphthochalcogenepin **12**.

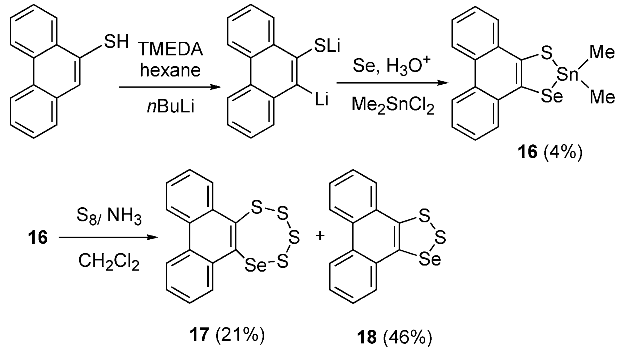
The construction of the same ring was also established at the $C^1$–$C^2$ position although this position is more liable to bear cyclic polysulfides.[11] Lithiation of 1-naphthalenethiol has already been performed.[12] Selenation of a lithiated mixture of 1-naphthalenethiol and successive air oxidation afforded the well-known naphtho[1,8-*cd*]-1,2-selenathiole (**13**) in 30% yield along with some insoluble oligomers (Scheme 4).[13] Protection of naphthalenedichalcogenols in bulk under neutral conditions with dimethyltin(IV) dichloride gave compound **14** in only 16% yield. Finally, compound **15** was obtained in low yield (14%) after thiation with $S_8/NH_3$.



Scheme 4. Synthesis of naphthochalcogenepin **15**.

### Synthesis of Phenanthro[9,10-*f*][1,2,3,4,5,]tetrathiaselenepin

Phenanthrene has some structural advantages[6b] over naphthalene to bear cyclic polychalcogenides at its 9,10-positions, as adjacent *peri* protons provide extra stability similar to substituents for the polychalcogen rings. Phenanthro[9,10-*d*][1,3,2]thiaselenastannole (**16**) was synthesized by an established procedure.[11] Lithiation occurred predominantly at the *peri* positions of phenanthrene; hence, compound **16** was isolated in low yield (4%). Interestingly, sulfurization of **16** with $S_8$/$NH_3$ afforded two products, **17** and **18**, in 21 and 46% yields, respectively (Scheme 5). Phenanthrene stabilized both the seven- and five-membered ring polychalcogenides. An interesting feature is that five-membered polychalcogenides were not observed at all when naphthalene was used as the substrate; hence, the phenanthrene $\pi$ system is considered to provide extra thermodynamic stability to unstable polychalcogenides.



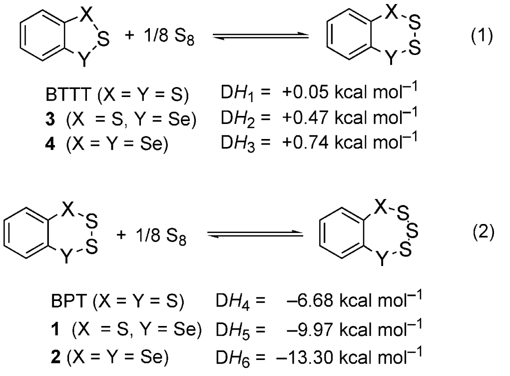
Scheme 5. Synthesis of phenanthrochalcogenenide **17**and **18**.

### Steric Factors of the Isopropyl Groups

The introduction of two isopropyl groups in proximity to the polychalcogen ring afforded only five-membered rings in excellent yields (Table 1, Entries 4, 7), whereas a substrate bearing only a single isopropyl group gave two stable products (Table 1, Entry 2). The steric bulkiness of the isopropyl groups forces the seven-membered polychalcogenides to extrude two sulfur atoms from the ring system, which results in the formation of a kinetically relaxed five-membered ring. This is considered to be a more favorable ring size surrounding two isopropyl groups. The results were completely opposite for two methoxy groups. In many cases, large-size polysulfides and polychalcogenides extrude one or more chalcogen atoms from their rings.[20]

### Homodesmotic Equations

The comparative energies for unstable cyclic benzopolysulfides and benzopolychalcogenides are frequently explained by homodesmotic equations.[14,15] The breaking propensities of large-sized rings and selenium extrusion are common phenomena for cyclic polychalcogenides.[10] Our preliminary communication[1] described that some unstable species were generated in the reaction mixture, but it was difficult to isolate them in a pure form. Therefore, various electronic and kinetic factors were adjusted to establish various sizes of rings. Theoretical calculations were performed to understand the comparative energies of these molecules by hypothetical equations starting from the corresponding trichalcogenoles or tetrachalcogenins with one atom equivalent of sulfur. The enthalpy of formation revealed realistic insight regarding their relative stabilities. Comparative energy distributions of different polychalcogenides were calculated according to the homogeneous Equations (1) and (2) (Scheme 6).



Scheme 6. Homodesmotic reactions among benzotrichalcogenoles, benzotetrachalcogenins, and benzopentachalcogenepins. Heat of formation was calculated by B3LYP//6-31G(d) levels.

It is well-established that parent benzotrichalcogenoles are unstable molecules. All reactions are slightly endothermic in Equation (1), indicating that benzotetrachalcogenins (BTTT, **3**, and **4**) are more unstable than the corresponding benzotrichalcogenoles. However, according to Equation (2), benzopentachalcogenepins (BPT, **1**, and **2**) are more stable than the corresponding benzotetrachalcogenins, as the reactions are highly exothermic. Therefore, seven-membered benzopentachalcogenepins are comparatively more stable than benzotrichalcogenoles or benzotetrachalcogenins, although there is no evidence so far for the isolation of substituent-free analogues.

### $^{77}$Se NMR Spectroscopy for the Structural Elucidation of Cyclic Polychalcogenides

$^{77}$Se NMR spectroscopy is an efficient alternative experimental tool to trace the existence of selenium in selenium-

Table 2. $^{77}$Se NMR spectroscopic data for selenium bearing compounds.

| Dichalcogenastannole | | Trichalcogenole | | Tetrachalcogenin | | Pentachalcogenepin | |
|---|---|---|---|---|---|---|---|
| Compound | $\delta$ $^{77}$Se [ppm][a] | Compound | $\delta$ $^{77}$Se [ppm][a] | Compound | $\delta$ $^{77}$Se [ppm][a] | Compound | $\delta$ $^{77}$Se [ppm][a] |
| **5a** | 57.9 | – | – | – | – | – | – |
| **5b** | 64.2 | **7b** | 662.1 | – | – | **6b** | 711.2 |
| **5c** | 72.0 | **7c** | 633.0 | **9** | 488.9 | **6c** | 606.6 |
| **5d** | 83.2 | **7d** | 628.0 | – | – | – | – |
| **5e** | 109.0 | – | – | **10** | 496.2 | **6f** | 611.9 |
| **5f** | 72.0 | **7f** | 651.0 | – | – | – | – |
| **5g** | 83.2 | **7g** | 653.9 | – | – | – | – |
| **11** | 53.7 | – | – | – | – | **12** | 709.3 |
| **14** | 79.5 | – | – | – | – | **15** | 933.1 |
| **16** | 50.5 | **18** | 624.4 | – | – | **17** | 862.5 |

[a] Relative to neat $Me_2Se$.

bearing molecules. Unfortunately, we were unable to obtain X-ray quality crystals of the tetrachalcogenins and pentachalcogenepins. However, $^{77}$Se NMR spectra showed pertinent information regarding the generation of dichalcogenastannoles, trichalcogenoles, tetrachalcogenins, and pentachalcogenepins (Table 2). The data facilely assigned the number of Se–S bonds in the ring.[18] Although it is difficult to differentiate among trichalcogenoles, tetrachalcogenins, and pentachalcogenepins by only $^{77}$Se NMR spectroscopy, all signals significantly clarified the presence of divalent selenium atom in their structures.[9] Previously, multinuclear NMR spectroscopic experiments were employed to identify the selenium atom that is bonded to aromatic carbon and tin (C–Se–Sn). The signals for the selenium atoms in selenachalcogenastannoles were observed at $\delta < 100$ ppm. The same results were also reflected for all benzochalcogenastannoles (Table 2). The $\delta$ values for five-membered polychalcogenoles are also very much consistent with already assigned authentic data.[9a,9f] Pentachalcogenepins were found to show signals at $\delta > 700$ ppm, whereas tetrachalcogenin showed $\delta$ values around 500 ppm.

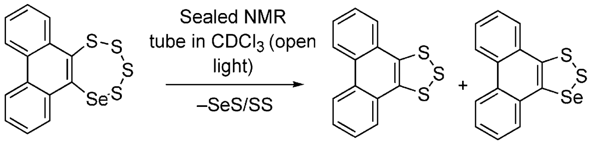
## The Effects of Heat, Light, Air, and Polar Solvents

Tetrachalcogenins are very unstable in solution. Compounds **9** and **10** delivered several uncharacterized products, including small amounts of five-membered rings, on standing in polar solvents. During heating at higher temperatures, the products decomposed to several coagulated pasty oligomers. Tetrathiaselenepins fused to naphthalene were found to be more stable than their corresponding benzo analogues. Compounds **12** and **15** were unchanged both in the solid state and in polar/nonpolar solvents for more than one month on standing. The reasons for the surprising stability of the naphthalene moiety are yet unclear. During purification and NMR spectroscopic measurements in solution, all cyclic polychalcogenides, except benzotrichalcogenoles, slowly deposited elemental selenium, which has been reported to be characteristics of labile selenium compounds.[10,19] Five-membered polychalcogenides are the most stable compounds and environmental factors such as heat, light, air, and polar solvents do not interfere with the ring systems. Phenathro[9,10-*d*][1,2,3]dithiaselenole (**18**) was also found to be a stable product under all experimental conditions. Compound **18** is the first example of an isolated, selenium-containing, five-membered polychalcogenide, and it is thermodynamically stabilized by the extended π system. For polychalcogenides fused to polyaromatics, the density gradients of the virtual HOMOs are dispersed on both the polychalcogen and the aromatic rings, which results in extra stabilization of the unstable cyclic polychalcogenides.

## Unusual Selenium Extrusion from Phenanthro[9,10-*f*]-[1,2,3,4,5]tetrathiaselenepin by Natural Light

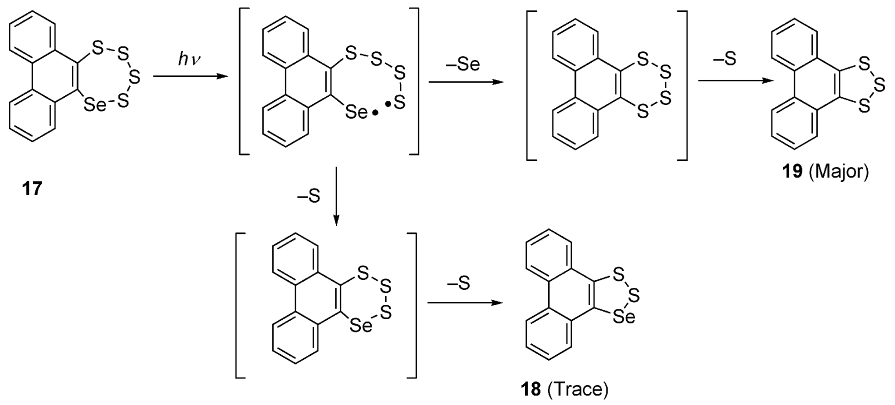
After measurement of the $^1$H NMR spectrum of compound **17**, the NMR tube was stored under ambient conditions. Three days later, it was observed that the bright yellow solution of **17** in $CDCl_3$ had changed into a reddish one.

Previously, spectroscopic and X-ray structural data of authentic compound **19** was reported.[6b] Both the $^1$H and $^{13}$C NMR spectra clarified that at ambient light the seven-membered ring was slowly changing into **19** and **18** as the major and minor products, respectively, by elimination of both sulfur and selenium (Scheme 7 and Figure 2). For generation of **19**, both sulfur and selenium were eliminated from **17**, whereas **18** resulted from the extrusion of two sulfur atoms. The ring cleavage was initiated from the Se–S bond. Breaking of the C–Se or S–S bond requires higher energy than the S–Se bond. We also examined a similar sample in another NMR tube for the same period in the dark by covering it with aluminum foil and the compound remained unchanged.



**17** **19** (Major) **18** (Trace)

Scheme 7. Selenium extrusion from phenanthroselenepin **17**.



Scheme 8. Plausible sulfur and selenium extrusion pathway of **17**.

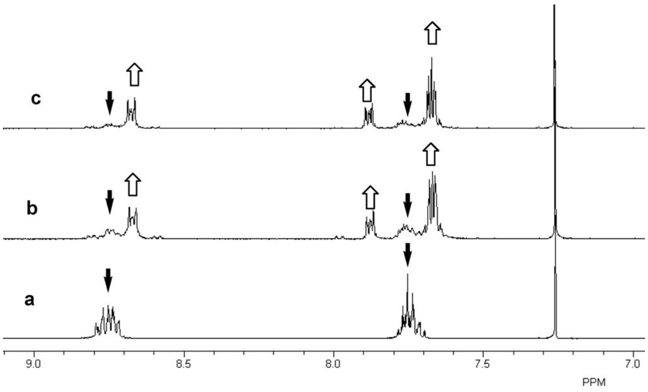


Figure 2. Partial $^1$H NMR (400 MHz, $CDCl_3$) spectra of compound **17**: (a) $^1$H NMR spectra of **17** in $CDCl_3$; (b) After two weeks compound **17** was converted into **19** (major) and **18** (trace); (c) After 4 weeks almost all **17** was converted into **19**.

The plausible mechanism for the extrusion of selenium, starting from cleavage of the Se–S bond, is shown in Scheme 8. During ring dissociation, compound **18** was also generated in a small amount. The results provided additional agreement for light-induced bond breaking through radical pathway.[18] After extrusion of one Se or S atom, form **17**, the six-membered rings were expected to be formed in the reaction system and further degraded into more stable trichalcogenoles (**18** or **19**) by extrusion of one more Se/S. Ando et al. also observed selenium extrusion by using a medium pressure mercury lamp for the same ring on sterically crowded selenadiazole.[16] In our case, however, selenium extrusion occurred by natural light in polar solvent. The ring cleavage afforded more stable trithiole rings, which were traced by NMR spectroscopic signals of the authentic samples. Interestingly, phenanthrene derivatives **16** and **18** showed good stability in both solid state and in solution.

## Conclusions

Novel benzotetrachalcogenins and benzopentachalcogenepins containing selenium and fused to an aromatic carbon were successfully synthesized by using methoxy and isopropyl groups as substituents in close proximity to the chalcogen rings. The bulky substituents act kinetic stabilizer units for the unstable polychalcogen rings. Methoxy groups showed the best results for stabilization of all five-, six- and seven-membered cyclic polychalcogenides. Concerning thermodynamic stabilization, the π system was extended from benzene to naphthalene or phenanthrene to stabilize the similar cyclic polychalcogenides. Consequently, conjugated π systems displayed remarkable thermodynamic stability to unstable polychalcogen rings. Almost all synthesized polychalcogenides were sensitive to heat, light, air, and polar solvents. A novel selenium extrusion reaction was also examined in ambient light in $CDCl_3$ for phenanthro[1,2,3,4,5]tetrathiaselenepin.

## Experimental Section

**General:** Melting points were measured with a MEL-TEMP capillary melting point apparatus and are uncorrected. $^1$H (400 MHz), $^{13}$C (101 MHz), and $^{77}$Se (76 MHz) NMR spectra were recorded with a Bruker AC-400P instrument and with $CDCl_3$ as the solvent. $^1$H NMR chemical shifts are given relative to internal TMS. $^{13}$C and $^{77}$Se NMR chemical shifts are given relative to internal $CDCl_3$ and external standard $Me_2Se$. Mass spectra were recorded with a Hitachi M-2000 or JEOL JMS SX 102 spectrometer under electron ionization (70 eV). IR spectra were recorded as KBr disks with a JASCO FTIR-7300 spectrometer. Hexane, $CH_2Cl_2$, and THF were freshly distilled according to standard laboratory procedure prior to use. Commercial grade TMEDA was purified by atmospheric distillation before use. Wakogel C-200 was used for silica gel column chromatography. Elemental analyses were recorded by using a Yanaco MT5 apparatus at the elemental analysis division of Iwate University.

**General Method for the Synthesis of Dichalcogenastannoles:** In a typical procedure (Table 1, Entry 2), 2-isopropylbenzenethiol (1.0 mmol, 0.152 g) was dissolved in hexane (30–40 mL) and TMEDA (10 mL). The solution was placed in an ice bath and *n*BuLi (3 to 4 equiv.) was slowly added to the reaction mixture. The lithiated mixture was stirred for 8 h at room temperature and elemental selenium was added to the reaction mixture. The mixture was further stirred for 12 h at room temperature, quenched with ice water, acidified with dilute HCl, and extracted with $CH_2Cl_2$. The extracted solution was dried with anhydrous $MgSO_4$, and the residual solvents were removed under reduced pressure. The reaction mixture was further dissolved in dry THF and reduced with $LiAlH_4$ at 0 °C. The reduced mixture was quenched with water, acidified with dilute HCl, and protected with $Me_2SnCl_2$. The organic product was extracted with $CH_2Cl_2$ and dried with anhydrous $MgSO_4$, and the resulting solid was purified by column chromatography (dry bed silica gel; $CHCl_3/CCl_4$, 1:1). Recrystallization from hexane/$CH_2Cl_2$ gave pure product **5b** in 52% (0.196 g) yield.

**7-Isopropyl-2,2-dimethylbenzo[1,3,2]thiaselenastannole (5b):** Colorless plates, m.p. 113.5–114.0 °C. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.02 (s, 6 H, $-SnCH_3$), 1.25 (d, $J$ = 6.8 Hz, 6 H, $-CH_3$), 3.61 (sept, $J$ = 6.8 Hz, 1 H, CH), 6.88 (t, $J$ = 7.6 Hz, 1 H, ArH), 6.96 (dd, $J$ = 7.6, 1.3 Hz 1 H, ArH), 7.43 (dd, $J$ = 7.6, 1.3 Hz, 1 H, ArH) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 1.9, 22.9, 34.4, 122, 124.4, 129.1, 134.8, 139.4, 149.3 ppm. IR (KBr): $\tilde{\nu}$ = 2958, 2924, 2864, 1919, 1686, 1554, 1454, 1434, 1400, 897, 776, 722 $cm^{-1}$. MS: $m/z$ = 378 $[M]^+$. $C_{11}H_{16}SSeSn$ (377.98): calcd. C 34.95, H 4.27; found C 35.02, H 4.33.

**2,2-Dimethylbenzo[1,3,2]thiaselenastannole (5a):** Colorless needles, 80%, m.p. 162.5–163.5 °C. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.04 (s, 6 H, $-CH_3$), 6.84 (dt, $J$ = 7.8, 1.4 Hz, 1 H, ArH), 6.93 (dt, $J$ = 7.8, 1.4 Hz, 1 H, ArH), 7.49 (dd, $J$ = 7.8, 1.4 Hz 1 H, ArH), 7.52 (dd, $J$ = 7.8, 1.4 Hz 1 H, ArH) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 2.4, 124.2, 125.1, 129.9, 131.8, 133.9, 140.6 ppm. $^{77}Se$ NMR (76 MHz, $CDCl_3$): $\delta$ = 57.9 ($J_{77Se\text{-}117Sn}$ = 1056 Hz, $J_{77Se\text{-}119Sn}$ = 1108 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2908, 1912, 1793, 1705, 1444, 746 $cm^{-1}$. MS: $m/z$ = 336 $[M]^+$. $C_8H_{10}SSeSn$ (335.90): calcd. C 28.61, H 3.00; found C 28.67, H 3.02.

**4,7-Dimethoxy-2,2-dimethylbenzo[1,3,2]thiaselenastannole (5c):** Colorless needles, 87%, m.p. 192.5–193.0 °C. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.02 (s, 6 H, SnMe), 3.85 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 6.55 (d, $J$ = 8.8 Hz, 1 H, ArH), 6.64 (d, $J$ = 8.8 Hz, 1 H, ArH) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 2.2, 56.5, 56.5, 106.8, 108.0, 125.8, 131.4, 153.0, 153.1 ppm. $^{77}Se$ NMR (76 MHz, $CDCl_3$): $\delta$ = 72.0 ($J_{77Se\text{-}117Sn}$ = 1043 Hz, $J_{77Se\text{-}119Sn}$ = 1093 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3083, 2987, 2948, 28.30, 1802, 1566, 1456, 1426, 1376, 1243, 1021, 786, 760, 706 $cm^{-1}$. MS: $m/z$ = 396 $[M]^+$. $C_{10}H_{14}O_2SSeSn$ (395.95): calcd. C 30.33, H 3.56; found C 30.24, H 3.84.

**2,2-Dimethyl[1,3,2]benzodiselenastannole (5e):** Colorless needles, 58%, m.p. 157–158 °C. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.08 (s, 6 H, $CH_3$), 7.36 (dd, $J$ = 5.9, 3.4 Hz, 2 H, ArH), 7.56 (dd, $J$ = 5.9, 3.4 Hz, 2 H, ArH) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 2.0, 125.0, 131.8, 136.9 ppm. $^{77}Se$ NMR (76 MHz, $CDCl_3$): $\delta$ = 109.9 ($J_{77Se\text{-}117Sn}$ = 1027 Hz, $J_{77Se\text{-}119Sn}$ = 1077Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2906, 1912, 1795, 1703, 1416, 747 $cm^{-1}$. MS: $m/z$ = 386 $[M]^+$. $C_9H_{10}Se_2Sn$ (382.79): calcd. C 25.10, H 2.63; found C 25.12, H 2.55.

**Compounds 5d, 5f, and 5g:** See ref.[9a]

**2,2-Dimethylnaphtho[2,3-*d*][1,3,2]thiaselenastannole (11):** Off white crystals, m.p. 159.9–160.1 °C. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.07 (s, 6 H, $CH_3$), 7.31–7.34 (m, 2 H, ArH), 7.58 (dd, $J$ = 6.8, 2.5 Hz, 2 H, ArH), 8.00 (s, 1 H, ArH), 8.06 (s, 1 H, ArH) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 1.86, 125.4, 125.7, 126.1, 126.2, 127.4, 128.1, 129.9, 131.0, 131.6, 133.4 ppm. IR (KBr): $\tilde{\nu}$ = 1561, 1482, 1481, 1090, 877, 767, 745, 601 $cm^{-1}$. MS: $m/z$ = 386 $[M]^+$. $C_{12}H_{12}SSeSn$ (385.96): calcd. C 37.34, H 3.13; found C 37.45, H 3.05.

**2,2-Dimethylnaphtho[1,2-*d*][1,3,2]thiaselenastannole (14):** Yellow crystals, m.p. 138.9–139.1 °C. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.07 (s, 6 H, $CH_3$), 7.37–7.41 (m, 2 H, ArH), 7.49 (t, $J$ = 7.2 Hz, 1 H, ArH), 7.60 (d, $J$ = 8.5 Hz, 1 H, ArH), 7.72 (d, $J$ = 8.0 Hz, 1 H, ArH), 8.40 (d, $J$ = 8.5 Hz, 1 H, ArH) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 2.37, 124.6, 124.9, 126.7, 127.3, 128.1, 128.9, 129.1, 131.5, 132.1, 134.3 ppm. IR (KBr): $\tilde{\nu}$ = 1542, 1495, 1331, 1255, 807, 767, 668, 539, 520 $cm^{-1}$. MS: $m/z$ = 386 $[M]^+$. $C_{12}H_{12}SSeSn$ (385.96): calcd. C 37.34, H 3.13; found C 37.70, H 3.10.

**2,2-Dimethylphenanthro[9,10-*d*][1,3,2]thiaselenastannole (16):** Yellow solid, m.p. 192.0 °C (decomp.). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.10 (s, 6 H, Me), 7.53–7.62 (m, 5 H, ArH), 8.39 (dd, $J$ = 8.0, 1.1 Hz, 1 H, ArH), 8.59–8.65 (m, 3 H, ArH) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 1.9, 122.7, 122.8, 125.7, 126.0, 127.1, 127.2, 128.8, 129.1, 129.4, 130.3, 132.9, 133.6, 134.2, 137.5 ppm. IR (KBr): $\tilde{\nu}$ = 1551, 1442, 1147, 1043, 754, 717 $cm^{-1}$. MS: $m/z$ = 436 $[M]^+$. $C_{16}H_{14}SSeSn$ (436.02): calcd. C 44.07, H 3.24; found C 43.75, H 3.21.

**General Procedure for the Synthesis of Benzopentachalcogenepins:** In a typical procedure (Table 1, Entry 2), substrate **5b** (1.00 mmol, 0.378 g) was dissolved in $CH_2Cl_2$ (20–30 mL) along with concentrated HCl (30 mL), and the acidic mixture was stirred for 7 h in the fume chamber at room temperature. The mixture was extracted with $CH_2Cl_2$, dried with anhydrous $MgSO_4$, and filtered. The filtrate was diluted by adding fresh $CH_2Cl_2$ (up to 200 mL). Elemental sulfur (2.0 equiv.) was added to the solution and dissolved well. Liquid $NH_3$ (5–7 mL) was flushed into the solution under constant stirring by using a titanium autoclave connected with a glass needle. The mixture was stirred for several hours for complete removal of the $NH_3$ by evaporation. At neutral pH, the solution was quenched with $H_2O$, extracted with $CH_2Cl_2$, and dried with anhydrous $MgSO_4$, and the remaining solvent was removed in vacuo. After silica gel column chromatography, products **6b** and **7b** were separated by GPLC column in 54 (0.175 g) and 6% (0.016 g) yields, respectively.

**9-Isopropylbenzo[1,2,3,4,5]tetrathiaselenepin (6b):** Yellow crystals, m.p. 46.0–47.0 °C. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.21 (d, $J$ = 3.4 Hz, 3 H, $CH_3$), 1.26 (d, $J$ = 3.4 Hz, 3 H, $CH_3$), 3.81 (sept, $J$ = 3.4 Hz, 1 H, CH), 7.26 (t, $J$ = 7.8 Hz, 1 H, ArH), 7.36 (dd, $J$ = 7.8, 1.4 Hz, 1 H, ArH), 7.71 (dd, $J$ = 7.8, 1.4 Hz, 1 H, ArH) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 23.9, 33.0, 33.5, 127.9, 130.2, 134.8, 143.0, 143.6, 155.0 ppm. IR (KBr): $\tilde{\nu}$ = 2959, 2919, 2858, 1571, 1459, 1438, 1103, 1051, 739, 740 $cm^{-1}$. MS: $m/z$ = 326 $[M]^+$. $C_9H_{10}S_4Se$ (325.40): calcd. C 33.22, H 3.10; found C 33.22, H 3.13.

**6,9-Dimethoxybenzo[1,2,3,4,5]tetrathiaselenepin (6c):** Yellow needles, m.p. 119.0–120.0 °C (decomp.). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.85 (s, 3 H, $OCH_3$), 3.86 (s, 3 H, $OCH_3$), 6.95 (d, $J$ = 9.1 Hz, 1 H, ArH), 6.97 (d, $J$ = 9.1 Hz, 1 H, ArH) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 57.1, 57.2, 115.2, 115.3, 133.7, 134.2, 154.0, 155.3 ppm. IR (KBr): $\tilde{\nu}$ = 2993, 2936, 2830, 1576, 1555, 1460, 1426, 1260, 1182, 1099, 1035, 882, 804, 772, 709 $cm^{-1}$. MS: $m/z$ = 344 $[M]^+$. $C_8H_8O_2S_4Se$ (343.37): calcd. C 27.98, H 2.35; found C 27.80, H 2.07.

**6,9-Dimethoxybenzo[2,3,4,1,5]trithiadiselenepin (6f):** Orange needles, m.p. 109.5–112.0 °C (decomp.). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.84 (s, 6 H, OMe), 6.98 (s, 2 H, ArH) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 57.3, 115.2, 134.2, 154.7 ppm. IR (KBr): $\tilde{\nu}$ = 2935, 2830, 1573, 1551, 1459, 1425, 1258, 1181, 1091, 1034, 804 $cm^{-1}$. MS: $m/z$ = 328 $[M - 2S]^+$. $C_8H_8O_2S_3Se_2$ (390.26): calcd. C 24.62, H 2.07; found C 24.36, H 1.98.

**Naphtho[2,3-*f*][1,2,3,4,5]tetrathiaselenepin (12):** Yellow crystals, m.p. 129 °C. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.61 (dd, $J$ = 6.6, 3.9 Hz, 2 H, ArH), 7.83 (dd, $J$ = 5.6, 3.5 Hz, 2 H, ArH), 8.33 (s, 1 H, ArH) 8.48 (s, 1 H, ArH) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 127.9, 128.1, 128.7, 128.8, 132.7, 132.8, 136.5, 137.3, 137.8, 141.1 ppm. IR (KBr): $\tilde{\nu}$ = 1136, 888, 753, 478 cm$^{-1}$. MS: *m/z* = 334 [M]$^+$, 270 [M – 2S]$^+$. $C_{10}H_6S_4Se$ (333.37): calcd. C 36.03, H 1.81; found C 36.02, H 1.81.

**Naphtho[1,2-*f*][1,2,3,4,5]tetrathiaselenepin (15):** Yellow crystals, m.p. 109.9–110.1 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.55–7.64 (m, 3 H, ArH), 7.84–7.95 (m, 3 H, ArH) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 125.9, 126.5, 126.8, 128.0, 128.5, 128.6, 131.1, 132.0, 133.9, 134.5 ppm. IR (KBr): $\tilde{\nu}$ = 1482, 1298, 1136, 899, 887, 753, 480, 428 cm$^{-1}$. MS: *m/z* = 270 [M – 2S]$^+$. $C_{10}H_6S_4Se$ (333.37): calcd. C 36.03, H 1.81; found C 36.08, H 1.79.

**Phenanthro[9,10-*f*][1,2,3,4,5]tetrathiaselenepin (17):** Yellow powder, m.p. 149.2–149.5 °C (decomp.). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.69–7.78 (m, 4 H, ArH), 8.71–8.79 (m, 4 H, ArH) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 122.9, 123.3, 123.4, 127.7, 127.9, 128.0, 128.6, 128.6, 128.80, 129.7, 129.8, 132.0, 132.6, 132.7 ppm. IR (KBr): $\tilde{\nu}$ = 1472, 1128, 898, 889, 470 cm$^{-1}$. MS: *m/z* = 320 [M – 2S]$^+$, 272 [M – S – Se]$^+$. $C_{14}H_8S_4Se$ (383.43): calcd. C 43.85, H 2.10; found C 44.14, H 2.44.

**5,8-Dimethoxybenzo[1,2,3,4]trithiaselenin (9):** 3,6-Dimethoxy-2-mercaptobenzeneselenol (0.102 g, 0.4 mmol) was dissolved in THF (10 mL) under an argon atmosphere. The solution was cooled to –78 °C, and $S_2Cl_2$ (0.4 mmol) was gradually added into the reaction mixture under constant stirring. The reaction mixture was poured into cooled hexane (30 mL) by a two-way needle. The solvent was evaporated in vacuo and a product precipitated out as a crystalline solid. The solid was filtered and further dissolved in $CCl_4$. Silica gel column chromatography ($CCl_4$) gave pure product (0.024 mg, 19%) as yellow needles. M.p. 98.5–99.0 °C (decomp.). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.87 (s, 3 H, OMe), 3.8 (s, 3 H, OMe), 6.73 (d, *J* = 8.9 Hz, 1 H, ArH), 6.74 (d, *J* = 8.9 Hz, 1 H, ArH) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 57.0, 57.2, 107.7, 107.7, 116.2, 120.1, 150.8, 151.6 ppm. IR (KBr): $\tilde{\nu}$ = 2994, 2933, 2831, 1564, 1450, 1419, 1256, 1037, 787 cm$^{-1}$. MS: *m/z* = 312 [M]$^+$, 280 [M – S]$^+$. $C_8H_8O_2S_3Se$ (311.30): calcd. C 30.86, H 2.59; found C 30.86, H 2.51.

**5,8-Dimethoxybenzo[2,3,1,4]dithiadiselenin (10):** 2,2-Dimethylbenzo[1,3,2]diselenastannole (**5f**; 0.133 g, 0.3 mmol) in THF (20 mL) was taken under an argon atmosphere. The solution was cooled to –50 °C, and $S_2Cl_2$ (0.38 mmol) was added dropwise by a needle. The solution was stirred for 10 min at –50 °C and warmed up to room temperature. The reaction mixture was quenched with ice, extracted with $CH_2Cl_2$, and dried with anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure. Recrystallization of the crude solid from *n*-hexane/$CH_2Cl_2$ at low temperature gave 5,8-dimethoxybenzo[2,3,1,4]dithiadiselenin (0.026 g, 24%) as air-sensitive orange needles. M.p. 89.0–90.0 °C (decomp.). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.89 (s, 6 H, OMe), 6.74 (s, 2 H, ArH) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 57.2, 107.9, 116.6, 151.2 ppm. IR (KBr): $\tilde{\nu}$ = 3002, 2932, 2830, 1562, 1448, 1412, 1253, 1030, 787 cm$^{-1}$. MS: *m/z* = 328 [M – S]$^+$. $C_8H_8O_2S_2Se_2$ (358.20): calcd. C 26.82, H 2.25; found C 26.88, H 2.36.

**Synthesis of Benzotrichalcogenoles:** The products were synthesized along with pentachalcogenepins.

**7-Isopropylbenzo[1,2,3]dithiaselenole (7b):** Orange yellow oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.25 (d, *J* = 6.8 Hz, 6 H, $CH_3$), 3.09 (sept, *J* = 6.8 Hz, 1 H, CH), 7.04 (dd, *J* = 7.7, 1.8 Hz, 1 H, ArH), 7.07 (t, *J* = 7.7 Hz, 1 H, ArH), 7.28 (dd, *J* = 7.7, 1.8 Hz, 1 H, ArH) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 23.0, 36.0, 123.6, 124.0, 127.5, 138.7, 141.9, 146.3 ppm. IR (KBr): $\tilde{\nu}$ = 1412, 1136, 887, 753, 480 cm$^{-1}$. MS: *m/z* = 262 [M]$^+$. $C_8H_{10}S_2Se$ (261.27): calcd. C 41.37, H 3.86; found C 41.58, H 3.02.

**Compounds 7e, 7d, 7f, 7g:** See ref.[9a]

**Phenanthro[9,10-*d*][1,2,3]dithiaselenole (18):** Red needles, m.p. 136.0 °C (decomp.). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.61–7.67 (m, 5 H, ArH), 7.97 (dd, *J* = 7.7, 1.6 Hz, 1 H, ArH), 8.66 (d, *J* = 8.0 Hz, 2 H, ArH) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 123.2, 127.1, 127.2, 127.8, 128.1, 128.6, 128.8, 129.7, 130.1, 130.2, 130.4, 136.4, 137.1, 138.6 ppm. IR (KBr): $\tilde{\nu}$ = 1452, 1232, 1130, 753, 480 cm$^{-1}$. MS: *m/z* = 320 [M]$^+$. $C_{14}H_8S_2Se$ (319.30): calcd. C 52.66, H 2.53; found C 52.66, H 2.67.

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