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Preparation of Phthalocyanines with Eight Benzylchalcogeno Substituents from 5,6-Dibromo-4,7-diethylbenzo[1,2,3]trichalcogenoles

Takeshi Kimura,* Akinori Yomogita, Tomoya Matsutani, Takahiro Suzuki, Ichiro Tanaka, Yasushi Kawai,† Yutaka Takaguchi,‡ Takatsugu Wakahara,§ and Takeshi Akasaka§

Center for Instrumental Analysis, Iwate University, Morioka, Iwate 020-8551, Japan, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan, Department of Environmental Chemistry and Materials, Okayama University, Okayama, Okayama 700-8530, Japan, and Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan

kimura@iwate-u.ac.jp

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Benzo[1,2,3]trichalcogenoles with two bromine atoms on the benzene ring, 5,6-dibromo-4,7-diethylbenzo[1,2,3]trichalcogenoles (**1a**) and (**1b**) (chalcogen: **1a** = S; **1b** = Se), were first prepared by treating 2,3,5,6-tetrabromo-1,4-diethylbenzene (**TBDEB**) with elemental sulfur or amorphous selenium in DBU at 140 °C (for **1a**) and 100 °C (for **1b**) for 24 h. The structures of **1a** and **1b** were verified by NMR spectroscopy, mass spectrometry, and elemental analysis. X-ray crystallographic analysis ultimately showed that the substitution reactions of **TBDEB** proceeded at the two adjacent bromine atoms. To apply **1a** and **1b** to construction of phthalocyanine derivatives with sulfur or selenium functional groups, 4,5-bis(benzylchalcogeno)-3,6-diethylphthalonitriles (**5a**) and (**5b**) as key intermediates were prepared by way of introduction of alkyl groups (2-cyanoethyl or 4-nitrophenethyl groups) on two chalcogen atoms, substitution of two bromine atoms with nitrile groups, and subsequent exchange of alkyl groups with benzyl groups. Compound **5a** was treated with lithium in *n*-pentanol at 100 °C for 1 h to produce 2,3,9,10,16,17,23,24-octakis(benzylthio)-1,4,8,11,15,18,22,25-octaethylphthalocyanine (**6a**). A similar treatment of **5b** in *n*-hexanol at 100 °C for 2 h gave phthalocyanine **6b**. The structures of **6a** and **6b** were determined by ^{1}H NMR spectroscopy and MALDI-TOFMS. X-ray crystallographic analysis of **6a** was also performed. The Q-band absorptions (λ_{max}) for **6a** and **6b** in UV−vis spectra were observed at 755 nm (log ϵ = 5.1) and 757 nm (log ϵ = 5.1), respectively, and their electrochemical properties were verified by cyclic voltammetry in dichloromethane with Ag/$AgNO_3$ as a reference electrode. Compounds **6a** and **6b** were further treated with lithium in THF/NH_3 at −78 °C and then with dibutyltin dichloride to produce phthalocyanine derivatives **8a** and **8b** with four dichalcogenastannole rings by way of octachalcogenate phthalocyanines **7a** and **7b**.

Introduction

Phthalocyanines are important materials and continue to attract considerable attention because the molecules have a variety of potential applications including use as photosensitizers, catalysts, optical disks, charge-generating materials, and photodynamic therapy.[1−8] Unlike porphyrin derivatives, phthalocyanines have the prominent property of exhibiting intense absorption (Q-band) in the near-infrared region. An unadorned phthalocyanine and its metalated derivatives usually exhibit Q-band absorption at around 680 nm. Since a redshift of the Q-band wavelength is a critical element in the application of phthalocyanines to advanced materials, there have been many investigations regarding the design and preparation of functionalized phthalocyanines and their

† Kyoto University.
‡ Okayama University.
§ University of Tsukuba.

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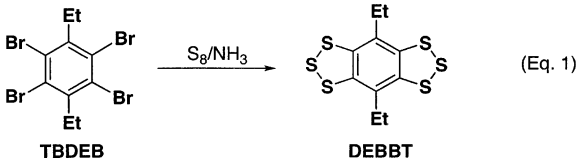
related molecules. For instance, a variety of characteristics have been added to the molecules (1) by introducing several heteroatoms to the periphery of the molecules,[8] (2) by distorting the molecular plane with steric congestion,[4c,e,f] and (3) by expanding the π-conjugation system (i) with the fusion of several aromatic rings,[4d,5a,7c] (ii) with the conjunction of phthalocyanines with alkynyl groups,[6,7a] and (iii) with the construction of binuclear phthalocyanines.[3a,5b]

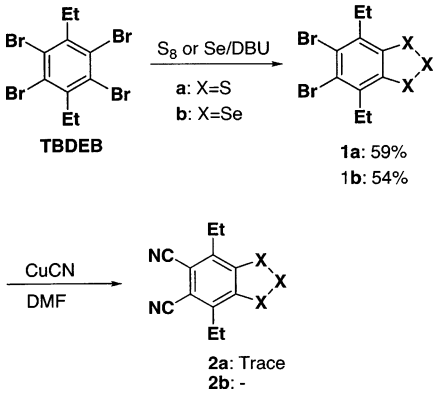
Conversely, we have reported on the preparation, structure, reactivity, and electrochemical properties of several benzoannelated oligosulfides, benzo[1,2,3,4,5]-pentathiepins, and benzo[1,2,3]trithioles.[9−12] In these reports, the preparation of 4,8-diethylbenzo[1,2-*d*:4,5-*d*′]-bis[1,2,3]trithiole (**DEBBT**) represents one of the most vital results. **DEBBT** was prepared in good yield in a one-step reaction by treating 2,3,5,6-tetrabromo-1,4-diethylbenzene (**TBDEB**) with elemental sulfur in liquid ammonia at 120 °C (eq 1).[9] From our continuing study



(Eq. 1)

of several cyclic oligosulfides, we serendipitously found that treatment of **TBDEB** with elemental sulfur in DBU at 140 °C, produced 5,6-dibromo-4,7-diethylbenzo[1,2,3]-trithiole (**1a**), a benzo[1,2,3]trithiole derivative with two adjacent bromine atoms, in moderate yield.[13] By a similar treatment, 5,6-dibromo-4,7-diethylbenzo[1,2,3]triselenole (**1b**), a selenium derivative, was obtained in good yield. Since these molecules have two bromine atoms, substituting the bromine atoms with two nitrile groups or with a diiminoisoindoline structure enables the application of

SCHEME 1



1a and **1b** to synthesize phthalocyanines with several sulfur or selenium functional groups. In this paper, we report on (1) the preparation of 4,5-bis(benzylchalcogeno)-3,6-diethylphthalonitriles **5a** and **5b** from **1a** and **1b** by three-step reactions; (2) their application to the synthesis of new phthalocyanines, 2,3,9,10,16,17,23,24-octakis(benzylchalcogeno)-1,4,8,11,15,18,22,25-octaalkylphthalocyanines with eight peripheral sulfur or selenium atoms; and (3) debenzylation of **6a** and **6b** and stannylation of octachalcogenate phthalocyanines **7a** and **7b** giving phthalocyanines **8a** and **8b** with four dichalcogenastannole rings. In addition, the results of measuring **6a** and **6b** by cyclic voltammetry and UV−vis spectra for **6a**, **6b**, **8a**, and **8b** are also described.

Results and Discussion

Preparation of 5,6-Dibromo-4,7-diethylbenzo-[1,2,3]trichalcogenoles (1a) and (1b). As a typical procedure for introducing sulfur atoms at adjacent positions on the benzene ring, **TBDEB** was treated with elemental sulfur in DBU at 140 °C for 24 h. We initially expected the production of **DEBBT** by this reaction, in a manner similar to the reaction of **TBDEB** with elemental sulfur in liquid ammonia (eq 1).[9] After the usual workup and purification by column chromatography and recrystallization, to our surprise, **1a** was obtained as orange crystals in 59% yield (Scheme 1), while no **DEBBT** was obtained at all. The result is different from the reaction shown in eq 1, and the reaction seems to depend on the solvent. The selenium derivative **1b** was also obtained in 54% yield by the reaction of **TBDEB** with amorphous selenium in DBU at 100 °C for 24 h. This is the first instance of the direct preparation of a benzo[1,2,3]triselenole derivative by a one-step reaction of 1,2-dibromobenzene with selenium reagents. The structures of **1a** and **1b** were verified by NMR spectroscopy, mass spectrometry, and elemental analysis. Since recrystallization of **1a** and **1b** gave orange and dark red crystals, respectively, which are suitable for crystallography, their structures were finally determined by X-ray crystallographic analysis. The crystal data, bond length, and bond angles of **1a** are shown in the Supporting Information. As shown in Figure 1, **1a** apparently has one trithiole ring and two bromine atoms on the benzene ring, clearly suggesting that the substitution reaction of **TBDEB** with the sulfur atoms proceeds at the two adjacent bromine atoms. The structure of the

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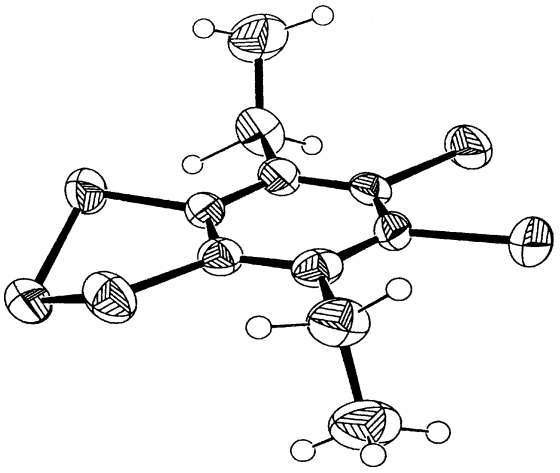


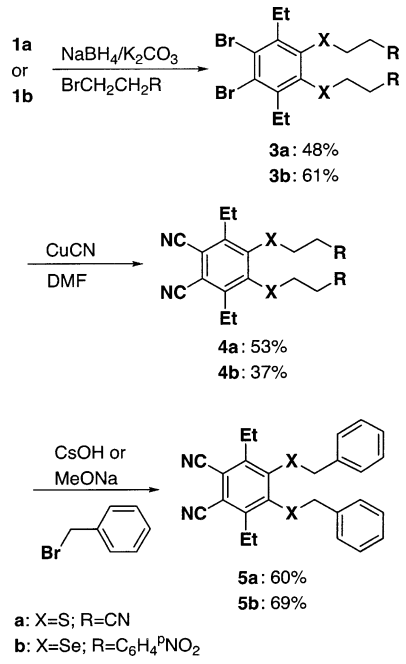
FIGURE 1. ORTEP drawing of **1a**.

benzotrithiole moiety is similar to that of **DEBBT**. The crystal data, ORTEP drawing, bond length, and bond angles of **1b** are also shown in Supporting Information. In contrast to **1a**, compound **1b** is shown to have one triselenole ring and two bromine atoms on the benzene ring. In the ^{77}Se NMR spectrum of **1b**, two signals were observed at δ = 457.5 and 576.8 ppm, and the Se−Se spin coupling constant of the two selenium atoms is J_{Se-Se}=260 Hz. To our knowledge, the benzo[1,2,3]-trithiole and benzo[1,2,3]triselenole derivatives with two bromine atoms on the benzene ring were obtained for the first time by these procedures.

In contrast, 1-(2-cyanoethylthio)-2,5-diethyl-3,4,6-tribromobenzene gave **1a** in 38% yield by treatment with elemental sulfur in DBU at 130 °C for 24 h.[14] The reaction is expected to proceed via 2,5-diethyl-3,4,6-tribromobenzenethiolate as an intermediate. On the basis of this reaction, we predicted a reaction mechanism of **TBDEB** with sulfur or selenium in DBU as follows. (1) The production of **1a** and **1b** is initiated by the aromatic nucleophilic substitution reaction of one bromine atom of **TBDEB** with activated sulfur or selenium atoms. (2) Subsequent intramolecular substitution and cyclization reactions give benzochalcogeniiren as an intermediate.[15] (3) Benzochalcogeniiren is further chalcogenized to produce **1a** and **1b**. However, the details of the mechanism of this substitution reaction are not clear.

Preparation of Phthalocyanines with Eight Benzylthio Groups. If it is possible to substitute the bromine atoms with the nitrile groups and get the corresponding phthalonitriles, **1a** and **1b** could be applied to the preparation of phthalocyanines with sulfur or selenium functional groups. To construct phthalocyanines with eight peripherally substituted chalcogeno substituents, transformation of **1a** and **1b** to the corresponding

SCHEME 2



phthalonitriles, as the key intermediates, was examined using following procedure. Compound **1a** was initially treated with copper(I) cyanide in DMF at 120 °C under an argon atmosphere.[16] Because of the instability of the trithiole ring under the reaction conditions, a complex mixture was obtained together with a trace amount of 5,6-dicyano-4,7-diethylbenzo[1,2,3]trithiole (**2a**).[17]

Because the trithiole ring was unstable under the reaction conditions and we were unable to improve the yield of **2a**, we tried to introduce two 2-cyanoethyl groups onto the sulfur atoms as a protecting group for the thiols (Scheme 2).[18] Compound **1a** was first treated with sodium borohydride and potassium carbonate and then 2-cyanoethyl bromide in THF/methanol at room temperature. After the usual workup and purification by column chromatography, 1,2-bis(2-cyanoethylthio)-3,6-diethyl-4,5-dibromobenzene (**3a**) was obtained in 48% yield. The substitution of the bromine atoms with the nitrile groups was then examined by a method similar to the one described above. The reaction of **3a** with copper(I) cyanide in DMF at 130 °C for 6 h under an argon atmosphere gave 4,5-bis(2-cyanoethylthio)-3,6-diethylphthalonitrile (**4a**) in 53% yield.

There are many procedures for preparing phthalocyanines. As preliminary experiments, according to the method for preparing phthalocyanines under the mild conditions reported by Kobayashi et al., **2a** and **4a** were

(14) 1-(2-Cyanoethylthio)-2,5-diethyl-3,4,6-tribromobenzene was obtained as a minor product together with **3a** when the crude product of **1a** was treated with sodium borohydride, potassium carbonate, and then 2-cyanoethyl bromide in THF/methanol.

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(17) Compound **2a** is the first instance of benzo[1,2,3]trithiole derivatives with two nitrile groups. The structure of **2a** was determined by NMR spectroscopy, IR spectroscopy, mass spectrometry, elemental analysis, and finally by X-ray crystallographic analysis (see the Experimental section and the Supporting Information). The structure of **2a** clearly has one trithiole ring and two nitrile groups on the benzene ring. The oxidation potentials of **2a** are listed in Table 2.

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then treated by sodium methoxide in THF solution.[19] These reactions, however, gave complex mixtures and no phthalocyanines with the trithiole ring or 2-cyanoethylthio groups. We then chose the benzyl group as a protecting group for the thiols instead of the 2-cyanoethylthio groups, and 4,5-bis(benzylthio)-3,6-diethylphthalonitrile (**5a**) was prepared in 45% yield by treating **4a** with cesium hydroxide and then benzyl bromide in THF/methanol at room temperature.

In contrast, to prepare **5a**, 1,2-bis(benzylthio)-3,6-diethyl-4,5-dibromobenzene was prepared from **1a** by treatment with sodium borohydride, potassium carbonate, and then benzyl bromide in THF/methanol and was subsequently reacted with copper(I) cyanide in DMF. In this reaction, however, elimination of the benzyl group seemed to proceed readily together under the reaction conditions with the substitution of the bromine atoms with the nitrile groups. The reaction resulted in complex products. Although **5a** was obtained in 10% yield after repeated column chromatography, the purification of **5a** prepared by this procedure was more difficult than that of **5a** obtained by the alkyl exchange reaction of **4a**.

We then tried to construct the target molecule by the method reported by Kobayashi et al., which is known as a good procedure for synthesizing sterically congested phthalocyanines.[4c] Compound **5a** was reacted with lithium in *n*-pentanol at 140 °C under an argon atmosphere. The solution immediately changed color to dark green. After being stirred for 1 h, the reaction mixture was cooled to room temperature and poured into methanol containing hydrochloric acid. A blue-green solid precipitated out of the solution. The precipitate was filtered, washed with methanol, and dried under vacuum. Through this treatment, a trace amount of **6a** was obtained as dark green crystals after purification by column chromatography. It seemed that the higher temperature and longer reaction time produced a lower yield. After several examinations of the reaction conditions, **5a** was treated with lithium in *n*-pentanol at 100 °C for 1 h under an argon atmosphere, giving the best result; **6a** was obtained in 39% yield (Scheme 3). Compound **6a** is a soluble molecule in several organic solvents (dichloromethane, chloroform, and THF), although it is insoluble in acetonitrile and methanol. The structure of **6a** was determined by ^{1}H NMR spectroscopy, UV−vis spectroscopy, and MALDI-TOFMS. As a conspicuous property of the ^{1}H NMR spectra measured in chloroform-*d*, the chemical shift for methylene protons of the two ethyl groups shows a large downfield shift ($\delta = 4.60$ ppm), suggesting that the two neighboring ethyl groups are in close proximity and that the methylene protons are affected by the steric congestion between them. The protons on the nitrogen atoms of the pyrrole rings could not be observed in the spectra. To determine the optical properties of **6a**, the absorption wavelength (λ_{max}) and molar-extinction coefficient (ϵ) were determined by UV−vis spectroscopy. The λ_{max} value of **6a** was observed at 755 nm ($\log \epsilon = 5.1$) in the spectrum, showing a large redshift of the λ_{max} value compared to that of unsubstituted phthalocyanines.

Preparation of Phthalocyanines with Eight Benzylseleno Groups. To our knowledge, there are no precedent reports with respect to phthalocyanine derivatives with selenium substituents, although porphyrazine derivatives with the selenadiazole ring were reported by Ercolani et al. and Barrett et al.[8] We then attempted to prepare phthalocyanines with selenium functional groups. In the process, the 4-nitrophenethyl group was used as an alkyl group instead of the 2-cyanoethyl group used in preparing the sulfur derivative. We did this because it is well-known that the bond energy of the Se−C bond is lower than that of the S−C bond, and the S−C bond of the 4-nitrophenethylthio group is known to be able to better bear the reaction conditions than that of the 2-cyanoethylthio group.[18] Therefore, 1,2-bis(4-nitrophenethylseleno)-3,6-diethyl-4,5-dibromobenzene (**3b**) was prepared by treating **1b** with sodium borohydride and potassium carbonate. Then, 4-nitrophenethylbromide was added to THF/methanol at 60 °C under an argon atmosphere. With this procedure, **3b** was produced in 61% yield. Preparation of phthalonitrile was subsequently attempted by reacting **3b** with copper(I) cyanide in DMF at 100 °C for 6 h under an argon atmosphere. After purification by column chromatography, 4,5-bis(4-nitrophenethylseleno)-3,6-diethylphthalonitrile (**4b**) was obtained in 37% yield. The higher reaction temperature gave a lower yield of **4b**. Since we can obtain **4b**, we attempted to prepare phthalocyanine with the 4-nitrophenethylseleno groups by the reaction of **4b** with lithium in *n*-pentanol at 100 °C under an argon atmosphere. However, we were unable to obtain the product.

Consequently, we tried to exchange the 4-nitrophenethylseleno groups with the benzylseleno groups. Thus, **4b** was treated with sodium methoxide in methanol/THF and then benzyl bromide at room temperature. This treatment produced 4,5-bis(benzylseleno)-3,6-diethylphthalonitrile (**5b**) in 57% yield.[20] When **5b** was treated with lithium in *n*-hexanol at 100 °C under an argon atmosphere, the solution immediately changed color to dark green. After being stirred for 2 h, the reaction mixture was treated by a procedure similar to that described above, and a dark green product **6b** was obtained in 25% yield. The structure of **6b** was determined by ^{1}H NMR spectroscopy, UV−vis spectroscopy, and MALDI-TOFMS. The solubility and ^{1}H NMR spectrum of **6b** are similar

SCHEME 3

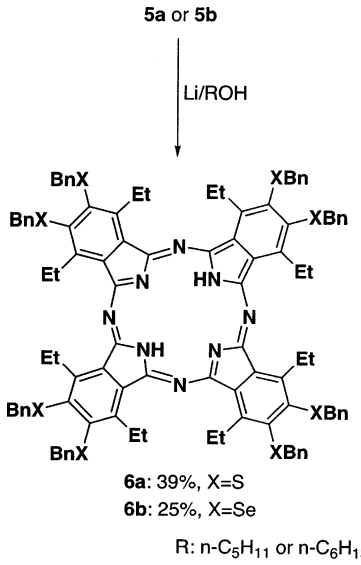

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TABLE 1. Crystal Data of 6a

	6a
crystal system	triclinic
space group	$P\bar{1}$
crystal color	dark green
a (Å)	15.301(7)
b (Å)	16.10(1)
c (Å)	21.64(1)
α (deg)	77.42(4)
β (deg)	89.92(4)
γ (deg)	70.89(4)
V (Å^3)	4903.3(4)
Z	2
D_{calc} (g/cm^3)	1.357
μ (cm^{-1})	4.00
refl/param ratio	11.44
R	0.046
R_w	0.065
GOF	1.12

to those of the sulfur derivative **6a**. Compound **6b** has eight selenium atoms arranged peripherally and, hence, we can characterize the molecule by the ^{77}Se NMR spectrum. In the spectrum, the signal of **6b** was observed at δ = 356.0 ppm, which is a value shifted upfield from those of **5b** (δ = 389.6 ppm) and 1,2-bis(benzylseleno)-4,5-dibromo-3,6-diethylbenzene (δ = 390.8 ppm). In the UV−vis spectrum, the λ_{max} value of **6b** is 757 nm (logϵ = 5.1), which is only 2 nm longer than that of **6a**. The HOMO−LUMO gaps of **6a** and **6b**, estimated from Q-band absorption, are both 1.64 eV.

X-ray Crystallography and Electrochemical Properties. Recrystallization of **6a** from chloroform/methanol gave dark green rhombic crystals, and they are suitable for single-crystal X-ray crystallography. We then performed X-ray crystallographic analysis and found that **6a** crystallizes in triclinic form and that the space group is $P\bar{1}$ (#2). The unit cell consists of two molecules of **6a** in the crystal, and four molecules of chloroform are further contained in the unit cell. The crystal data is shown in Table 1. Meanwhile, the ORTEP drawing reveals that the form of the phthalocyanine skeleton is nearly planar. In the structure, two benzylthio groups on the same benzene ring are directed in opposite directions and are perpendicular to the plane of the phthalocyanine, while the two ethyl groups in close proximity are also oriented in alternate directions (Figure 2). It seems that the two sterically congested ethyl groups cause a slight distortion in the phthalocyanine skeleton.

To determine the electrochemical properties, the redox potentials of **6a** and **6b** were then measured by cyclic voltammetry with silver nitrate used as the reference electrode (Table 2). As shown in Figure 3 and Table 2, two reversible oxidation potentials ($E_{1/2}$ = 0.49 and 0.72 V) and two reversible reduction potentials ($E_{1/2}$ = −1.02 and −1.31 V) were observed for **6a**, while one reversible oxidation potential ($E_{1/2}$ = 0.46 V), one irreversible oxidation potential (E_p = 0.74 V), and two reversible reduction potentials ($E_{1/2}$ = −1.03 and −1.32 V) were observed for **6b**. It appears that the oxidation potentials of **6b** are slightly lower than those of **6a**, while the reduction potentials of **6b** are similar to those of **6a**. The differences in potential (ΔE) between the first oxidation potential and the first reduction potential were calculated to estimate the HOMO−LUMO gap of **6a** and **6b**. The calculation reveals that the gaps of **6a** and **6b** are ΔE = 1.51 and 1.49 V, respectively.

In contrast, benzotrichalcogenoles **1a**, **1b**, **2a**, and **2b** show reversible oxidation potentials at $E_{1/2}$ = 0.99, 0.77, 1.10, and 0.87 V, respectively, which are higher than those of the benzotrichalcogenoles without the two bro-

(20) 5,6-Dicyano-4,7-diethylbenzo[1,2,3]triselenole (**2b**) was prepared by treating **4b** with CsOH·H$_2$O and then amorphous selenium in THF and MeOH. The structure of **2b** was determined by NMR spectroscopy, mass spectrometry, and elemental analysis (see the Experimental Section). In the ^{77}Se NMR spectrum of **2b**, two signals were observed at δ 463.5 and 563.5 ppm, and the Se−Se spin coupling constant of two selenium atoms is J_{Se-Se} = 271 Hz. X-ray crystallographic analysis shows that the structure of **2b** has one triselenole ring and two nitrile groups on the benzene ring (see the Supporting Information). The oxidation potentials of **2b** are listed in Table 2.

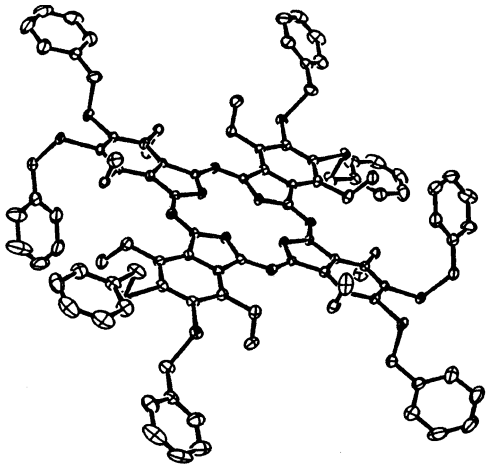


FIGURE 2. ORTEP drawing of **6a** (two $CHCl_3$ molecules and all hydrogen atoms are omitted).

TABLE 2. Redox Potentials (vs Ag/AgNO$_3$)

	$E_{1/2}$ (V)			
compd	second oxidation	first oxidation	first reduction	second reduction
1a[a]		0.99		
1b[a]		0.77		
2a[b]		1.09	−1.04[e]	
2b[b]		0.87	−0.68	
5a[b]		1.40[e]	−1.16[d]	
5b[b]		0.95[e]	−1.15[d]	
6a[c]	0.72	0.49	−1.02	−1.31
6b[c]	0.74[e]	0.46	−1.03	−1.32

[a] Measured in CH_2Cl_2/CH_3CN = 1:1. [b] Measured in CH_3CN. [c] Measured in CH_2Cl_2. [d] Quasi reversible. [e] Irreversible (Ep/V).

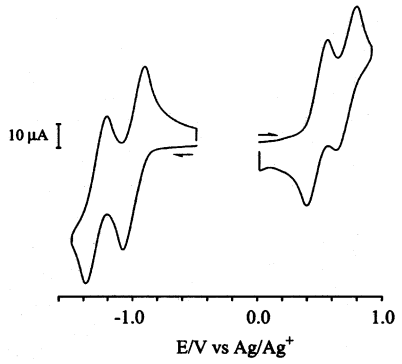
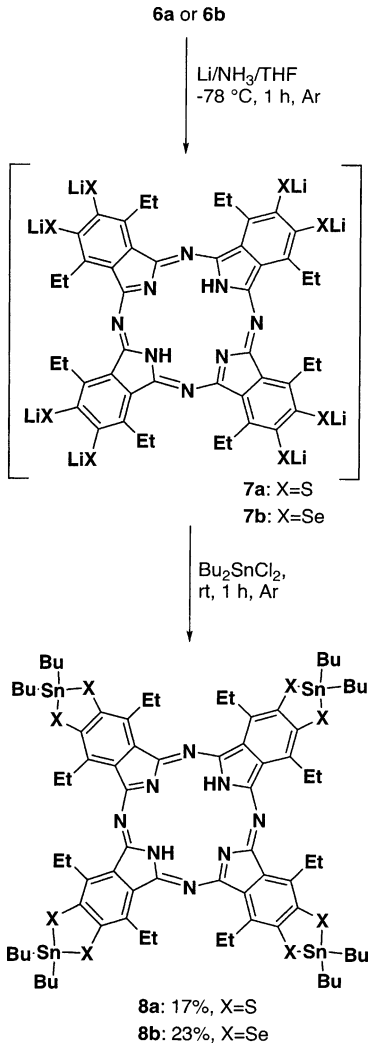


FIGURE 3. Cyclic voltammogram of **6a** (1.1 mmol/L).

mine atoms and two nitrile groups.[21] Interestingly, while the reduction potential of **2a** is observed at $E_p = -1.02$ V as an irreversible wave, **2b** shows a reversible reduction potential at $E_{1/2} = -0.68$ V, revealing that **2b** acts as both an electron donor and acceptor.

Debenzylation of 6a and 6b and Cyclization of Lithium Octachalcogenate with Bu_2SnCl_2. To prepare phthalocyanines modified peripherally, debenzylation and functionalization reactions of **6a** and **6b** were attempted by Birch reduction using lithium metal in THF/liquid ammonia.[22] First, **6b** was treated with lithium metal in THF/liquid ammonia and then elemental selenium. However, no soluble product was obtained by this reaction, suggesting that debenzylated phthalocyanine derivatives have low solubility. We then selected dibutyltin dichloride as an electrophile in a method similar to that reported by Hoffman.[23,24] The benzyl groups of **6b** were removed by using lithium metal in THF/liquid ammonia (Scheme 4). The octaselenolate **7b** generated was very air sensitive. After removal of the ammonia, dibutyltin dichloride in THF/methanol was added to the THF solution of **7b**, and the solution was stirred for 1 h at room temperature. Then the solvent was evaporated, and the product was separated by silica gel column chromatography to produce phthalocyanine with four diselenastannole rings in 23% yield. Similar treatment of **6a** with lithium/ammonia/THF and resulting octathiolate **7a** with dibutyltin dichloride yielded **8a** in 18% yield. The structures of **8a** and **8b** were determined by ^{1}H, ^{77}Se, and ^{119}Sn NMR spectroscopy and MALDI-TOFMS. In the ^{77}Se NMR spectrum, the signal of **8b** was observed at $\delta = 82.4$ ppm, while ^{119}Sn NMR signals appeared at 177.6 for **8a** and 88.2 for **8b**. These chemical shifts are similar to those of benzodichalcogenastannoles.[21] Under UV−vis spectroscopy, the λ_{max} value of **8b** is 766 nm ($\log\epsilon = 5.14$) while that of **8a** is 763 nm ($\log\epsilon = 5.14$) revealing that the construction of the dichalcogenastannole ring affects the UV−vis spectra of phthalocyanine.

SCHEME 4



Conclusion

Compounds **1a** and **1b** with two adjacent bromine atoms were first prepared by the reaction of **TBDEB** with elemental sulfur or selenium in DBU. To apply **1a** and **1b** to the construction of phthalocyanine derivatives with several sulfur or selenium functional groups, **5a** and **5b** were prepared as key intermediates in a three-step process. The phthalonitrile derivatives **5a** and **5b** were then treated with lithium in alcohol to produce corresponding phthalocyanines **6a** and **6b**, respectively, in moderate yields as dark green solids. X-ray crystallographic analysis showed that the structure of **6a** is somewhat distorted. The absorptions of the Q-band of **6a** and **6b** were observed at 755 and 757 nm, respectively, suggesting that the redshift of the Q-band is more strongly affected by the substitution of the ethyl group at the α-positions than that of the chalcogene atoms at the β-positions. The electrochemical properties of the phthalocyanines and benzotrichalcogenoles were determined by cyclic voltammetry with $Ag/AgNO_3$ used as the reference electrode. The cyclic voltammogram of **6a** shows two reversible oxidation potentials and two reversible reduction potentials, while the differences in potential between the first oxidation potential and the first reduction potential of **6a** and **6b** are similar in value. Phthalocyanine derivatives with four dichalcogenastannole rings were obtained by the removal of the benzyl group of **6a** and **6b** and the stannylation of **7a** and **7b**. Studies of further functionalization of **7a** and **7b** are currently in progress in our laboratory.

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(24) Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre: the deposition numbers are CCDC 237554 for **6a**, 237555 for **1a**, 237556 for **1b**, 237557 for **2a**, and 237558 for **2b**.

Experimental Section

Oxidation Potentials. All measurements were performed by cyclic voltammetry, using Ag/0.01 M $AgNO_3$ as a reference electrode, Pt wire as a counter electrode, and glassy carbon as a working electrode. *n*-Bu_4ClO_4 (0.1 M) was used as an electrolyte, and CH_2Cl_2, CH_3CN and CH_3CN/CH_2Cl_2=1:1 were used as solvents. The scan rate was 200 mV s^{-1} for all measurements.

5,6-Dibromo-4,7-diethylbenzo[1,2,3]trithiole (1a). TBDEB (6.76 g, 15 mmol) and elemental sulfur (4.84 g, 151 mmol) were placed in a glass reactor, and DBU (90 mL) was added. The solution was stirred for 24 h at 140 °C and then for 24 h at room temperature. The solution was treated with an aqueous H_2SO_4 solution and extracted with $CHCl_3$. After distillation of the solvent and purification by column chromatography (Wakogel C-300HG, *n*-hexane) and recrystallization from Et_2O, **1a** was obtained in 59% yield (3.44 g); orange crystals; mp 87−87.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, J = 7.5 Hz, 6H), 2.95 (q, J = 7.5 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 12.7, 34.5, 126.6, 138.6, 141.3; MS (*m*/*z*) 386 (M^+); UV ($CHCl_3$) λ_{max} nm (log ϵ) 330 (3.1), 282 (4.0), 241 (4.1). Anal. Calcd for $C_{10}H_{10}Br_2S_3$: C, 31.10; H, 2.61. Found: C, 31.43; H, 2.64.

5,6-Dibromo-4,7-diethylbenzo[1,2,3]triselenole (1b). TBDEB (9.04 g, 20 mmol) was reacted with elemental selenium (11.1 g, 141 mmol) in DBU (80 mL) at 100 °C for 24 h. The solution was treated with an aqueous H_2SO_4 solution under O_2 bubbling and extracted with $CHCl_3$. After distillation of the solvent and purification by column chromatography (Wakogel C-300HG, *n*-hexane/$CHCl_3$ = 1:1), **1b** was obtained in 54% yield (5.76 g): dark-red crystals; mp 141−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, J = 7.5 Hz, 6H), 3.05 (q, J = 7.5 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 12.9, 37.9, 127.1, 141.8, 142.4; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 457.5, 576.8 (J_{Se-Se} = 260 Hz); MS (*m*/*z*) 528 (M^+). Anal. Calcd for $C_{10}H_{10}Br_2Se_3$: C, 22.80; H, 1.91. Found: C, 22.80; H, 2.10.

1,2-Bis(2-cyanoethylthio)-3,6-diethyl-4,5-dibromobenzene (3a). To a solution of **1a** (2.67 g, 6.91 mmol) in THF (90 mL)/methanol (30 mL) was slowly added $NaBH_4$ (0.567 g, 15 mmol), and the solution was stirred for 30 min. After addition of K_2CO_3 (2.06 g, 15 mmol), 3-bromopropionitrile (1.5 mL, 18 mmol) was added, and the solution was stirred at room temperature for 12 h. After the usual workup, the solution was extracted with $CHCl_3$ and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane/$CHCl_3$ = 1:1) to produce **3a** in 48% yield (1.55 g): colorless crystals; mp 95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J = 7.4 Hz, 6H), 2.63 (t, J = 7.1 Hz, 4H), 3.23 (t, J = 7.1 Hz, 4H), 3.37 (q, J = 7.4 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.1, 18.1, 32.9, 33.4, 117.9, 130.8, 138.8, 149.6; MS (*m*/*z*) 462 (M^+); IR (KBr) 2249 cm^{-1} (CN). Anal. Calcd for $C_{14}H_{18}Br_2N_2S_3$: C, 41.57; H, 3.92; N, 6.06. Found: C, 41.77; H, 3.91; N, 6.11.

1,2-Bis(4-nitrophenethylseleno)-3,6-diethyl-4,5-dibromobenzene (3b). Compound **1b** (1.72 g, 3.3 mmol), 4-nitrophenethyl bromide (3.04 g, 13 mmol), and K_2CO_3 (1.30 g, 9.4 mmol) were placed in a glass reactor, and THF (20 mL) and methanol (10 mL) were added. $NaBH_4$ (0.462 g, 12 mmol) was added slowly, and the solution was stirred at 60 °C for 6 h. After the usual workup, the solution was extracted with $CHCl_3$ and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-400, *n*-hexane/$CHCl_3$ = 1:1) to produce **3b** in 61% yield (1.50 g): colorless crystals; mp 95−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, J = 7.4 Hz, 6H), 3.05 (t, J = 7.6 Hz, 4H), 3.24 (t, J = 7.6 Hz, 4H), 3.34 (q, J = 7.4 Hz, 4H), 7.28 (d, J = 8.6 Hz, 4H), 8 11 (d, J = 8.6 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.3, 32.2, 36.2, 36.2, 123.7, 129.1, 129.2, 139.1, 146.7, 148.1, 148.7; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 317.7, MS (*m*/*z*) 748 (M^+). Anal. Calcd for $C_{26}H_{26}Br_2N_2O_4Se_2$: C, 41.74; H, 3.50; N, 3.74. Found: C, 41.89; H, 3.71; N, 3.80.

4,5-Bis(2-cyanoethylthio)-3,6-diethylphthalonitrile (4a). Compound **3a** (3.22 g, 6.96 mmol) and CuCN (6.30 g, 70.3 mmol) were placed in a glass reactor, DMF (10 mL) was added under Ar, and the solution was stirred at 120 °C for 5 h. After the reactor was cooled, $FeCl_3 \cdot 6H_2O$ (19.2 g, 71.0 mmol) and trace amounts of aqueous HCl were added, and the solution was stirred at 70 °C for 15 min. After the reactor was cooled by the addition of ice−water, the product was extracted with $CHCl_3$ and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-300HG, $CHCl_3$) to produce **4a** in 53% yield (3.75 g): yellow crystals; mp 65−67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, J = 7.5 Hz, 6H), 2.68 (t, J = 6.8 Hz, 4H), 3.28 (q, J = 7.5 Hz, 4H), 3.32 (t, J = 6.8 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 15.3, 18.4, 29.0, 32.9, 114.5, 117.2, 117.4, 146.0, 152.8; MS (*m*/*z*) 354 (M^+); IR (KBr) 2255, 2230 cm^{-1} (CN). Anal. Calcd for $C_{18}H_{18}N_4S_2$: C, 60.99; H, 5.12; N, 15.80. Found: C, 60.96; H, 5.51; N, 15.53.

4,5-Bis(4-nitrophenethylseleno)-3,6-diethylpthalonitrile (4b). Compound **4b** was obtained in 37% yield (1.20 g) by treatment of **3a** (3.75 g, 5.0 mmol) with CuCN (1.82 g, 20 mmol) in DMF (12 mL) at 120 °C for 6 h under Ar: orange crystals; mp 90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, J = 7.5 Hz, 6H), 3.10 (t, J = 7.6 Hz, 4H), 3.24 (q, J = 7.5 Hz, 4H), 3.28 (t, J = 7.6 Hz, 4H), 7.35 (d, J = 8.6 Hz, 4H), 8 12 (d, J = 8.6 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 15.4, 31.9, 32.7, 36.0, 114.9, 116.0, 123.8, 129.1, 146.5, 146.9, 147.4, 152.1; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 309.9, MS (*m*/*z*) 642 (M^+); IR (KBr) 2225 cm^{-1} (CN). Anal. Calcd for $C_{28}H_{26}N_4O_4Se_2$: C, 52.51; H, 4.09; N, 8.75. Found: C, 52.18; H, 4.33; N, 8.55.

4,5-Bis(benzylthio)-3,6-diethylphthalonitrile (5a). Compound **4a** (0.495 g, 1.39 mmol) in THF (80 mL)/MeOH (20 mL) was treated with $CsOH \cdot H_2O$ (0.937 g, 5.58 mmol) at room temperature. Benzyl bromide (0.5 mL, 4.2 mmol) was then added, and the solution was stirred for 24 h. After the usual workup, the product was extracted with $CHCl_3$ and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-300HG, $CHCl_3$) to produce **5a** in 60% yield (0.838 g): yellow crystals; mp 142−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (t, J = 7.5 Hz, 6H), 2.99 (q, J = 7.5 Hz, 4H), 4.23 (s, 4H), 7.04−7.09 (m, 4H), 7.19−7.23 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 15.0, 28.6, 42.1, 114.9, 115.8, 127.7, 128.5, 128.8, 136.4, 147.5, 152.7; MS (*m*/*z*) 428 (M^+); IR (KBr) 2226 cm^{-1} (CN). Anal. Calcd for $C_{26}H_{24}N_2S_2$: C, 72.86; H, 5.64; N, 6.54. Found: C, 74.74; H, 6.06; N, 6.62.

4,5-Bis(benzylseleno)-3,6-diethylphthalonitrile (5b). Compound **4b** (652 mg, 1.0 mmol) in THF (20 mL)/MeOH (10 mL) was treated with MeONa (227 mg, 4.2 mmol) at 60 °C for 1 h under Ar. Benzyl bromide (0.5 mL, 4.2 mmol) was then added, and the solution was stirred at 60 °C for 6 h. After the usual workup, the product was extracted with $CHCl_3$ and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-300HG, $CHCl_3$) to produce **5b** in 69% yield (365 mg): orange crystals; mp 150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, J = 7.5 Hz, 6H), 3.04 (q, J = 7.5 Hz, 4H), 4.22 (s, 4H), 6.99−7.04 (m, 4H), 7.14−7.19 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 15.2, 31.6, 36.5, 115.1, 115.6, 127.4, 128.5, 128.7, 137.2, 147.1, 152.4; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 389.6; MS (*m*/*z*) 524 (M^+); IR (KBr) 2224 cm^{-1} (CN). Anal. Calcd for $C_{26}H_{24}N_2Se_2$: C, 59.78; H, 4.63; N, 5.36. Found: C, 59.45; H, 4.73; N, 5.25.

1,4,8,11,15,18,22,25-Octaethyl-2,3,9,10,16,17,23,24-(benzylthio)phthalocyanine (6a). Lithium (36 mg, 5.2 mmol) was placed in a glass reactor, *n*-pentanol (2 mL) was added under Ar, and the solution was stirred at 100 °C for several minutes. Compound **5a** (215 mg, 0.5 mmol) was added to the solution, which was then stirred at 100 °C for 1 h. After the reactor was cooled, aqueous HCl and MeOH were added, and a green precipitate was filtered out. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane/$CHCl_3$ = 1:1) to produce **6a** in 39% yield (84 mg): green crystals; mp 82−84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (t, J = 7.3 Hz, 24H), 4.45 (s, 16H), 4,60 (q, J = 7.3 Hz, 16H),

7.11−7.17 (m, 8H), 7.17−7.23 (m, 16H), 7.29−7.33 (m, 16H); UV ($CHCl_3$) λ_{max} nm (log ϵ) 755 (5.1); MALDI-TOFMS (*m*/*z*) 1714.71 (M^+).

1,4,8,11,15,18,22,25-Octaethyl-2,3,9,10,16,17,23,24-(benzylseleno)phthalocyanine (6b). Compound **6b** was obtained in 25% yield (134 mg) by treatment of **5b** (528 mg, 1.0 mmol) with lithium (35 mg, 5.0 mmol) in *n*-hexanol (2 mL) at 100 °C for 2 h under Ar: dark-green powder; mp 75−76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (t, J = 7.3 Hz, 24H), 4.45 (s, 16H), 4,67 (q, J = 7.3 Hz, 16H), 7.05−7.11 (m, 8H), 7.12−7.18 (m, 16H), 7.23−7.28 (m, 16H); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 356.0; UV ($CHCl_3$) λ_{max} nm (log ϵ) 757 (5.1); MALDI-TOFMS (*m*/*z*) 2091.56 (M^+).

Debenzylation of 6b and Cyclization of Lithium Octathiolate with Bu_2SnCl_2. Compound **6b** (106 mg, 0.051 mmol) and lithium (29 mg, 4.1 mmol) were placed in a glass reactor, THF (5 mL) was added under Ar, and the solution was cooled to −78 °C. NH_3 (30 mL) was introduced into the reactor (15 min) and was condensed. The solution was stirred for 45 min at this temperature and gradually warmed to room temperature. NH_3 gas was generated, and Ar gas was introduced into the reactor. After the generation of NH_3 was complete, NH_4Cl (268 mg, 5 mmol) was added slowly. Bu_2SnCl_2 (156 mg, 0.5 mmol) in THF (15 mL)/MeOH (25 mL) was added to the solution, and the solution was stirred for 1 h at room temperature. The solution was then evaporated and the product separated by column chromatography (Wakogel C-300HG, *n*-hexane/$CHCl_3$ = 1:1) to produce **8b** in 23% yield (27 mg): green powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, J = 7.3 Hz, 24H), 1.42−1.51 (m, 16H), 1.67 (t, J = 7.3 Hz, 24H), 1.82−1.91 (m, 32H), 4.86 (bs, 16H); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 82.4; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ 88.2; UV ($CHCl_3$) λ_{max} nm (log ϵ) 766 (5.13); MALDI-TOFMS (*m*/*z*) 2294.38 (M^+).

Debenzylation of 6a and Cyclization of Lithium Octaselenolate with Bu_2SnCl_2. Compound **6a** (63 mg, 0.037 mmol) was similarly treated as described above [lithium (22 mg, 3 mmol) in THF/NH_3, NH_4Cl (162 mg, 3 mmol) and Bu_2SnCl_2 (113 mg, 0.37 mmol)] to produce **8a** in 17% yield (12 mg): green powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, J = 7.3 Hz, 24H), 1.42−1.53 (m, 16H), 1.68 (t, J = 7.3 Hz, 24H), 1.76−1.94 (m, 32H), 4.80 (bs, 16H); ^{119}Sn NMR (76 MHz, $CDCl_3$) δ 177.6; UV ($CHCl_3$) λ_{max} nm (log ϵ) 763 (5.13); MALDI-TOFMS (*m*/*z*) 1919.34 (M^+).

5,6-Dicyano-4,7-diethylbenzo[1,2,3]trithiole (2a). Compound **4a** (296 mg, 0.84 mmol) in THF (20 mL)/MeOH (5 mL) was treated with $CsOH\cdot H_2O$ (582 mg, 3.46 mmol) at room temperature for 2 h. Elemental sulfur (90 mg, 2.8 mmol) was then added, and the solution was stirred for 12 h. After the usual workup, the product was extracted with $CHCl_3$ and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-400HG, *n*-hexane/$CHCl_3$ = 1:1) to produce **2a** in 13% yield (31 mg): orange crystals; mp 169−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, J = 7.6 Hz, 6H), 2.93 (q, J = 7.6 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 13.6, 30.2, 114.2, 114.9, 141.9, 148.0; MS (*m*/*z*) 278 (M^+); IR (KBr) 2227 cm^{-1} (CN); UV ($CHCl_3$) λ_{max} nm (log ϵ) 448 (2.5), 341 (3.5), 299 (4.3), 269 (3.9). Anal. Calcd for $C_{12}H_{10}N_2S_3$: C, 51.77; H, 3.62; N, 10.06. Found: C, 51.99; H, 3.75; N, 9.80.

5,6-Dicyano-4,7-diethylbenzo[1,2,3]triselenole (2b). Compound **4b** (692 mg, 1.08 mmol) in THF (20 mL)/MeOH (10 mL) was treated with MeONa (225 mg, 4.2 mmol) at 60 °C under Ar. Amorphous selenium (410 mg, 5.0 mmol) was then added, and the solution was stirred at 60 °C for 6 h. After the usual workup, the product was extracted with $CHCl_3$ and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-300HG, $CHCl_3$) to produce **2b** in 28% yield (127 mg): dark-red crystals; mp 151−152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, J = 7.6 Hz, 6H), 3.01 (q, J = 7.6 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.0, 33.2, 114.5, 115.2, 145.2, 150.0; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 463.5, 563.5 (J_{Se-Se} = 271 Hz); Anal. Calcd for $C_{12}H_{10}N_2Se_3$: C, 34.39; H, 2.41; N, 6.68. Found: C, 34.66; H, 2.66; N, 6.65.

1,2-Bis(benzylseleno)-4,5-dibromo-3,6-diethylbenzene. Compound **1b** (2.64 g, 5.0 mmol) and K_2CO_3 (1.39 g, 10 mmol) were placed in a glass reactor, and THF (40 mL) and methanol (10 mL) were added under Ar. $NaBH_4$ (0.568 g, 15 mmol) was added slowly, and then benzyl bromide (2.38 mL, 20 mmol) was dropped from syringe. The solution was stirred for 6 h. After the usual workup, the solution was extracted with $CHCl_3$ and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-400, *n*-hexane/$CHCl_3$ = 1:1) to produce 1,2-bis(benzylseleno)-4,5-dibromo-3,6-diethylbenzene in 68% yield (2.17 g): colorless crystals; mp 83−86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (t, J = 7.4 Hz, 6H), 3.22 (q, J = 7.4 Hz, 4H), 4.16 (s, 4H), 7.07−7.13 (m, 4H), 7.15−7.23 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.1, 35.9, 36.5, 127.0, 128.3, 128.8, 129.0, 138.1, 140.1, 148.9; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 390.8; MS (*m*/*z*) 630 (M^+). Anal. Calcd for $C_{22}H_{24}Br_2Se_2$: C, 45.74; H, 3.84. Found: C, 45.76; H, 3.95.

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Supporting Information Available: Crystallographic data of **1a**,**b**, **2a**,**b**, and **6a**; UV−vis spectra of **6a** and **6b**; ^{1}H NMR spectra of **6a**,**b**, and **8a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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