Macromolecules **2002,** *35,* 3539−3543 **3539**

π-Conjugated Poly(dithiafulvene)s and Poly(diselenafulvene)s: Effects of Side Alkyl Chains on Optical, Electrochemical, and Conducting Properties

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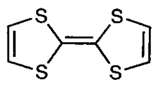
Received November 6, 2001; Revised Manuscript Received February 12, 2002

ABSTRACT: Electron-donating π-conjugated polymers with dithiafulvene moiety (**4**) or with diselenafulvene moiety (**5**) were prepared by cycloaddition polymerization of chalcogenoketenes derived from aromatic diynes (**3**). The solubilities of the polymers strongly depended on the structures. The diselenafulvene polymers (**5**) showed lower solubilities than the corresponding dithiafulvene polymers (**4**). Attachment of long alkyl chains enhanced the solubilties in nonpolar solvents. The structures of the polymers were confirmed by IR and ^{1}H NMR spectra. UV−vis measurements indicated that π-conjugations of the polymers were expanded; in particular, those of polymers containing the long alkoxy side chains were developed effectively. All the polymers showed electron-donating properties in cyclic voltammometry measurements and formed soluble charge-transfer complexes with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ). After the complexation with TCNQ, the conductivities of the polymers increased.

Introduction

Dichalcogenafulvene derivatives have been widely used as electron donor components in the preparation of charge-transfer (CT) complexes and radical ion salts.[1] In the chemistry of the dichalcogenafulvenes, especially the focus has been centered on derivatives of tetrathiafulvalene (TTF, **1**). Since the discoveries of a high electrical conductivity in a chloride salt of TTF[2] and metallic behavior in the charge-transfer (CT) complex with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ),[3] there have been many studies of TTF-based materials that possess unusual electronic and magnetic properties.[4] The recent developments in synthetic TTF chemistry have allowed the ready preparation of large quantities of derivatized TTFs, which are utilized not only for components of the molecular conductor but also for π-rich redox-active supramolecular systems.[5] Meanwhile, replacement of sulfur by chalcogens with more diffuse orbitals (Se, Te) would enhance the interstack interaction to increase dimensionality of the conduction state. The resulting high dimensionality improves the conducting performance of such organic metals at low temperature. For example, cation radicals of tetramethylselenafulvalene (TMTSF, **2**) have been reported to exhibit superconductivity below 5 K due to the Se−Se interaction between the units.[6]



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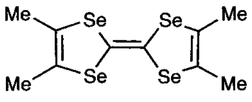

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Hybridization between the dichalcogenafulvene derivatives and π-conjugated polymers is an attraction.[7,8] The association of structural characters and properties may contribute to mutual fertilization by development of new materials of fundamental and technological interest. The conjugated polymers are basically low-dimensional conductors, similar to the dichalcogenafulvene-based CT salts. When intermolecular CT units between the dichalcogenafulvenes and π-acceptors are incorporated into conjugated polymers, electron mobility along the polymer backbone via π-conjugation as well as along the stacking direction via π-orbital overlap would be improved (high dimension of conducting state).[8] Furthermore, inter- and intramolecular Coulombic repulsions between the charged species would be suppressed to enhance the stacking CT formations due to the large number of chalcogene atoms in the π-conjugated dichalcogenafulvene-based polymers.[7a,8]

We have reported[9] on a series of π-conjugated polymer with the dithiafulvene unit, which formed CT complexes with TCNQ. Resulting polymer CT complexes showed highly improved electrical conductivities. In this article, we report on a general synthesis of π-conjugated poly(dichalcogenafulvene)s by cycloaddition polymerizations of chalcogenoketenes. Comparison between the new poly(dithiafulvene)s and poly(diselenafulvene)s is interesting. We also studied effects of the polymer side chains on chemical and physical properties of the poly(dichalcogenafulvene)s.

Results and Discussion

Polymer Synthesis. We employed three monomers (**3a**−**c**) with different side alkyl chains to prepare the poly(dichalcogenafulvene)s (**4**, **5**). Cycloaddition polymerizations of chalcogenoketenes and their alkynechalcogenol tautomer derived from **3** in situ successfully produced the poly(dithiafulvene)s **4** and the poly(diselenafulvene)s **5** (Scheme 1). End-capping by piperidine to convert thioamides or selenoamides resulted in better solubilities of the obtained polymers than those of the polymers without end-capping. Synthetic details of poly(dithiafulvene) **4a** were reported in 1999.[9b] The report showed that molecular weights of the poly(dithiafulvene)s varied with the change of the reaction solvent, and Et$_2$O was the best reaction medium to achieve satisfactory degrees of the polymerization. In present work, Et$_2$O was the most effective solvent to synthesize the poly(dithiafulvene)s **4b** and **4c**, but the poly(disel-

10.1021/ma011939n CCC: $22.00

Scheme 1

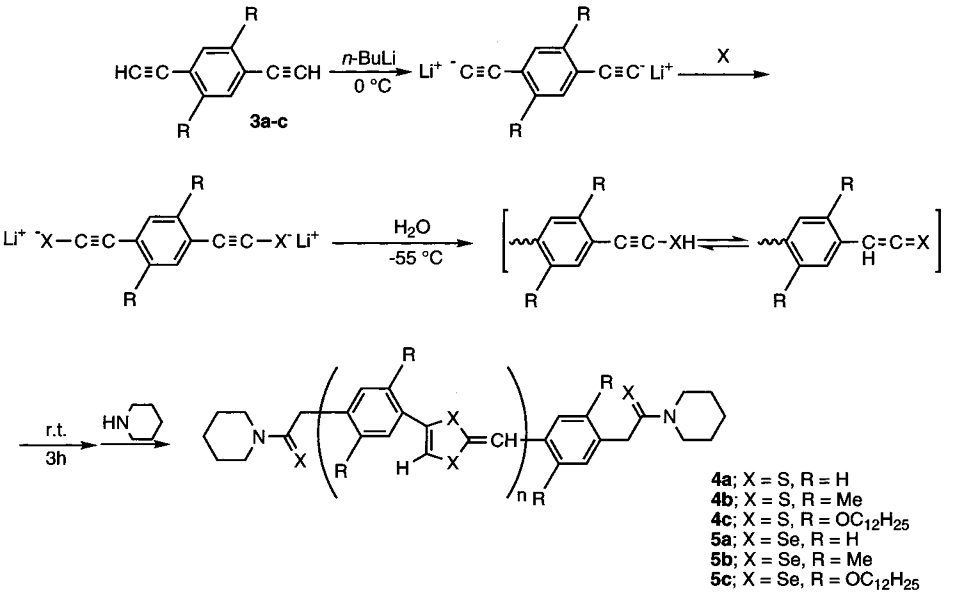


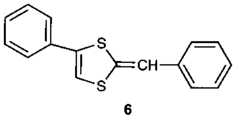
Table 1. Preparation of Poly(dichalcogenafulvene)s

entry	compd	yield (%)	solubility	mol wt (M_n)
1	**4a**	76	DMSO, DMF	6810[a]
2	**4b**	37	DMSO, DMF	3090[a]
3	**4c**	68	$CHCl_3$, CH_2Cl_2, THF	8870
4	**5a**	95	insoluble	
5	**5b**	85	partially soluble in DMSO	2110[a,c]
6	**5c**	98	partially soluble in $CHCl_3$, THF	5220[b,d]

[a] GPC was carried out by using DMSO as an eluent at 50 °C after calibration with standard poly(ethylene glycol). [b] GPC were performed in chloroform at 25 °C by use of polystyrene standard samples. [c] DMSO-soluble part. [d] Chloroform-soluble part.

enafulvene)s **5** could not be obtained in Et_2O; however, in THF polymerization toward **5** underwent smoothly.

Solubilities of the polymers are summarized in Table 1. Similar to **4a**, the poly(dithiafulvene) **4b** was soluble in aprotic polar solvents such as DMSO and DMF. Because of the long alkoxy chains, polymer **4c** showed good solubility in $CHCl_3$, CH_2Cl_2, and THF and was hardly soluble in DMSO and DMF. Solubilities of the poly(diselenafulvene)s were found to be very limited; e.g., polymer **5a** was completely insoluble in any solvent, preventing further investigations of its chemical and physical properties. Despite the long alkoxy substitutions on the phenylene unit, polymers **5b** and **5c** showed partial solubilities in organic solvents. 31% of **5b** was soluble in DMSO, and the $CHCl_3$-soluble part of **5c** was 46%. The polymers obtained in this work were subjected to gel permeation chromatography (GPC) measurement to determine molecular weights (Table 1). In the case of the poly(diselenafulvene)s, the soluble parts of the polymers were examined.



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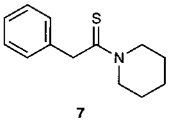

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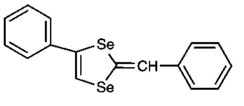

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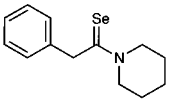

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The structures of the new poly(dithiafulvene)s (**4b**, **4c**) were confirmed by IR and ^1H NMR spectroscopies compared with those of the model compounds reported previously(**6**, **7**).[9b] To support the structures of the poly(diselenafulvene)s, two model compounds (**8**, **9**) were synthesized. 2,6-Bisphenyl-1,4-diselenafulvene (**8**)[10] was used as a model compound for the diselenafulvene unit of **5** and selenoamide (**9**)[10] as a model for the terminal unit of the poly(diselenafulvene)s. In the IR spectrum of **8**, peaks corresponding to the double bonds of the diselenafulvene moiety appeared at 1576 and 1558 cm^{-1}. The IR spectra of the soluble parts as well as insoluble parts of the poly(diselenafulvene)s **5** showed similar peaks between 1550 and 1580 cm^{-1}, suggesting that the structures of both parts of **5** are basically the same containing diselenafulvene moieties in the structures. The model diselenafulvene compound **8** was observed to show less solubility than **6**, and the molecular weights of **5** were lower than those of the corresponding poly(dithiafulvene)s **4**, suggesting that strong Se−Se interactions might induce interunit stackings between the diselenafulvene moieties to give the low solubilities of **5**. The ^1H NMR spectrum of the DMSO-d_6 soluble part of **5b** showed a broad peak corresponding to diselenole ring proton at 7.5 ppm and peaks for the terminal selenoamide moiety at 3.6, 4.3, and 4.4 ppm. In the ^1H NMR spectrum of the $CDCl_3$-soluble part of **5c**, satisfactory peaks attributed to the diselenafulvene protons and the terminal selenoamide moiety were observed.

Optical Properties. The UV−vis absorption of the polymers in the solution is seen in Figure 2. The peaks due to $\pi-\pi^*$ transitions of **4** and the soluble parts of **5** were located at longer wavelengths than those of the corresponding model compounds, indicating efficient π-electron delocalizations in the polymer systems. In the series of the poly(dithiafulvene)s, methyl substitution on benzene ring gave rise to a blue shift from the absorption of **4a** due to a steric distortion of **4b** in CH_3CN. UV−vis measurement of **4c** showed a notable feature of the conjugation. The π-conjugation system of **4c** in $CHCl_3$ was the most effectively expanded among those of the poly(dithiafulvene)s. Each soluble part of the poly(diselenafulvene) (**5b** in CH_3CN, **5c** in $CHCl_3$)

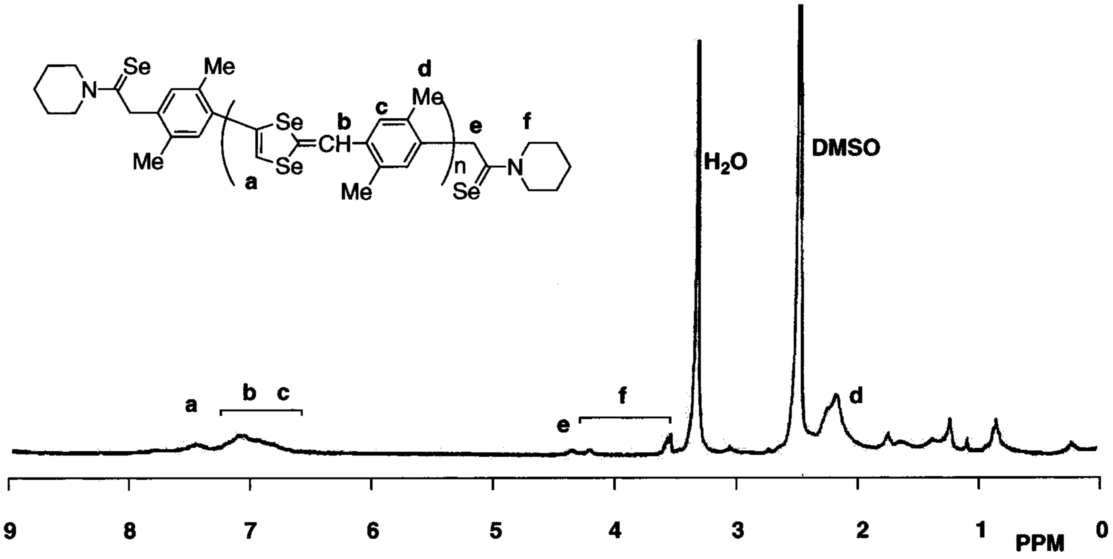

Figure 1. ^{1}H NMR spectrum of the soluble part of **5b** in DMSO-d_6.

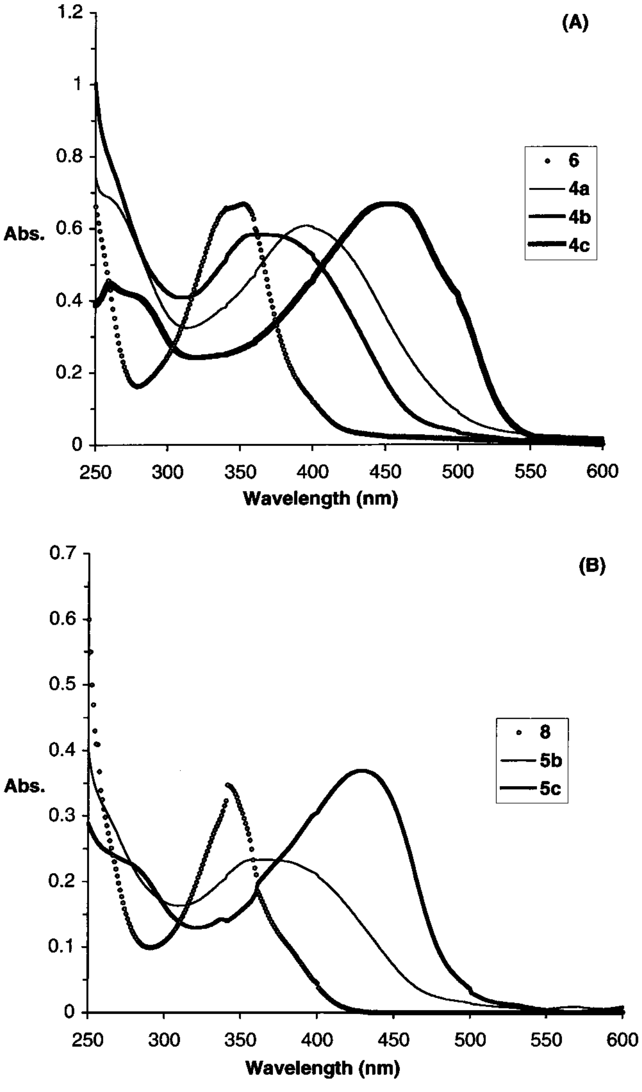

Figure 2. UV–vis absorption spectra of (A) **4a** and **4b** in CH$_3$CN, **4c** and **6** in CHCl$_3$ and (B) the soluble part of **5b** in CH$_3$CN, the soluble part of **5c** and **8** in CHCl$_3$.

had an absorption with a similar peak position to its analogous poly(dithiafulvene). The π-conjugation system of **5c** was also highly developed by the long alkoxy chain.

Table 2. Physical Properties of Poly(dichalcogenafulvene)s

				conductivity[d]	
entry	compd	UV λ_{max} (nm)	oxidation peak (V)[c]	nondoped, S/cm	TCNQ complex, S/cm
1	**4a**	398[a]	0.60	3×10^{-7}	2×10^{-4}
2	**4b**	366[a]	0.55	8×10^{-7}	9×10^{-4}
3	**4c**	451[b]	0.74	$<10^{-7}$	4×10^{-6}
4	**5b**	377[a]	0.59	2×10^{-6}	2×10^{-4}
5	**5c**	429[b]	0.79	1×10^{-7}	4×10^{-6}
6	**6**	358[b]	0.40		
7	**8**	341[b]	0.44		

[a] UV spectra were measured in CH$_3$CN. [b] UV spectra were measured in CHCl$_3$. [c] Cyclic voltamograms were obtained in CH$_3$CN solution containing 0.1 M [NEt$_4$]BF$_4$. Scan rates were 300 mV/s. [d] Electrical conductivities were measured at room temperature by the two-probe technique.

The effective π-conjugations in **4c** and **5c** should be induced by electron-donating effects of the alkoxy groups. Several examples have shown that the introduction of strong electron-donating alkoxy groups significantly reduces the band gaps of poly(thiophene) and poly(thienylene vinylene).[11]

Electrochemical Study. The electrochemical redox behaviors of the donors were studied by cyclic voltammetry (CV) (Table 2). The model compounds **6** and **8** showed single oxidation peaks at 0.40 and 0.44 V vs Ag/Ag$^+$, respectively. The value of the oxidation peak for the dithiafulvene **6** was less positive by 0.04 V than that of **8**, indicating that the electron-donating ability of **6** is slightly stronger than that of **8**. The cast films of the polymers (**4** and **5**) showed irreversible broad oxidation waves between 0.5 and 0.8 V vs Ag/Ag$^+$. UV–vis and CV measurements suggested that the oxidation potential and the π-electron delocalizations of the polymers are correlative. The oxidation potentials of the polymers shifted positively with the development of the π-conjugations and may also be finely tuned by substituents on the benzene ring in the systems of the poly(dichalcogenafulvene)s.

TCNQ Complexes. The poly(dichalcogenafulvene)s formed CT complexes with TCNQ. After adding an excess amount of TCNQ to a polymer solution, it gradually turned to be dark green. The unreacted TCNQ was filtered off, and then the filtrate was evaporated to obtain a dark green powder as a polymer CT complex. The resulting complexes derived from **4a**, **4b**, and **5b** were soluble in acetonitrile, DMSO, DMF, acetone, and MeOH. The CT complexes composed of **4c** or **5c** were soluble in THF, $CHCl_3$, and CH_2Cl_2. The UV−vis absorptions of the polymer CT complexes exhibited λ_{max} at 845, 762, and 745 nm, which were responsible for the anion radical of TCNQ.[12] The conductivities of the polymers were measured at room temperature by the two-probe technique and are summarized in Table 2. After complexation with TCNQ, the conductivities of the polymers increased remarkably. In the case of **4a** and **4b**, the values raised approximately 1000 times higher than those of the uncomplexed polymers. The relatively low conductivities of **4c** and **5c** complexes suggested incomplete complexations with TCNQ in the solid states because of the steric hindrances of the long alkoxy groups.

Conclusion

We presented here the synthesis and properties of the π-conjugated polymers with the electron-donating dichalcogenafulvene units. UV absorption analysis indicated that π-conjugations in **4** and **5** were developed efficiently. In particular, the most effective π-conjugations were achieved in the systems of the polymers attaching the long alkoxy side chains. The polymers acted as good electron donors, similarly to the low molecular weight model compounds. The polymers formed semiconducting CT complexes with TCNQ. Some polymers showed highly improved conductivities (3 orders of magnitude greater than the uncomplexed polymers) upon TCNQ complexation.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried and distilled under N_2. 1,4-Diethynyl-2,5-dimethylbenzene (**3b**)[13] and 1,4-diethynyl-2,5-bis(dodecyloxy)benzene (**3c**)[14] were synthesized according to the literature. Syntheses of the dithiafulvene **6** and the thioamide **7** have been described in a previous paper.[9b]

Measurements. ^1H NMR and IR spectra were recorded on a JEOL JNM-EX270 spectrometer and a Perkin-Elmer 1600 spectrometer, respectively. GPC measurements of **4b** and **5b** were carried out on TSK gel a-3000 by using DMSO as an eluent at 50 °C after calibration with standard poly(ethylene glycol) samples. GPC of **4c** and **5c** were performed with a Shodex K-803 in chloroform at 25 °C by use of polystyrene as standard samples. UV−vis spectra were obtained on a JASCO V-530 spectrophotometer. Cyclic voltammetry was carried out with a BAS CV-50W electrochemical analyzer in CH_3CN solution of 0.1 M $[NEt_4]BF_4$ as a supporting electrolyte. Platinum wire auxiliary electrode and Ag/AgCl RE-5 reference electrode were used in the CV measurements. For the CV of the polymers, thin polymer films were prepared on indium tin oxide (ITO) coated glass electrodes by casting from their solutions. The electrodes were dried under vacuum. For the CV of the model compounds, they were dissolved in the CH_3CN solution containing the supporting electrolyte. A platinum working electrode was used, instead of ITO. Electrical conductivities were measured at room temperature by the two-probe technique using a Keithley 2400 source meter. The polymer films were prepared by dropping of the polymer solutions onto glass plates equipped with platinum electrodes, followed by drying in vacuo.

Polymerization. A typical procedure was as follows. To a solution of a diethynyl compound (0.50 mmol) in a solvent (Et_2O or THF, 4.0 mL), 1.6 M solution of *n*-butyllithium in hexane (0.65 mL, 1.04 mmol) was added at 0 °C. The reaction mixture was kept at 0 °C for 0.5 h, and powder of sulfur or selenium (1.00 mmol) was added. After stirring the mixture for 2 h at 0 °C, water (18 mg) was carefully added at −55 °C. The temperature of the mixture was allowed to rise at room temperature, and the reaction mixture was stirred for 3 h. The mixture was then poured into a large quantity of Et_2O or hexane. The obtained precipitate was washed with water to remove inorganic salts. After drying under reduced pressure, the polymeric compound was obtained.

4b. Yield: 37%. ^1H NMR (DMSO-d_6, ppm): δ 1.2−1.6 (CH_2 of piperidine unit), 2.3 ($-CH_3$ on phenyl moiety), 3.6 ($N-CH_2$ of piperidine unit), 4.2 ($N-CH_2$ of piperidine unit and $-CH_2C(=S)N\langle$), 6.7 (benzylidene and aromatic protons), 7.2 (aromatic and 1,3-dithiole ring protons). IR (KBr, cm^{-1}): 1576, 1550, 1290, 1262.

4c. Yield: 68%. ^1H NMR ($CDCl_3$, ppm): δ 0.9 ($-OC_{11}H_{22}-CH_3$), 1.1−1.6 ($-OC_2H_4-C_9H_{18}-CH_3$ and CH_2 of piperidine unit), 1.8 ($-OCH_2-CH_2-C_{10}H_{21}$), 3.8−4.2 ($-OCH_2-C_{11}H_{23}$ and $N-CH_2$ of piperidine unit), 4.3 ($N-CH_2$ of piperidine unit and $-CH_2C(=S)N\langle$), 6.8 (benzylidene and aromatic protons), 7.0−7.2 (aromatic and 1,3-dithiole ring protons). IR (KBr, cm^{-1}): 1580, 1288, 1262.

5a. Yield: 95%. IR (KBr, cm^{-1}): 1575, 1556.

5b. Yield: 85%. ^1H NMR (DMSO-d_6 soluble part, ppm): δ 1.2−1.5 (CH_2 of piperidine unit), 2.2 ($-CH_3$ on phenyl moiety), 3.6 ($N-CH_2$ of piperidine unit), 4.3 ($N-CH_2$ of piperidine unit), 4.4 ($-CH_2C(=S)N\langle$), 6.7−7.4 (benzylidene and aromatic protons), 7.5 (1,3-diselenole ring proton). IR (KBr, cm^{-1}): 1576, 1553, 1292.

5c. Yield: 68%. ^1H NMR ($CDCl_3$, ppm): δ 0.9 ($-OC_{11}H_{22}-CH_3$), 1.1−1.5 ($-OC_2H_4-C_9H_{18}-CH_3$ and CH_2 of piperidine unit), 1.8 ($-OCH_2-CH_2-C_{10}H_{21}$), 3.8−4.1 ($-OCH_2-C_{11}H_{23}$ and $N-CH_2$ of piperidine unit), 4.2 ($N-CH_2$ of piperidine unit and $-CH_2C(=S)N\langle$), 6.9 (aromatic protons), 7.1 (benzylidene proton), 7.5 (1,3-diselenole ring protons). IR (KBr, cm^{-1}): 1577, 1555, 1291.

Model Reactions. a. 2,6-Bisphenyl-1,4-diselenafulvene (8).[10] A 1.6 M solution of *n*-butyllithium in hexane (0.65 mL, 1.04 mmol) was added to a stirred solution of phenylacetylene (102 mg, 1 mmol) in THF (2 mL), cooled at 0 °C. When the addition was completed, the reaction mixture was stirred at 0 °C for 0.5 h, and powder of selenium (79 mg, 1.00 mmol) was added. After stirring the mixture for an additional 2 h at 0 °C, water (1 mL) was carefully added at −78 °C. The temperature of the mixture was allowed to rise at room temperature, and the two layers were separated. The organic solution was dried with $MgSO_4$, and the solvent was removed, yielding the diselenafulvene **8** (146 mg, 81%). IR (NaCl): 1576, 1558 cm^{-1}. ^1H NMR (270 MHz, DMSO-d_6): δ 7.23−7.48 (m, 11H), 7.85 (s, 1H).

b. 1-(2-Phenyl-1-selenoxoethyl)piperidine (**9**).[10] To a solution of piperidine (2.5 mL, 25 mmol) in Et_2O (1 mL) was added 1.6 M solution in hexane of *n*-butyllithium (1.56 mL, 2.50 mmol) at −30 °C. Phenylacetylene (255 mg, 2.50 mmol) was added to the reaction mixture. The temperature of the mixture was allowed to rise to 80 °C. The powder of selenium (197 mg, 2.5 mmol) was added, the mixture was stirred for 2 h, and then 1 N HCl (5 mL) was added. The brown organic layer was separated, and the aqueous phase was extracted with Et_2O. The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated to give the yellow product (604 mg, 91%). ^1H NMR ($CDCl_3$): δ 1.28 (m, 2H), 1.73 (m, 4H), 3.55 (t, 2H), 4.39 (t, 2H), 4.52 (s, 2H), 7.35 (m, 5H).

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (No. 12650865) from the Ministry of Education, Culture, Sports, Science, and Technology, Government of Japan. T.U. appreciates Research Fellowship of the Japan Society for the Promotion of Science for Young Scientists for financial support.

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MA011939N