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Efficient Synthesis, Structure, and Redox Reactions of 1,4,6,9-Tetraisopropylchalcogenanthrenes

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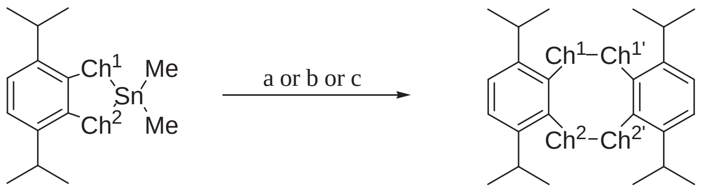
1,4,7,10-Tetraisopropyldibenzo[*c*,*g*][1,2,5,6]tetrachalcogenocins that were readily synthesized from 4,7-diisopropyl-2,2-dimethyl-1,3,2-benzodichalcogenastannoles underwent selective ring contraction under irradiation with a high-pressure mercury lamp to give the corresponding 1,4,6,9-tetraisopropylchalcogenanthrenes having bulky substituents on the benzene ring at adjacent positions of the 6-membered dichalcogenin unit in moderate yields. X-ray crystal structure determination of 1,4,6,9-tetraisopropylthianthrene revealed that the substituents of bulky substituents such as isopropyl groups scarcely affected the structure of the parent dithiin framework. Measurements of the cyclic voltammetry of thianthrene showed a well-defined reversible redox property, whereas the voltammograms of selenium-containing analogues showed irreversible oxidation waves. In contrast to electrical observations, facile reversible one-electron redox reaction systems were observed between the chalcogenanthrenes and the corresponding chalcogenanthrenium radical cations by chemical oxidation or reduction reactions.

The design of facile and reversible one-electron redox systems based on unusual π-electron framework is an attractive challenge for chemists. Recently, we have reported the construction of reversible one-electron redox systems using 4,7-disubstituted benzotrichalcogenoles.[1–8] Their one-electron oxidized species, radical cation salts, generated by treatment with a one-electron oxidant have a pseudoaromatic 7π electron framework.[6,9] Now, our research has been aimed at the design of a reversible one-electron redox system using 6-membered 1,4-dichalcogenins, 1,4,6,9-tetraisopropylchalcogenanthrenes, which have four bulky isopropyl groups on the benzene ring at adjacent positions for kinetic stabilization. Although many chalcogenanthrene derivatives have been reported,[10–16] there are few chalcogenanthrenes containing carbon substituents on the benzene ring due to their synthetic limitation.[17,18] In the present work, we report novel synthetic routes for the preparation of sulfur- and/or selenium-containing chalcogenanthrenes via formation of tetrachalcogenocins and the properties of the interconvertible redox structure bearing bulky substituents on the benzene ring.[19] Obviously, these chalcogenanthrene derivatives can serve as efficient precursors for novel one-electron redox systems.

Results and Discussion

Synthesis of 1,4,7,10-Tetraisopropyldibenzo[*c*,*g*][1,2,5,6]-tetrachalcogenocins (2a–2d). 4,7-Diisopropyl-2,2-dimethyl-1,3,2-benzodichalcogenastannoles (**1a**–**1c**)[1] served as ideal starting materials for all the preparative work. The reaction of stannoles with 2 equiv of *n*-butyllithium, followed by acidification and air oxidation gave the corresponding tetrachalcogenocins **2a**–**2d** as stable products in moderate yields after the usual work-up (Scheme 1, condition a). Alternatively, sequential treatment of the stannoles with $SOCl_2$/THF, $LiAlH_4$/THF, H^+/H_2O, and $Et_3N–I_2/CH_2Cl_2$ (condition b), or with HCl gas/THF and air oxidation (condition c) followed by the same work-up gave **2a**–**2d** in good to high yields. All physical and spectroscopic data supported the molecular structures of **2a**–**2d**. Interestingly, the methyl protons of the isopropyl groups of **2a** showed a pair of doublets in the ^1H NMR spectrum. This spectral feature should imply that the tetrachalcogenocin ring has a chair conformation with slow ring-interconversion via a twist-boat form in the NMR time scale at room temperature.

Photo-Irradiation Reaction of 1,4,7,10-Tetraisopropyldibenzo[*c*,*g*][1,2,5,6]tetrachalcogenocins (2a–2d). Irradiation of a benzene solution of the tetrachalcogenocins **2a**–**2d** in a Pyrex vessel with a 100 W high-pressure mercury lamp under an argon atmosphere gave the corresponding chalcogenanthrenes **3a**–**3c** in moderate yields (Scheme 2 and Table 1). For instance, tetrathiocin **2a** was quantitatively converted to thianthrene **3a** in the photochemical reaction accompanied with the extrusion of two sulfur atoms. This ring contraction, however, did not occur thermally. It seems that these reactions proceeded via an excited singlet state because the reaction was not quenched under irradiation in the presence of some triplet quenchers such as oxygen (Table 1, Entry 3). To explore the generality of the photochemical ring contraction, tetraselenocin **2b** and dithiadiselenocins **2c** and **2d** were examined. Photolysis of tetraselenocin **2b** in benzene gave the desired 6-membered selenanthrene **3b** accompanied, however, with the 5-membered triselenole **4**. Furthermore, photolysis of two types of dithiadiselenocins **2c** and **2d** in benzene gave the 6-membered thiaselenanthrene **3c** and thianthrene **3a** with 5-membered thiadiselenole **5** and 7-membered dithiaselenepin **6**, respectively. The yields in Table 1 are those optimized after examination of the reaction conditions, and no further improvement was observed, even with longer irradiation time (total of 100 h). All



1a: $Ch^1 = Ch^2 = S$

1b: $Ch^1 = Ch^2 = Se$

1c: $Ch^1 = S, Ch^2 = Se$

2a: $Ch^1 = Ch^2 = Ch^{1'} = Ch^{2'} = S$

2b: $Ch^1 = Ch^2 = Ch^{1'} = Ch^{2'} = Se$

2c: $Ch^1 = Ch^{1'} = S, Ch^2 = Ch^{2'} = Se$

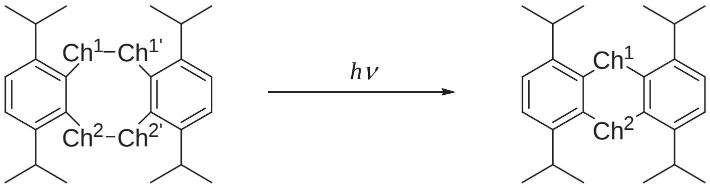
2d: $Ch^1 = Ch^{2'} = S, Ch^2 = Ch^{1'} = Se$

condition a: **2a** 66%, **2b** 60%, **2c** 28%, and **2d** 5%.

condition b: **2a** 85%, **2c** 68%, and **2d** 26%

condition c: **2a** quant.

Scheme 1. Condition a: 1) *n*BuLi/THF, 0 °C, under N_2, 2) H^+/H_2O, 3) O_2 gas/CH_2Cl_2. Condition b: 1) $SOCl_2$/THF, 0 °C, under N_2, 2) $LiAlH_4$/THF, rt, 3) H^+/H_2O, 4) Et_3N–I_2/CH_2Cl_2, 0 °C. Condition c: 1) HCl gas/THF, rt, 2) H_2O, 3) O_2 gas/CH_2Cl_2.



2a: $Ch^1 = Ch^2 = Ch^{1'} = Ch^{2'} = S$

2b: $Ch^1 = Ch^2 = Ch^{1'} = Ch^{2'} = Se$

2c: $Ch^1 = Ch^{1'} = S, Ch^2 = Ch^{2'} = Se$

2d: $Ch^1 = Ch^{2'} = S, Ch^2 = Ch^{1'} = Se$

3a: $Ch^1 = Ch^2 = S$

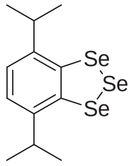
3b: $Ch^1 = Ch^2 = Se$

3c: $Ch^1 = S, Ch^2 = Se$

Scheme 2. Photo-irradiation reaction of tetrachalcogenocins **2a–2d**.

Table 1. Yields of Photoreaction of Tetrachalcogenocins

Substrate	Time/h	Solvent	Atmosphere	Yields/%
2a	24	benzene	Ar	**3a**: 98%
2a	6	toluene	Ar	**3a**: 96%
2a	24	benzene	O_2	**3a**: 94%
2b	50	benzene	Ar	**3b**: 54%, **4**: 31%
2c	48	benzene	Ar	**3a**: 21%, **3c**: 14%, **5**: 10%, **6**: 19%
2d	48	benzene	Ar	**3a**: 19%, **3c**: 11%, **5**: 7%, **6**: 19%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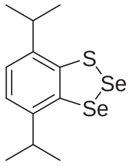
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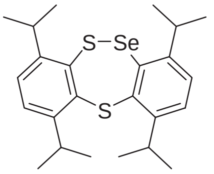
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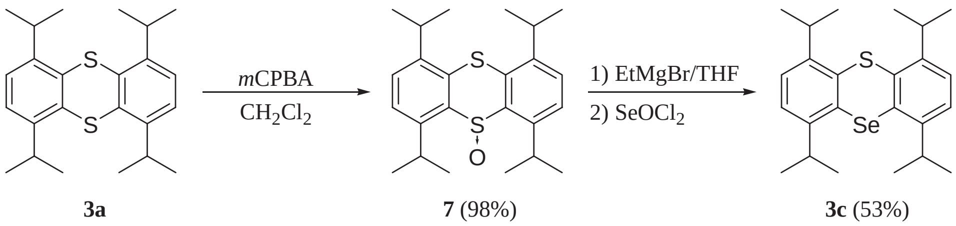
physical and spectroscopic data supported the molecular structures of **3a–3c**. Especially, ^{77}Se NMR measurement strongly revealed the presence of a selenium atom in the molecules ($\delta = 381.5$ ppm for **3b**, $\delta = 337.6$ ppm for **3c**), and these chemical shift values are in good agreement with those of the divalent selenium compounds bound to the aromatic ring in the literature.[20]

Selective Synthesis of 1,4,6,9-Tetraisopropyl-5-thia-10-selenanthrene (3c). Although the thianthrene **3a** and the selenanthrene **3b** were obtained almost selectively in moderate to excellent yields by photochemical ring contraction from the corresponding tetrathiocin and tetraselenocin, the synthesis of **3c** by the same procedures from **2c** or **2d** gave the thiaselenanthrene **3c** with mixed chalcogen atoms, S and Se, in low yield together with compounds **3a**, **5**, and **6**, along with a mixture inseparable by several chromatographic techniques. Therefore,



Scheme 3. Selective synthesis of thiaselenanthrene **3c**.

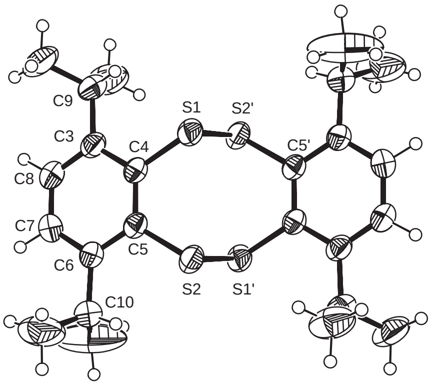


Fig. 1. ORTEP drawing of **2a**.

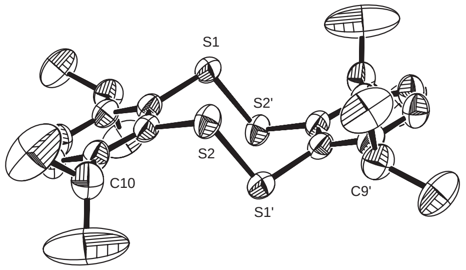


Fig. 2. Bottom view of crystal structure for **2a**. All hydrogen atoms were omitted for clarity.

Table 2. Selected Bond Lengths (Å), Angles (°), and Torsion Angle (°) for **2a**[a)]

Bond lengths		Bond angles	
S1–S2′	2.0602(9)	S2′–S1–C4	103.31(8)
S1–C4	1.777(2)	S1′–S2–C5	101.94(8)
S2–C5	1.779(2)	S1–C4–C5	120.0(2)
C4–C5	1.414(3)	S2–C5–C4	120.9(2)
C4–C3	1.400(4)	C4–C3–C9	123.2(2)
C5–C6	1.406(4)	C5–C6–C10	122.9(2)
C3–C8	1.385(4)		
C7–C8	1.348(4)	Torsion angle	
C6–C7	1.392(4)	C4–S1–S2′–C5′	117.4(1)

a) Values in parentheses are the greater of the range or the estimated SD.

we attempted selective architectural preparation of a 6-membered mixed chalcogen framework by ligand exchange reactions of diaryl sulfoxide derivatives.[21] Compound **3a** was readily oxidized by *m*CPBA to give the thianthrene 5-monooxide **7** quantitatively. Furthermore, sequential treatment of **7** with two equivalents of EtMgBr and a equimolar amount of $SeOCl_2$ in THF gave **3c** in 53% yield as the sole product together with the starting material **7** (Scheme 3).

X-ray Crystallographic Analyses of 1,4,7,10-Tetraisopropyldibenzo[*c*,*g*][1,2,5,6]tetrathiocin (2a) and 1,4,6,9-Tetraisopropylthianthrene (3a). The X-ray crystallographic analyses provided the most diagnostic information as to the cyclic constitution of **2a** and **3a**. The ORTEP drawing of the tetrathiocin **2a** (Fig. 1) showed the striking feature of a chair conformation for the 8-membered ring. There are some reports of X-ray analysis of tetrachalcogenocins and their dibenzo-derivatives, namely, those that have chair conformation or twist conformation.[22–29] Figure 2 shows that the bulky substituents, isopropyl groups, and lone pairs on the sulfur atoms are arranged so as to avoid contact. Especially, the bond lengths and angles of the benzene ring and their isopropyl substituents show a distorted arrangement generated by steric hindrance; for example, the C–C distances of the benzene ring bound to the tetrathiocin side were over 1.4 Å, while other distances were less than 1.4 Å (Table 2). The isopropyl groups also showed slight distortion; the bond angles of C4–C3–C9 and C5–C6–C10 were about 123°. The thianthrene **3a** has a boat-form in the central ring, which is commonly referred to as a butterfly molecule with bulky parts in both wings (Fig. 3). The bond lengths in the central dithiin ring and the butterfly angle of **3a** are 1.77 Å for S–C bonds, 1.39 Å for C–C bonds, and 127.72° (Fig. 4 and Table 3), which are in good agreement with those of the parent thianthrene in the literature.[30,31]

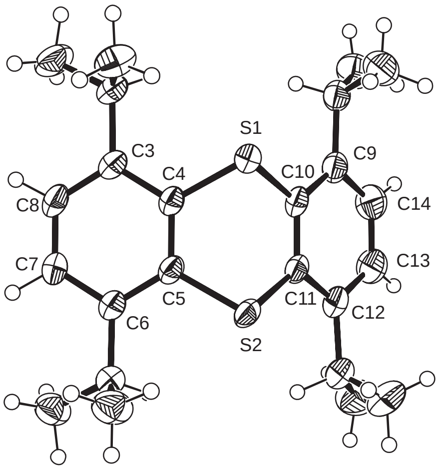


Fig. 3. ORTEP drawing of **3a**.

Electrochemical Studies. Analysis of cyclic voltammetric responses is a diagnostic for an essentially electrochemically reversible anodic step. Cyclic voltammograms of **3a**–**3c** were measured in acetonitrile containing 0.1 M Bu_4NClO_4 as a supporting electrolyte using a glassy-carbon working electrode

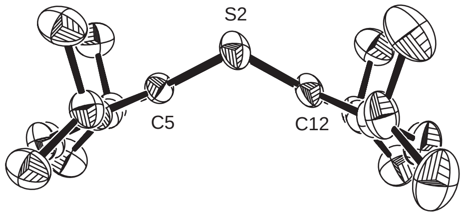


Fig. 4. Bottom view of crystal structure for **3a**. All hydrogen atoms were omitted for clarity.

Table 3. Selected Bond Lengths (Å), Angles (°), and Butterfly Angle (°) for **3a**[a)]

Bond lengths		Bond angles	
S1–C4	1.773(3)	C4–S1–C10	101.8(1)
S1–C10	1.774(3)	C5–S2–C11	102.1(1)
S2–C5	1.776(2)	S1–C4–C5	119.1(2)
S2–C11	1.772(3)	S1–C10–C11	118.9(2)
C4–C5	1.393(3)	S2–C5–C4	119.1(2)
C10–C11	1.395(4)	S2–C11–C10	119.3(2)
		Butterfly angle[b)]	127.72

a) Values in parentheses are the greater of the range or the estimated SD. b) Butterfly angle was estimated least-squares planes between S1, S2, C3, C4, C5, C6, C7, C8 and S1, S2, C9, C10, C11, C12, C13, C14.

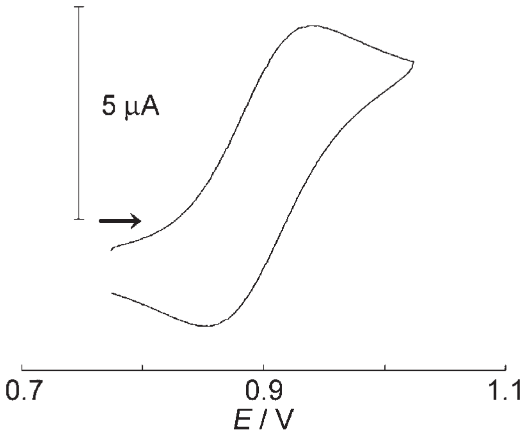


Fig. 5. Cyclic voltammogram of **3a**.

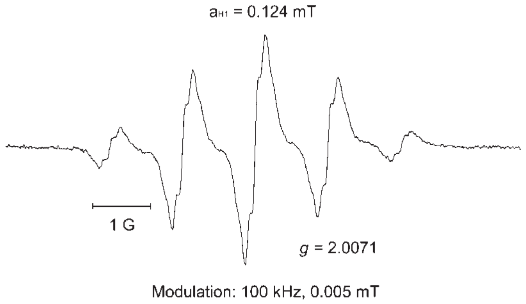
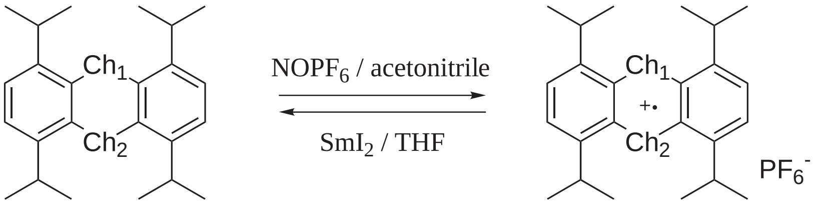


Fig. 6. ESR spectrum of **8a** at 0.005 mT field modulation.



3a: $Ch^1 = Ch^2 = S$
3b: $Ch^1 = Ch^2 = Se$

8a: $Ch^1 = Ch^2 = S$
8b: $Ch^1 = Ch^2 = Se$

Scheme 4. Chemically reversible one-electron redox systems.

and Ag/0.01 M $AgNO_3$ couple in the electrolyte solution as a reference electrode at 20 °C under an argon atmosphere. The cyclic voltammogram curve of **3a** exhibited a well-defined reversible redox wave (Fig. 5; $E_{pa} = 0.94$, $E_{pc} = 0.85$), while **3b** and **3c** showed irreversible waves (**3b**: $E_{pa} = 0.90$; **3c**: $E_{pa} = 0.94$). It is well-known that increasing the selenium substitution from sulfur normally leads to the lowering of the oxidation potential of the donor. As expected, with increasing the selenium substitution, lowered oxidation peaks and less reversible sweeps were obtained that could be explained by assuming a higher degree of localization of electron deficiency to the selenium rather than the sulfur. This reflects the higher reactivity of the corresponding radical cation containing a selenium atom compared with sulfur derivatives. Another possibility of the irreversibility of the selenium-containing **3b** and **3c** is due to the fast escape of the corresponding radical cations from the solution of the CV measurements.

Radical Cations and ESR Spectra. Treatment of the chalcogenanthrenes **3a** and **3b** with 1 equiv of $NOPF_6$ in acetonitrile gave the corresponding radical cation salts **8a** and **8b** quantitatively as a dark blue or dark purple powder (Scheme 4). These salts **8a** and **8b** were stable and their structures were determined by physical and spectroscopic means.[32–39] In particular, the measurement of ^{31}P NMR spectra in CD_3CN showed a septet signal (**8a**: $\delta = -143.7$, $J_{PF} = 706$ Hz; **8b**: $\delta = -143.8$, $J_{PF} = 707$ Hz), which clearly indicated the presence of PF_6^- as a counter anion in the solutions of **8a** and **8b**. In addition, treatment of the radical cation salt **8a** with water gave the corresponding colorless mixture of **3a** and **7**, resulting in disproportionation and hydrolysis. The ESR spectra of **8a** and **8b** in acetonitrile showed the presence of radical cation character (**8a**: $g = 2.0071$; **8b**: $g = 2.0241$). Especially, in the case of **8a**, the signal showed a quintet of the quintet derived from spin-H hyperfine coupling ($a_{H1} = 0.124$, $a_{H2} = 0.013$; Figs. 6 and 7). Unfortunately, the hyperfine coupling constants of **8b** could not be estimated because

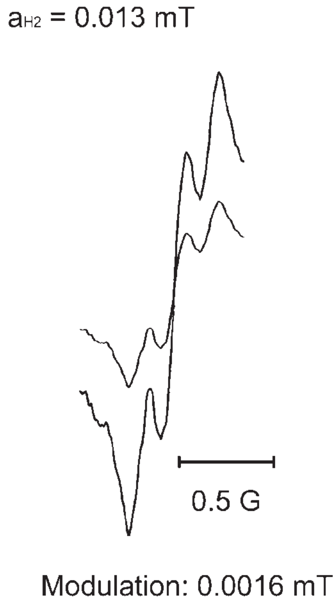


Fig. 7. Part of ESR spectrum of **8a** at 0.0016 mT field modulation.

the signal was observed as a broad peak. The theoretical hyperfine coupling constants of the **3a** cation radical were calculated by using the C_{2v} symmetrical structure with UB3LYP/6-311+G**//UB3LYP/6-31G* level.[40] The theoretical constants, −0.125 mT for aromatic protons and −0.027 mT for methine protons, were in good agreement with the experimental ones, which indicated that the constant of a_{H1} was coupled with aromatic protons and that of a_{H2} was coupled with methine protons. The salts **8a** and **8b** underwent one-electron reduction by treatment with 1 equiv of samarium(II) iodide in THF to give **3a** and **3b** quantitatively. Thus, chemical one-electron redox systems have been achieved by the isolation of both chalcogenanthrenes **3a** and **3b**, and chalcogenanthrenium radical cations **8a** and **8b** (Scheme 4).

We have succeeded in preparing chalcogenanthrenes with bulky substituents by a novel photochemical ring contraction of tetrachalcogenocins. These functionally substituted stable compounds should be useful materials for the construction of a new reversible one-electron redox system.

Experimental

General. Melting points were determined on a MEL-TEMP capillary melting point apparatus and are uncorrected. ^{1}H (400 MHz), ^{13}C (101 MHz), ^{31}P (162 MHz, H_3PO_4 as an external standard), and ^{77}Se (76 MHz, Me_2Se as an external standard) NMR spectra were recorded on a Bruker AC-400 instrument; $CDCl_3$ was used as the solvent if not mentioned otherwise. Mass spectra were recorded on a Hitachi M-2000 spectrometer operating at 70 eV in EI mode. IR spectra were obtained on a JASCO FT-7300 spectrometer. The silica gel used for column chromatography was Wakogel C-200. Preparative HPLC was performed on a JAI LC-908. Elemental analyses were obtained using Yanako MT-5 apparatus at the Elemental Analysis Division of Iwate University. Cyclic voltammetric experiments were performed using a Cypress Systems CS-1090. A three-electrode system was used that consisted of a glassy-carbon working electrode, a platinum wire auxiliary electrode, and a Ag/0.01 M $AgNO_3$ reference electrode. The measurements were carried out in a CH_3CN solution with scan rates 50–500 mV s^{-1} at 20 °C. ESR data were taken with a JEOL RE 2X spectrometer operating in X-band with DPPH and Mn^+ on MgO as field markers.

Materials. THF, diethyl ether, and benzene were distilled from sodium diphenylketyl. CH_2Cl_2 and CH_3CN were distilled from CaH_2. Reagents, except for the solvent given above, were purchased from commercial suppliers and used without further purification.

General Procedure for the Synthesis of 1,4,7,10-Tetraisopropyldibenzotetrachalcogenocins 2a–2c. Condition a: For a typical run, to a stirred solution of 4,7-diisopropyl-2,2-dimethyl-1,3,2-benzodithiastannole (**1a**) (933 mg, 2.5 mmol) in THF (50 mL) was added 1.63 M *n*-BuLi (3.4 mL, 5.5 mmol) at 0 °C under a nitrogen atmosphere, and stirred for 10 min. The mixture was then treated with oxygen as an oxidant, and stirred for 50 min at room temperature. The resulting mixture was poured into ice water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed. The residue was purified by column chromatography on silica gel with hexane as an eluent to give 371 mg of 1,4,7,10-tetraisopropyldibenzo[*c*,*g*][1,2,5,6]tetrathiocin (**2a**) in 66% yield as yellow needles. mp 259.0–260.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (d, 12H, $J = 6.9$ Hz, CH_3), 1.34 (d, 12H, $J = 6.9$ Hz, CH_3), 3.96 (sept, 4H, $J = 6.9$ Hz, CH), 7.36 (s, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.8, 24.2, 32.4, 128.0, 141.7, 152.0; IR (KBr) 2962, 2865, 1462, 1383, 1361, 1239, 1065, 1038, 827, 640 cm^{-1}; UV ($CHCl_3$) λ_{max} 316 (ε 4800) nm; MS (70 eV) m/z 448 (M^+); Anal. Calcd for $C_{24}H_{32}S_4$: C, 64.23; H, 7.19%. Found: C, 64.06; H, 7.25%. Condition b: For a typical run, to a stirred solution of 4,7-diisopropyl-2,2-dimethyl-1,3,2-benzodithiastannole (**1a**) (375 mg, 1.0 mmol) in THF (20 mL) was added thionyl chloride (0.1 mL, 1.38 mmol) in THF (10 mL) at 0 °C under a nitrogen atmosphere, and stirred for 1 h at 0 °C. The resulting mixture was poured into ice water, neutralized with sodium hydrogencarbonate, and then extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed. The residue was purified by column chromatography on silica gel with CCl_4 as an eluent to give 272 mg trithiole 2-oxide (1.0 mmol) as a yellow oil quantitatively. To a stirred solution of 4,7-diisopropyl-1,2,3-benzotrithiole 2-oxide (272 mg, 1.0 mmol) in THF (20 mL) was added $LiAlH_4$ (152 mg, 4.0 mmol) at 0 °C, and the mixture was stirred for 5 min at room temperature. The resulting mixture was poured into ice water, acidified with hydrochloric acid, and then extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed. To a stirred solution of the residue in CH_2Cl_2 (25 mL) were slowly added triethylamine (0.138 mL, 1.0 mmol) in CH_2Cl_2 (25 mL) and iodine (254 mg, 1.0 mmol) in CH_2Cl_2 (25 mL) at 0 °C, and the mixture was stirred for 2.5 h at 0 °C. The resulting mixture was poured into ice water, acidified with hydrochloric acid, and then extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, and the solvent removed. The residue was purified by column chromatography on silica gel with hexane as an eluent to give 191 mg 1,4,7,10-tetraisopropyldibenzo[*c*,*g*][1,2,5,6]tetrathiocin (**2a**) in 85% yield as yellow needles. Condition c: To a stirred solution of 4,7-diisopropyl-2,2-dimethyl-1,3,2-benzodithiastannole (**1a**) (500 mg, 1.34 mmol) in THF (300 mL) was bubbled HCl gas at room temperature, and stirred for 8 h. The resulting mixture was poured into ice water and then extracted with CH_2Cl_2. The organic layer was washed with water, dried over anhydrous sodium sulfate, and the solvent was removed. The stirred solution of the mixture was treated with air as an oxidant and stirred for 48 h at room temperature. The solution was dried over anhydrous sodium sulfate, and the solvent was removed. The residue was purified by column chromatography on silica gel with CCl_4 as an eluent to give 301 mg 1,4,7,10-tetraisopropyldibenzo[*c*,*g*][1,2,5,6]tetrathiocin (**2a**) quantitatively as yellow needles.

1,4,7,10-Tetraisopropyldibenzo[*c*,*g*][1,2,5,6]tetraselenocin (2b): Red crystals; mp 219.0–219.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (d, 12H, $J = 6.9$ Hz, CH_3), 1.30 (d, 12H, $J = 6.9$ Hz, CH_3), 3.89 (sept, 4H, $J = 6.9$ Hz, CH), 7.33 (s, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.9, 24.5, 36.0, 127.7, 142.5, 152.2; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 470.3; IR (KBr) 2961, 2862, 1457, 1432, 1381, 1361, 1232, 1071, 1034, 826, 632 cm^{-1}; UV ($CHCl_3$) λ_{max} 263 (ε 13400), 322 (4600) nm; MS (70 eV) m/z 480 ($M^+ - 158$(^{80}Se, ^{78}Se)); Anal. Calcd for $C_{24}H_{32}Se_4$: C, 45.30; H, 5.07%. Found: C, 45.42; H, 4.94%.

1,4,7,10-Tetraisopropyldibenzo[*c*,*g*][1,2,5,6]dithiadiselenocin (2c): Red needles; mp 246.0–247.5 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (d, 6H, $J = 6.9$ Hz, CH_3), 1.22 (d, 6H, $J = 6.9$ Hz, CH_3), 1.31 (d, 6H, $J = 6.9$ Hz, CH_3), 1.34 (d, 6H, $J = 6.9$ Hz, CH_3), 3.86 (sept, 2H, $J = 6.9$ Hz, CH), 3.98 (sept, 2H, $J = 6.9$ Hz, CH), 7.32 and 7.36 (A_2B_2, 4H, $J = 8.3$ Hz, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.7, 24.0, 24.38, 24.40, 33.0, 35.2, 127.8, 141.4, 142.5, 151.7, 152.5; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 433.8; IR (KBr) 2961, 2864, 1459, 1384, 1361, 1236, 1076, 1058, 1038, 827, 637 cm^{-1}; UV ($CHCl_3$) λ_{max} 317 (ε 3700) nm; MS (70 eV) m/z 544 (M^+); Anal. Calcd for $C_{24}H_{32}S_2Se_2$: C, 53.13; H, 5.94%. Found: C, 53.16; H, 5.94%.

1,4,7,10-Tetraisopropyldibenzo[*c*,*g*][1,5,2,6]dithiadiselenocin (2d): Orange needles; mp 248.5–249.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (d, 6H, $J = 6.9$ Hz, CH_3), 1.23 (d, 6H, $J = 6.9$ Hz, CH_3), 1.32 (d, 12H, $J = 6.9$ Hz, CH_3), 3.88 (sept, 2H, $J = 6.9$ Hz, CH), 3.95 (sept, 2H, $J = 6.9$ Hz, CH), 7.34 (brs, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.7, 23.9, 24.2, 24.7, 33.2, 35.2, 127.6, 128.1, 142.5, 142.7, 151.7, 152.4; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 535.1; IR (KBr) 2961, 2864, 1459, 1383, 1361, 1236, 1076, 1059, 1038, 827, 637 cm^{-1}; UV ($CHCl_3$) λ_{max} 255 (ε 26700), 319 (7500) nm; MS (70 eV) m/z 544 (M^+); Anal. Calcd for $C_{24}H_{32}S_2Se_2$: C, 53.13; H, 5.94%. Found: C, 52.97; H, 5.88%.

General Procedure for the Synthesis of 1,4,6,9-Tetraisopropylchalcogenanthrenes by Ring Contraction Reaction of 1,4,7,10-Tetraisopropyldibenzotetrachalcogenocins 2a–2d. A stirred solution of 1,4,7,10-tetraisopropyldibenzo[*c*,*g*][1,2,5,6]tetrathiocin (**2a**) (45 mg, 0.1 mmol) in toluene (15 mL) was irradiated by a 100 W high-pressure mercury lamp for 6 h under an argon atmosphere at room temperature. The solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with hexane as an eluent to give 37 mg 1,4,6,9-tetraisopropylthianthrene (**3a**) in 96% yield as colorless crystals. mp 162.5–163.5 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (d, 24H, $J = 6.9$ Hz, CH_3), 3.78 (sept, 4H, $J = 6.9$ Hz, CH), 7.22 (s, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.5, 31.3, 124.3, 136.2, 145.9; IR (KBr) 2961, 2928, 2868, 1460, 1387, 1364, 1070, 822 cm^{-1}; UV ($CHCl_3$) λ_{max} 262 (ε 10500), 287 (2300), 295 (2100) nm; MS (70 eV) m/z 384 (M^+); Anal. Calcd for $C_{24}H_{32}S_2$: C, 74.94; H, 8.39%. Found: C, 74.90; H, 8.25%.

1,4,6,9-Tetraisopropylselenanthrene (3b): Colorless crystals; mp 191.0–192.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (d, 24H, $J = 6.9$ Hz, CH_3), 3.73 (sept, 4H, $J = 6.9$ Hz, CH), 7.25 (s, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.8, 34.3, 124.6, 137.3, 147.5; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 381.5; IR (KBr) 2959, 2865, 1466, 1385, 1361, 1078, 1062, 826 cm^{-1}; UV ($CHCl_3$) λ_{max} 270 (ε 6800), 300 (4100) nm; MS (70 eV) m/z 480 (M^+); Anal. Calcd for $C_{24}H_{32}Se_2$: C, 60.25; H, 6.74%. Found: C, 60.35; H, 6.67%.

1,4,6,9-Tetraisopropylthiaselenanthrene (3c): Colorless crystals; mp 156.0–156.5 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (d, 24H, $J = 6.9$ Hz, CH_3), 3.65 (sept, 2H, $J = 6.9$ Hz, CH), 3.94 (sept, 2H, $J = 6.9$ Hz, CH), 7.25 and 7.28 (A_2B_2, 4H, $J = 7.8$ Hz, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.6, 23.7, 31.8, 33.7, 124.7, 136.0, 137.2, 146.78, 146.84; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 337.6; IR (KBr) 2960, 2926, 2866, 1460, 1387, 1364, 1321, 1204, 1066, 910, 829, 820 cm^{-1}; UV ($CHCl_3$) λ_{max} 266 (ε 13400), 288 (4500), 297 (4800) nm; MS (70 eV) m/z 432 (M^+); Anal. Calcd for $C_{24}H_{32}SSe$: C, 66.80; H, 7.47%. Found: C, 66.64; H, 7.74%.

4,7-Diisopropylbenzotriselenole (4): Reddish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (d, 12H, $J = 6.8$ Hz, CH_3), 3.02 (sept, 2H, $J = 6.8$ Hz, CH), 7.05 (s, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.4, 38.7, 125.0, 141.5, 146.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 440.9 ($J_{Se\text{–}Se} = 258$ Hz), 547.0 ($J_{Se\text{–}Se} = 258$ Hz); IR (neat) 2958, 2865, 1885, 1754, 1462, 1385, 1367, 1160, 1104, 906, 820 cm^{-1}; HRMS Calcd for $C_{12}H_{16}Se_3$ (M^+, ^{78}Se^{80}Se × 2): 397.8761, (^{80}Se × 3): 399.8753. Found (M^+, ^{78}Se^{80}Se × 2): 397.8743, (^{80}Se × 3): 399.8662.

4,7-Diisopropyl-1,2,3-benzothiadiselenole (5): Reddish brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (d, 6H, $J = 6.8$ Hz, CH_3), 1.25 (d, 6H, $J = 6.8$ Hz, CH_3), 2.94 (sept, 1H, $J = 6.8$ Hz, CH), 3.22 (sept, 1H, $J = 6.8$ Hz, CH), 6.98 and 7.01 (A_2B_2, 2H, $J = 8.0$ Hz, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.1, 23.3, 35.6, 38.6, 124.6, 124.9, 140.4, 142.1, 144.7, 145.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 509.0 ($J_{Se\text{–}Se} = 275$ Hz), 574.7 ($J_{Se\text{–}Se} = 275$ Hz); IR (neat) 2959, 2924, 1634, 1464, 1385, 818; HRMS Calcd for $C_{12}H_{16}SSe_2$ (M^+): 351.9304. Found (M^+): 351.92702.

1,4,6,9-Tetraisopropyldibenzo[*c*,*f*][1,5,2]dithiaselenepin (6): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (d, 6H, $J = 6.8$ Hz, CH_3), 1.23 (d, 6H, $J = 6.8$ Hz, CH_3), 1.25 (d, 6H, $J = 6.8$ Hz, CH_3), 1.26 (d, 6H, $J = 6.8$ Hz, CH_3), 3.28 (sept, 1H, $J = 6.8$ Hz, CH), 3.67 (sept, 1H, $J = 6.8$ Hz, CH), 3.92 (sept, 1H, $J = 6.8$ Hz, CH), 4.10 (sept, 1H, $J = 6.8$ Hz, CH), 7.14 and 7.20 (A_2B_2, 2H, $J = 8.2$ Hz, ArH), 7.23 and 7.25 (A_2B_2, 2H, $J = 8.2$ Hz, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.4, 23.6, 23.7, 23.9, 30.6, 31.5, 31.6, 31.8, 125.3, 125.6, 125.9, 126.4, 132.8, 134.9, 136.4, 142.3, 146.0, 147.0, 150.4, 151.1; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 501.0; IR (neat) 2960, 2867, 1578, 1464, 1386, 1362, 1318, 1247, 1206, 1159, 1105, 1066, 907, 825; MS (70 eV) m/z 464 (M^+); Anal. Calcd for $C_{24}H_{32}S_2Se$: C, 62.18; H, 6.96%. Found: C, 62.47; H, 6.99%.

Synthesis of 1,4,6,9-Tetraisopropylthianthrene 5-Oxide (7). A solution of *m*CPBA (23 mg, 0.125 mmol) in CH_2Cl_2 (50 mL) was added slowly to a stirred solution of 1,4,7,10-tetraisopropylthianthrene (**3a**) (48 mg, 0.125 mmol) in CH_2Cl_2 (50 mL) at 0 °C. Then, the mixture was warmed to room temperature gradually, and stirred for 13 h. The reaction mixture was washed with sodium hydrogencarbonate solution, and extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, and concentrated in vacuo. The mixture was purified by silica-gel column chromatography with CH_2Cl_2 and then ethyl acetate as eluents to give 48 mg 1,4,6,9-tetraisopropylthianthrene 5-oxide (**7**) in 98% yield as colorless crystals. mp 226.5–227.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (d, 6H, $J = 6.8$ Hz, CH_3), 1.32 (d, 6H, $J = 6.8$ Hz, CH_3), 1.36 (d, 6H, $J = 6.8$ Hz, CH_3), 1.47 (d, 6H, $J = 6.8$ Hz, CH_3), 3.70 (sept, 2H, $J = 6.8$ Hz, CH), 4.05 (sept, 2H, $J = 6.8$ Hz, CH), 7.37 and 7.41 (A_2B_2, 4H, $J = 8.2$ Hz, CH); ^{13}C NMR

(101 MHz, $CDCl_3$) δ 22.8, 22.9, 23.9, 24.4, 29.7, 30.5, 124.2, 127.7, 131.6, 135.2, 145.3, 147.0; IR (KBr) 1037 (SO) cm^{-1}; MS (70 eV) m/z 400 (M^+); Anal. Calcd for $C_{24}H_{32}OS_2$: C, 71.95; H, 8.05%. Found: C, 71.82; H, 8.18%.

Synthesis of 1,4,6,9-Tetraisopropylthiaselenanthrene (3c) from 7. To a stirred solution of 1,4,6,9-tetraisopropylthianthrene 5-oxide (**7**) (40 mg, 0.1 mmol) in THF (5 mL) was added EtMgBr (2.5 mL, 0.1 M, 0.25 mmol) in THF at 0 °C under a nitrogen atmosphere. After stirring for 1 h at room temperature, seleninyl chloride (0.02 mL, 2.5 mmol) in THF (5 mL) was added slowly to the mixture at 0 °C. The reaction mixture was stirred for 5 h, and poured into ice water. The resulting mixture was extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent to give 23 mg 1,4,6,9-tetraisopropylthiaselenanthrene (**3c**) in 53% yield.

X-ray Diffraction Data for 2a and 3a. **2a**: $C_{24}H_{32}S_4$, monoclinic, space group $P2_1/n$ (#14), $a = 11.471(1)$ Å, $b = 5.958(1)$ Å, $c = 18.039(1)$ Å, $\beta = 102.284(8)°$, $V = 1204.6(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.237$ g cm^{-3}. The intensity data were collected on a Rigaku AFC7R diffractometer with filtered Cu Kα radiation at 295 K. Of the 2552 reflections that were collected, 2424 were unique. The structure was solved by the direct method (SHELXS86[41]) and expanded using Fourier techniques (DIRDIF94[42]). The final cycle of full-matrix least-squares refinement was based on 2046 observed reflections ($I > 1.00\sigma(I)$) and 144 variable parameters with $R = 0.046$ and $R_w = 0.081$. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC-139895). **3a**: $C_{24}H_{32}S_2$, monoclinic, space group $P2_1/n$ (#14), $a = 11.050(2)$ Å, $b = 16.593(2)$ Å, $c = 11.936(2)$ Å, $\beta = 91.95(1)°$, $V = 2187.2(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.168$ g cm^{-3}. The intensity data were collected on a Rigaku AFC7R diffractometer with filtered Cu Kα radiation at 295 K. Of the 5520 reflections that were collected, 4192 were unique. The structure was solved by a direct method (SIR92[43]) and expanded using Fourier techniques (DIRDIF94[42]). The final cycle of full-matrix least-squares refinement was based on 3478 observed reflections ($I > 1.50\sigma(I)$) and 364 variable parameters with $R = 0.053$ and $R_w = 0.069$. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC-139896). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

General Procedure for the Synthesis of 1,4,6,9-Tetraisopropylthianthreniumyl Hexafluorophosphate (8a). 1,4,6,9-Tetraisopropylthianthrene (**3a**) (77 mg, 0.2 mmol) and nitrosyl hexafluorophosphate (36 mg, 0.2 mL) were dissolved in CH_3CN (4 mL) under an argon atmosphere. The reaction mixture was stirred for 1 h at room temperature, and the solvent was removed under reduced pressure to give 106 mg (0.20 mmol, 100%) of 1,4,6,9-tetraisopropylthianthreniumyl hexafluorophosphate as a dark blue powder. mp 164.5–165.0 °C (decomp.); ^{31}P NMR (162 MHz, CD_3CN) δ −143.7 (sept, $J_{PF} = 706$ Hz), UV (CH_2Cl_2) λ_{max} 253 (ε 9300), 280 (20000), 321 (19700), 381 (1100), 554 (6500) nm; Anal. Calcd for $C_{24}H_{32}F_6PS_2$: C, 54.43; H, 6.09%. Found: C, 54.54; H, 6.06%.

1,4,6,9-Tetraisopropylselenanthreniumyl Hexafluorophosphate (8b): Dark purple powder; mp 78.5–79.0 °C (decomp.); ^{31}P NMR (162 MHz, CD_3CN) δ −143.8 (sept, $J_{PF} = 707$ Hz), UV (CH_2Cl_2) λ_{max} 253 (ε 9300), 280 (20000), 321 (19700), 381 (1100), 554 (6500) nm; Anal. Calcd for $C_{24}H_{32}F_6PSe_2$: C, 46.24; H, 5.17%. Found: C, 45.88; H, 5.37%.

General Procedure for the One-Electron Reduction of 1,4,-6,9-Tetraisopropylthianthreniumyl Hexafluorophosphate (8a). To a solution of 1,4,6,9-tetraisopropylthianthreniumyl hexafluorophosphate (**8a**) (53 mg, 0.1 mmol) in THF (10 mL) was added 1 mL (1.0 mL, 0.1 M, 0.1 mmol) of samarium iodide in THF at −78 °C under an argon atmosphere. After stirring for 30 min, the reaction mixture was warmed up to room temperature, and then the mixture was treated as follows: poured into water, washed with sodium hydrogensulfite aqueous solution, and extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, and concentrated in vacuo. The mixture was purified by silica-gel column chromatography with CH_2Cl_2 as an eluent to give 37 mg 1,4,6,9-tetraisopropylthianthrene (**3a**) in 96% yield.

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