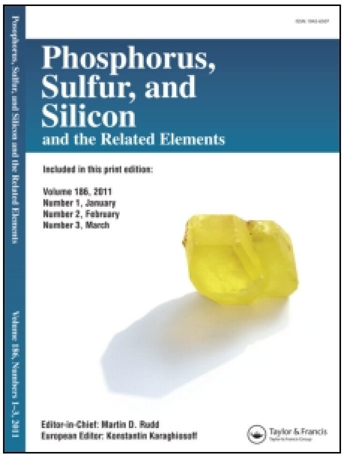

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Preparation, Characterization, and Electrochemical Properties of Selenylfullerenes

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Preparation, Characterization, and Electrochemical Properties of Selenylfullerenes

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The photochemical reaction of C_{60} with selenium-containing bicyclooctanes affords for the first time the selenylfullerenes, which were characterized by mass, UV-vis absorption, and NMR spectroscopic and X-ray crystallographic analyses.

Keywords C_{60}; chalcogen; dibenzocyclooctane; photochemical reaction; selenylfullerene

INTRODUCTION

Chemical functionalization of fullerenes has attracted much attention for application in material science and biochemistry.[1] A chalcogen atom shows its unique characteristics, such as various oxidation states,

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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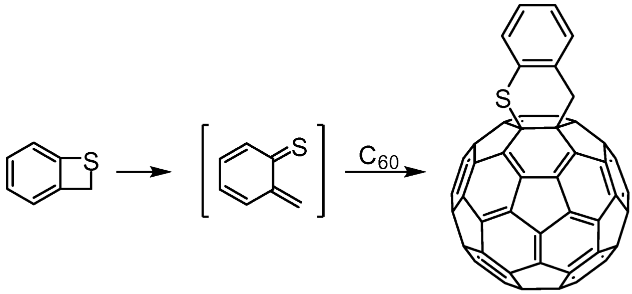
specific reactivity, neighboring-group assistance, and so forth.[2–4] Although chalcogen-containing C_{60} derivatives have been reported,[5–9] only a few derivatives in which a chalcogen atom is directly connected with a fullerene skeleton have been found.[6,7,9] The C_{60} derivatives bonded with a chalcogen atom can be synthesized by 1,3-dipolar cycloaddition,[6] hetero Diels–Alder reaction[7] (Scheme 1), and radical-type reaction[9] of C_{60} with the corresponding oxygen or sulfur compounds. To the best of our knowledge, it is noteworthy that the fullerene derivatives directly bonded with heavier chalcogens such as selenium and tellurium have not been reported yet.



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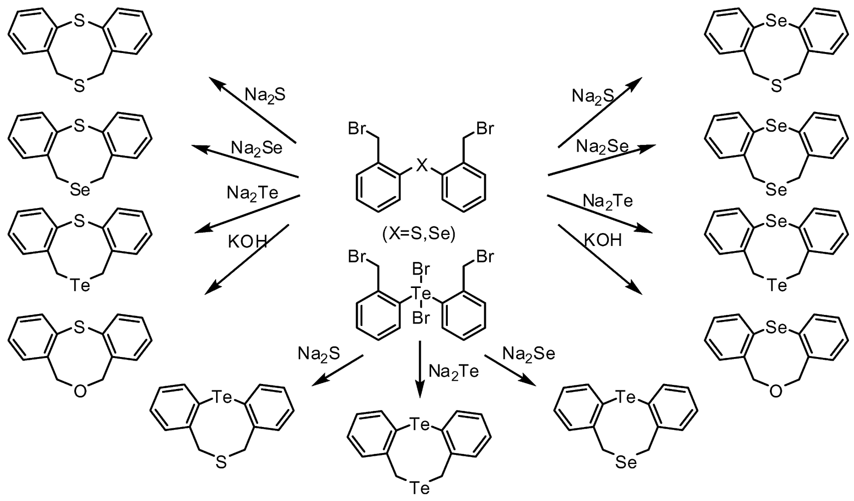
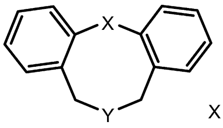
SCHEME 1

Meanwhile, organic chalcogen compounds have been used as a precursor or an initiator of chalcogen radical and carbon radical, which reacts with a C=C double bond to afford the addition product.[3,4] In view of these reactions, chalcogen-containing dibenzo[*b*, *g*]cyclooctane (**1**) plays an important role.[2] A variety of chalcogen species can be easily incorporated into the 1- and 5-position of a cyclooctane skeleton (Scheme 2). We have utilized the chalcogen-containing dibenzo[*b*, *g*]cyclooctane as a reactant to synthesize the corresponding chalcogenylfullerene.[7] In order to obtain a selenylfullerene, we prepared two kinds of selenium-containing dibenzo[*b*, *g*]cyclooctanes, dibenzo[*b*, *g*][1,5]diselenocin (**1a**)[10] and dibenzo[b,g][1,5]oxaselenacin (**1b**),[11] and allowed them to react with C_{60}. Herein we demonstrate for the first time the photochemical reaction of C_{60} with Se-containing dibenzo[*b*, *g*]cyclooctanes to result in the formation of selenylfullerene derivatives (**3** and **4**) (Scheme 3). Their structures and redox properties were also well characterized.



Compound 1



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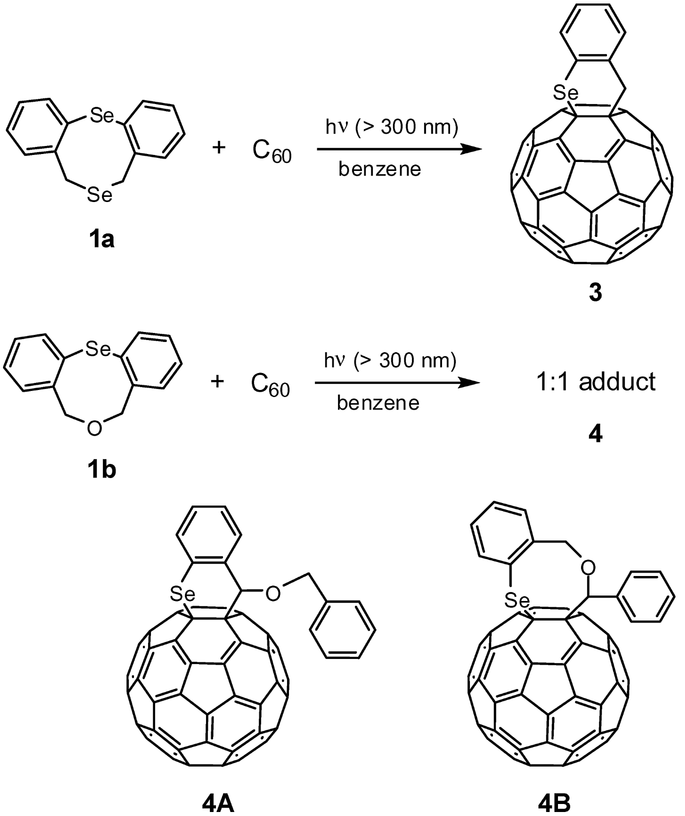
SCHEME 2

RESULTS AND DISCUSSION

The irradiation of a benzene solution of an equivalent amount (5.6×10^{-4} M) of C_{60} and **1a** in a sealed Pyrex tube with a high-pressure mercury arc lamp (cutoff $<$ 300 nm) for 2 h at room temperature resulted in the formation of the selenylfullerene derivative **3** in 30% yield (Scheme 3). Derivative **3** was easily isolated from the reaction mixture by preparative HPLC using a Buckyprep column (Nacalai Tesque, Inc.) (Figure 1). The color of the reaction mixture changed from purple to brownish-red. Meanwhile, no change was observed upon photoirradiation with a halogen-tungsten lamp using a filter solution (cutoff $<$ 400 nm) for 3 h. This suggests that the photochemical reaction may proceed via the excitation of **1a**, not that of C_{60}.[12]

The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of **3** displays a molecular ion peak at m/z 890, corresponding to the molecular formula of $C_{67}H_6Se$ as well



SCHEME 3

as one for C_{60} at *m/z* 720 due to the loss of the selenium-containing *o*-quinodimethane moiety. An isotopic pattern of the observed peak was also in good agreement with that of the calculated (Figure 2). The visible absorption spectrum of **3** shows a shoulder-like absorption maximum at 450 nm, which is characterized as the result of 6,6-addition on C_{60} (Figure 3).[13]

The ^{1}H and ^{13}C-NMR spectra of **3** clearly displays the proton signals on the 1,2-substituted phenyl ring at 6.86 (2H), 7.04 (1H), and 7.31 (1H) ppm and on the isolated methylene group at 3.91 (1H, d, $J = 13$ Hz) and 4.41 (1H, d, $J = 13$ Hz) ppm, and also the carbon signal of the methylene group at 54.92 ppm (Figures 4 and 5). These data are very similar to the sulfur analogue **2** reported by Ohno and coworkers.[7] The ^{13}C-NMR spectrum also shows two quaternary carbon peaks corresponding to the sp^3 carbon signals for the C_{60} skeleton at 66.30 and 69.48 ppm, and

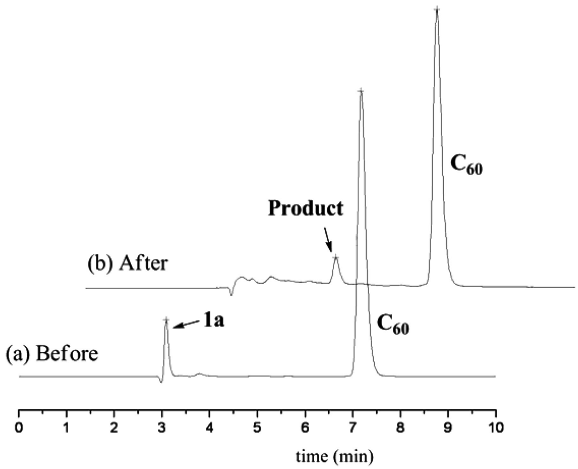


FIGURE 1 HPLC profiles of the reaction mixture of **1a** with C_{60} (a: before irradiation, b: after irradiation for 120 min); toluene eluent, 1.0 mL/min, Buckyprep column ϕ 4.6 mm × 2.5 mm, 284 nm UV detection.

the sp^2 carbon signals [64 carbons (8 signals overlapped)] for the C_{60} cage in the range of 130–156 ppm assignable for a benzene ring (6C) and C_{60} (58C). If **3** has C_s symmetry with the plane passing through the 6,6-junction on C_{60}, the sp^2 carbon signals should be 36 including

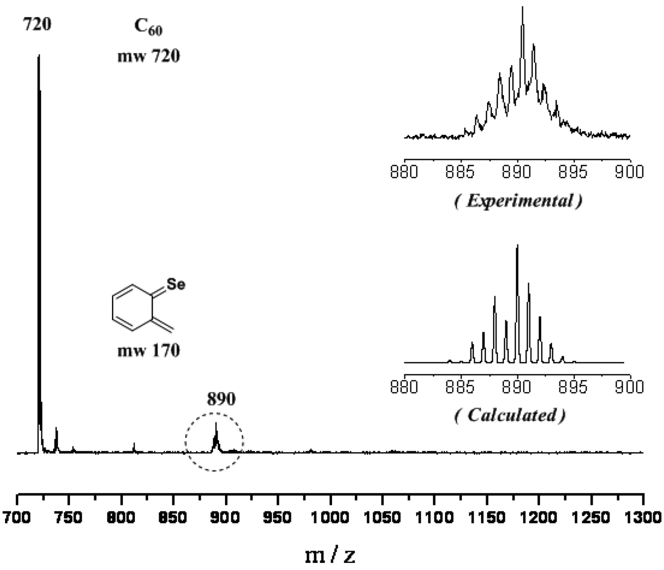


FIGURE 2 MALDI-TOF-MS spectra of **3**, matrix: 1,1,4,4-tetraphenylbutadiene.

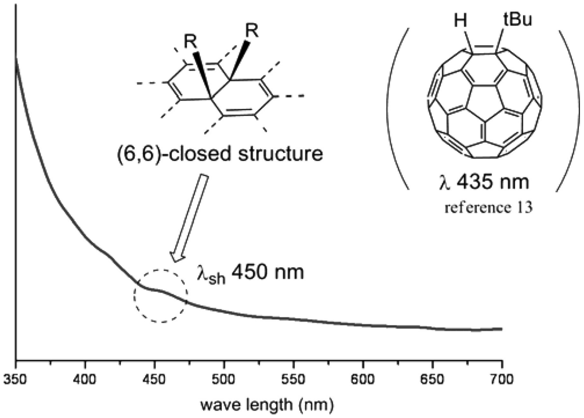


FIGURE 3 UV-vis absorption spectrum of **3** in benzene.

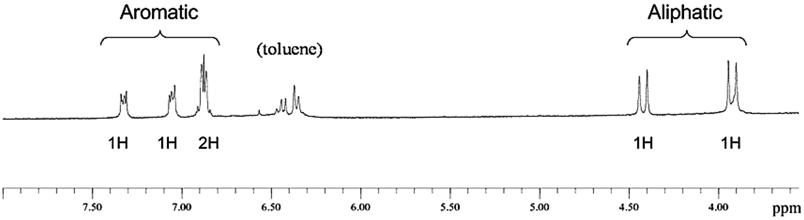


FIGURE 4 ^{1}H-NMR spectrum of **3**, 300 MHz, acetone-d_6 capillary in CS_2.

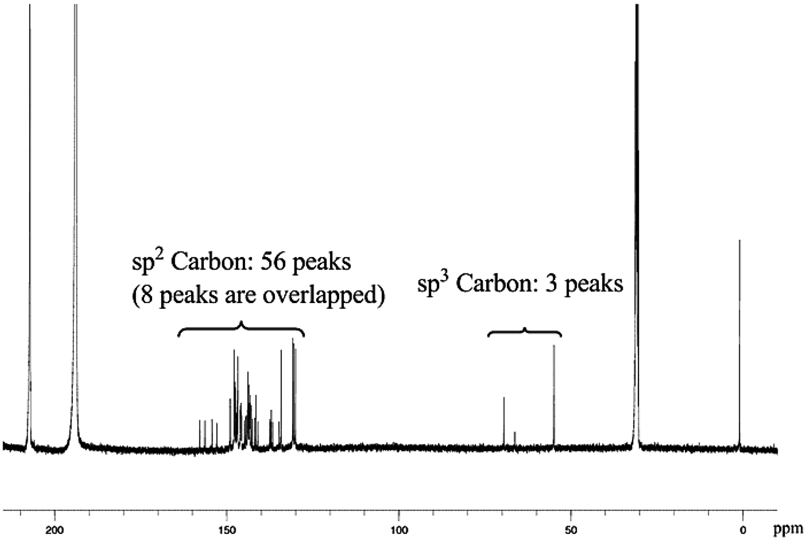


FIGURE 5 ^{13}C-NMR spectrum of **3**, 125 MHz, acetone-d_6 capillary in CS_2.

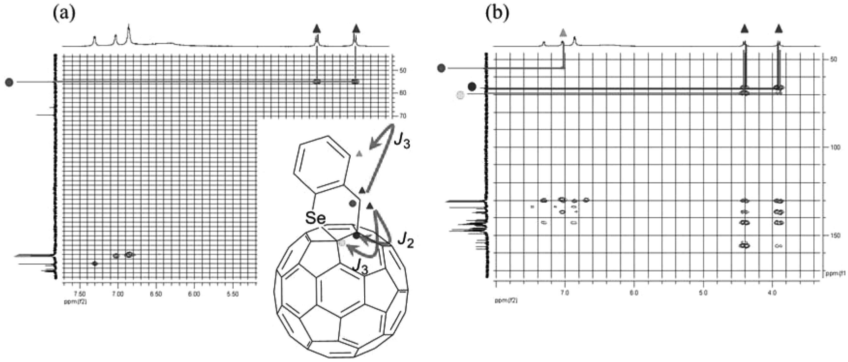


FIGURE 6 HMQC (a) and HMBC (b) spectra of **3**, 500 MHz, acetone-d_6 capillary in CS_2.

the phenyl carbons. The ^{13}C-NMR spectrum reveals that **3** has two conformers with C_1 symmetry inversing slower than NMR time scale, which is also observed in the case of **2**.[7]

In order to confirm the structure of **3**, the 2D NMR measurement was accomplished. The long-range C—H correlation between the phenyl proton and the methylene carbon, and also between the methylene protons and two sp^3 carbons of C_{60}, were observed (Figure 6). ^{77}Se-NMR spectrum of **3** shows a singlet signal at 580 ppm (Me_2Se used as external standard). These results confirm the structure of **3** as shown in Scheme 3.

To confirm the existence of two conformers in **3**, a variable temperature (VT) ^{1}H-NMR measurement was carried out by varying temperatures from 20 °C to 120 °C at intervals of 10°C in ODCB-d_6 (Figure 7). Two doublet signals of the methylene protons (δ 3.91 and 4.41) were coalesced at 70 °C, and one broad signal (δ 4.16) for these protons appeared at 100–120°C. The corresponding $\Delta G^\ddagger$ was calculated at 16.2 kcal/mol, which is the same value of **2**.[7]

This is the first fullerene derivative with the selenium atom directly bonded to the C_{60} cage. We also assume that the reaction proceeds via a formation of the selenium-containing *o*-quinodimethane intermediate followed by the Diels–Alder cycloaddition (Scheme 4).

The photochemical reaction of C_{60} with **1b** was also conducted in the same way for **1a** (Scheme 3), resulting in the formation of **4** in 53% yield.**4** was isolated from the reaction mixture by preparative HPLC (Figure 8). Irradiation at over 400 nm gave no product, similar to the reaction of **1a** with C_{60}.[12]

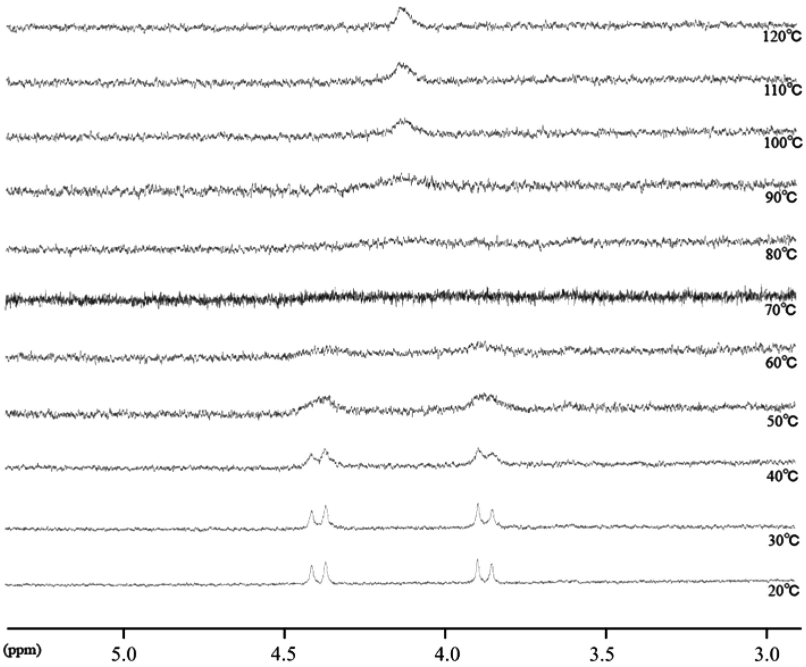
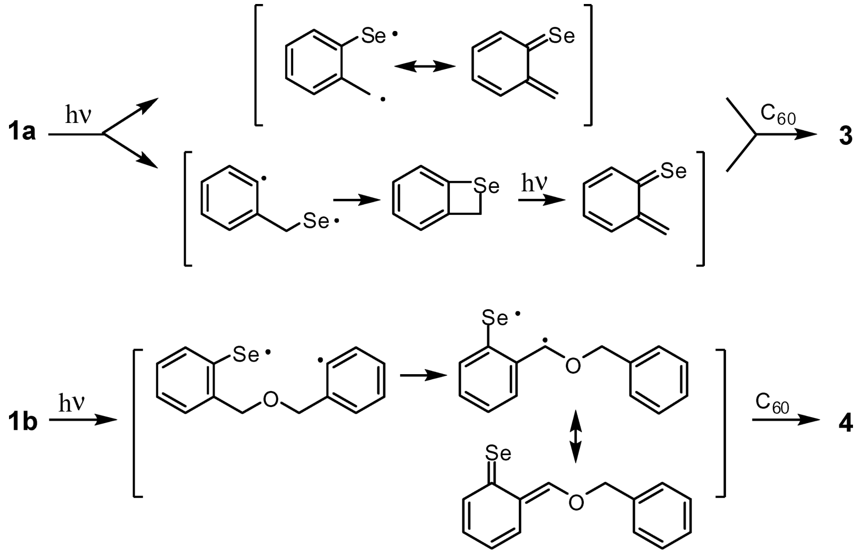


FIGURE 7 VT ^{1}H-NMR spectra of **3** (20–120°C) in ODCB-d_4, 300 MHz.



SCHEME 4

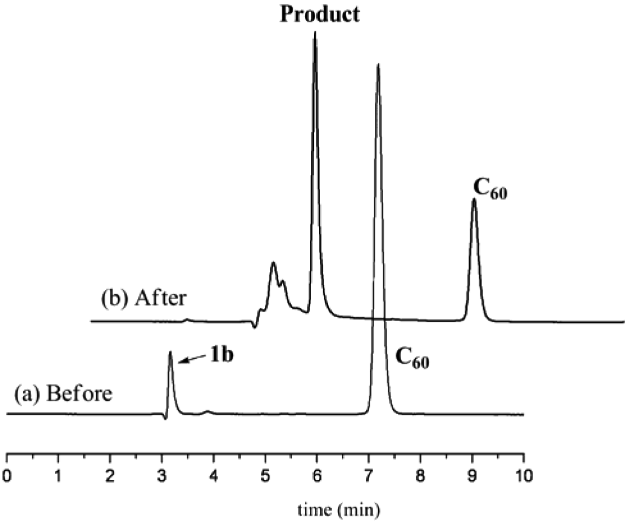


FIGURE 8 HPLC profiles of the reaction mixture of **1b** with C_{60} (a: before irradiation, b: after irradiation for 120 min); toluene eluent, 1.0 mL/min, Buckyprep column ϕ 4.6 mm × 2.5 mm, 284 nm UV detection.

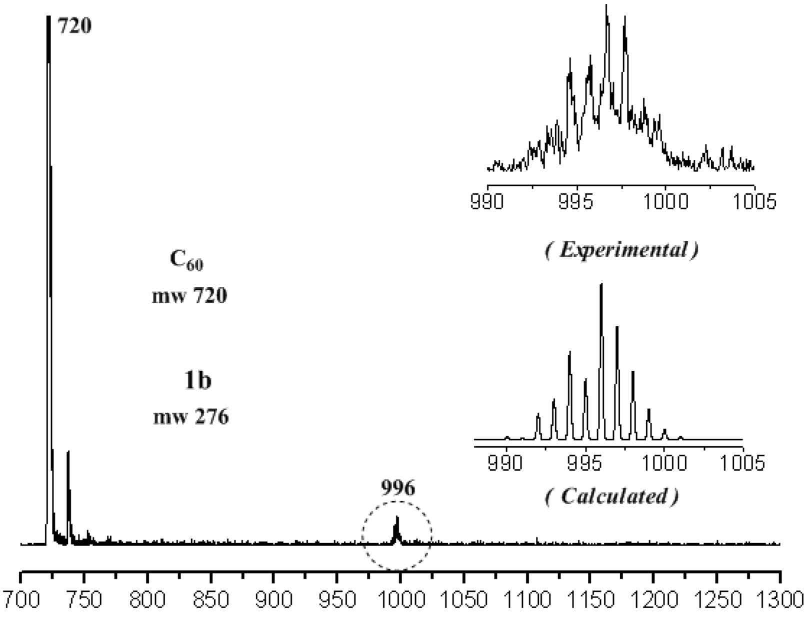


FIGURE 9 MALDI-TOF-MS spectra of **4**, matrix: 1,1,4,4-tetraphenylbutadiene.

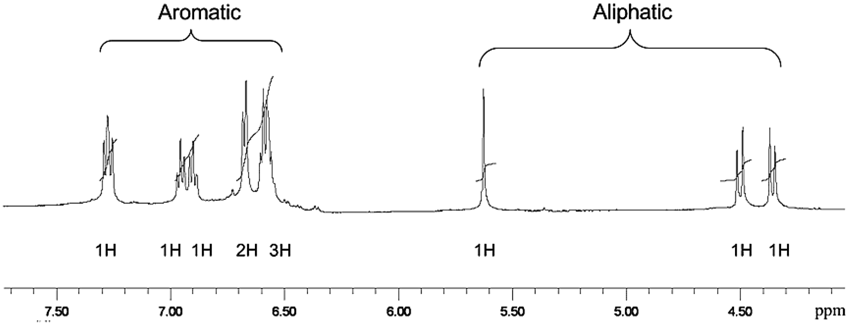


FIGURE 10 ^{1}H-NMR spectrum of **4**, 500 MHz, acetone-d_6 capillary in CS_2.

The MALDI-TOF mass spectrum of **4** shows a molecular ion peak at *m/z* 996 corresponding to $C_{74}H_{12}OSe$ and one for C_{60} due to the loss of the cyclooctane moiety (Figure 9). The absorption maximum at 450 nm in the visible absorption spectrum also suggests the 6,6-addition

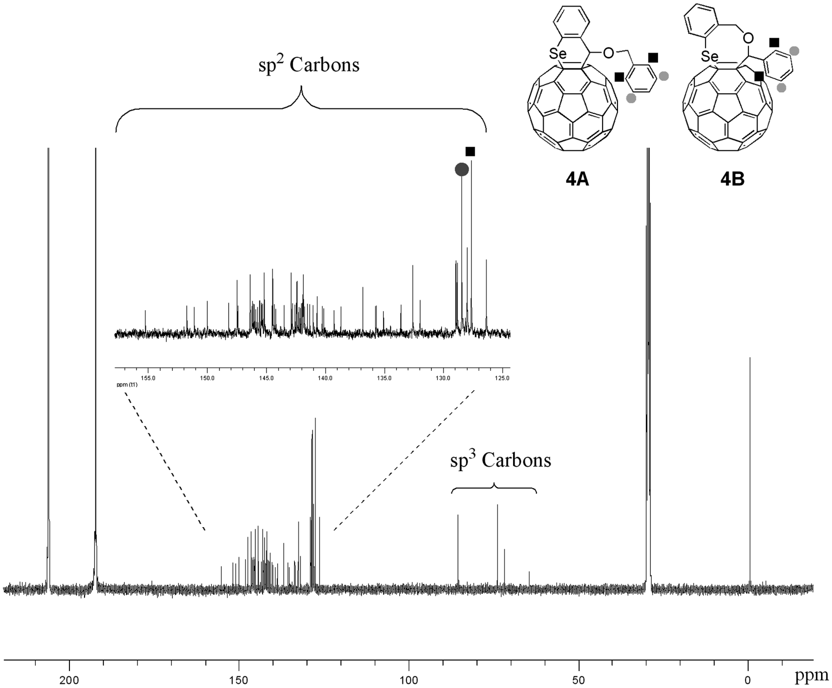


FIGURE 11 ^{13}C-NMR spectrum of **4**, 125 MHz, acetone-d_6 capillary in CS_2.

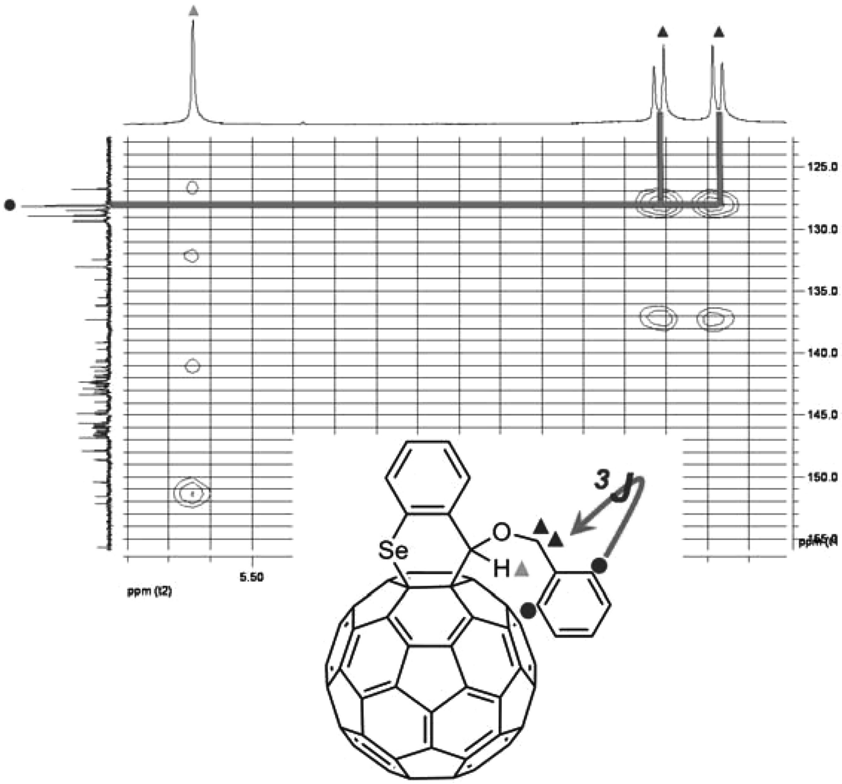


FIGURE 12 HMBC spectrum of **4**, 500 MHz, acetone-d_6 capillary in CS_2.

on C_{60}.[13] The ^{1}H and ^{13}C NMR spectra of **4** displays two methylene proton signals at 4.36 (1H, d, $J = 12$ Hz) and 4.50 (1H, d, $J = 12$ Hz) and the carbon at 73.88 ppm, and the methine proton signal at 5.62 (1H, s) ppm and the carbon signal at 85.49 ppm adjacent to the oxygen atom, and also two phenyl groups; i.e., one is mono-substituted and another is 1,2-substituted (Figures 10 and 11). In addition, the ^{13}C-NMR spectrum of **4** shows 53 peaks due to the overlapping of five peaks in the sp^2 carbon signals for the C_{60} skeleton in the range of 156–126 ppm and two quaternary carbon signals at 64.52 and 72.96 ppm for the C_{60} cage. ^{77}Se-NMR spectrum of **4** shows a signal at 550 ppm. These results suggest that the structure of **A** or **B** may be conceivable for **4**. The 2D HMBC spectrum displays the long-range correlation peaks between the methylene proton and the *ortho*-carbon in the phenyl

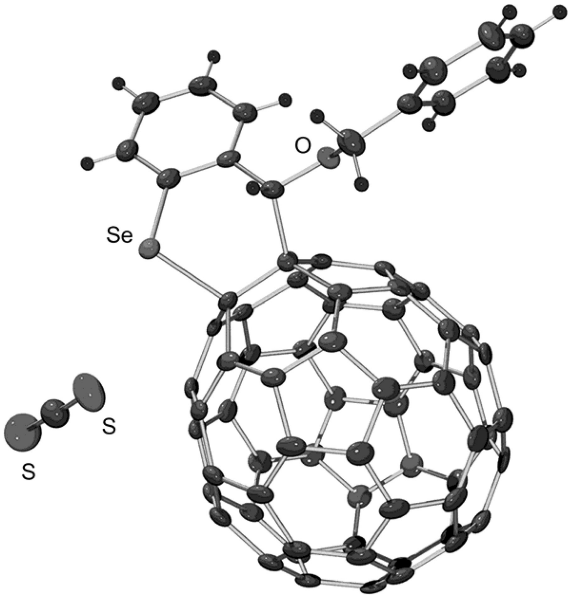


FIGURE 13 ORTEP drawing of $C_{60}SeCHC_6H_4OCH_2C_6H_5$ (**4**) + CS_2 at 100 K. Thermal ellipsoids are shown at 50% probability. CS_2 molecules are included as solvent.

group, between the methylene proton and the methine carbon, and also between the methine proton and the sp^3 carbons on the C_{60} cage (Figure 12). From these results, the structure of **A** may be concluded to be **4**.

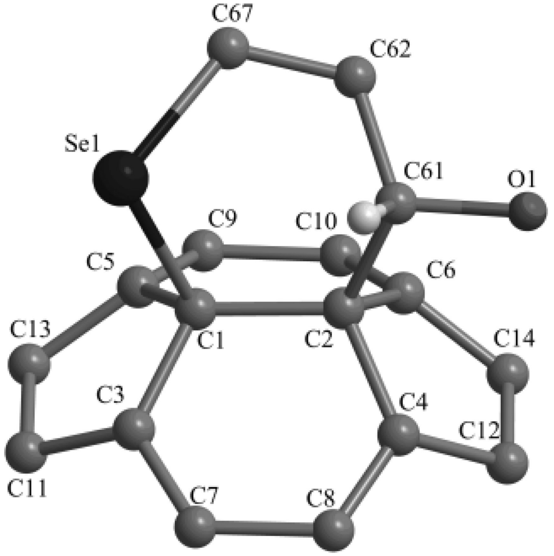
Finally, the X-ray crystallographic analysis of **4** unambiguously reveals the molecular structure of **A** for **4** (Figure 13). The selected bond lengths and dihedral angles around the addition site of a selenium atom are shown in Table I.

On the basis of these observations, the formation of the 1:1 adduct (**4**) of C_{60} and **1b** has been shown. It may be also considered that the reaction proceeds via a cleavage of the C-Se bond followed by a hydrogen abstraction of the phenyl radical once formed to afford **4** (Scheme 4).

In order to know the limit and scope of usefulness of dibenzo[*b*, *g*][1,5]dichalcogenides as a chalcogenation reagent to C_{60}, we carried out the photoreaction of C_{60} with other dibenzodichalcogenides **1c** and **1d**, which contain both selenium and sulfur atom, as well as **1e**, which contains only sulfur (Scheme 5). The reaction with **1c** afforded **2** together with **3** in the ratio of 2:1 (conversion yields of

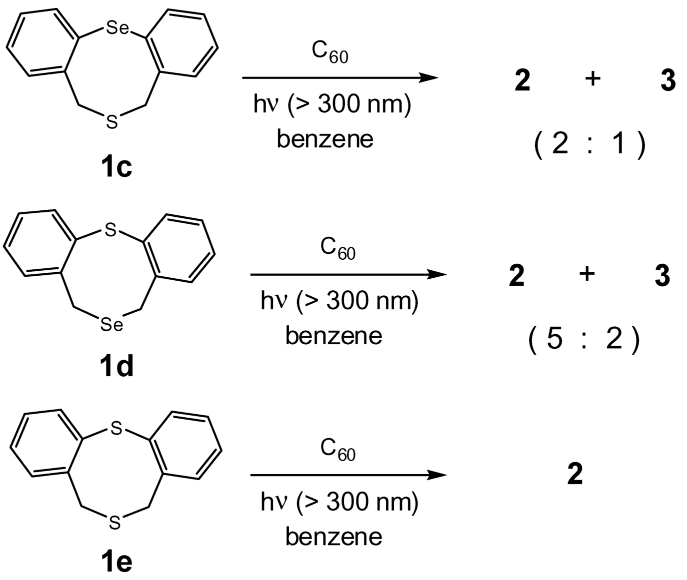
TABLE I Selected Bond Lengths (Å) and Dihedral Angles (°), and a View of $C_{60}SeCHC_6H_4OCH_2C_6H_5$ (4) in the Vicinity of the Addend

Bond length (Å)		Dihedral angles (°)	
Se1-C1	2.041	Se1-C1-C2-C4	122.7
Se1-C67	1.904	Se1-C1-C2-C6	125.7
C1-C2	1.599	Se1-C1-C5-C9	115.7
C5-C9	1.377	Se1-C1-C5-C13	93.0
C3-C7	1.376	Se1-C1-C3-C7	113.9
		Se1-C1-C3-C11	94.2



2 and **3** are 41% and 20%, respectively), and the reaction with **1d** also afforded **2** and **3** in the ratio of 5:2 (40% and 16%). **1e** reacted with C_{60} to afford **2** in a low yield (11%). These reactions are assumed to proceed in a similar manner with those of **1a** via a formation of both selenium and sulfur-containing *o*-quinodimethane intermediates.

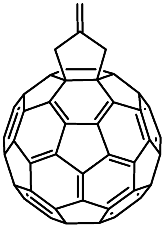
The redox potentials of **3** and **4** were characterized by cyclic (CV) and differential pulse voltammetry (DPV) measurements in *o*-dichlorobenzene using $(n\text{-Bu})_4NPF_6$ as a supporting electrolyte. The redox potentials of **3** and **4** are summarized in Table II, together with those of C_{60} and other fullerene adducts **5**,[14] **6**,[15] and **7**[12] as references. These results reveal that the introduction of a selenyl group on the C_{60} cage lowers the oxidation potential of C_{60}.



SCHEME 5

TABLE II Redox Potentials (V *vs* Fc/Fc$^+$) of Selenylfullerenes 3 and 4, C$_{60}$, and Other Fullerene Adducts

Compounds	$^{ox}E_1$	$^{red}E_1$	$^{red}E_2$	$^{red}E_3$
3	+1.06	−1.20	−1.49	−1.64
4	+1.05	−1.18	−1.45	−1.62
C$_{60}$	+1.26	−1.12	−1.50	−1.95
5	+1.03	−1.23	−1.58	−2.11
6	+1.17	−1.13	−1.50	−1.99
7	+0.60	−1.29	−1.67	−2.18



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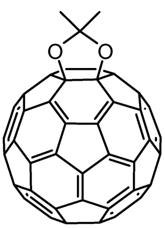

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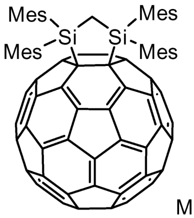

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Mes = mesityl

CONCLUSION

We have for the first time succeeded in the syntheses of the selenylfullerenes, **3** and **4**, by the photochemical reaction of C_{60} with selenium-containing dibenzo[*b*, *g*]cyclooctanes, **1a** and **1b**, and characterized their structures and electronic properties. Selenylfullerene **3** can be formed by the hetero Diels–Alder reaction of C_{60} with the selenyl diene intermediate derived from a C-Se bond cleavage in **1a**, similar to the case of the sulfur-analogue. The photochemical reaction with dibenzo[*b*, *g*][1,5]oxaselenacin (**1b**), however, afforded the unexpected and unique compound **4**, and its structure was determined by X-ray crystallographic analysis. The reaction mechanisms have also been presented in Scheme 4. Successful chemical functionalization of the fullerene with a chalcogen atom may promise application of the derivatized fullerene in material science and biochemistry.

EXPERIMENTAL

General Procedure

Benzene was distilled over benzophenone sodium ketyl under argon atmosphere prior to use in the reactions. HPLC isolation was performed on a LC-908 (Japan Analytical Industry Co., Ltd.). Toluene was used as the eluent. Mass spectrometry was performed on a Bruker BIFLEX III in negative mode with 1,1,4,4-tetraphenylbutadiene as matrix. The UV-vis spectra were measured in benzene solution by using a SHIMADZU UV-3150 spectrophotometer. NMR spectra were obtained with Bruker AVANCE 300 and AVANCE 500. The ^{1}H and ^{13}C shifts were calibrated with TMS as an internal reference ($\delta = 0.0$), and the ^{77}Se shifts were calibrated with Me_2Se as an external reference ($\delta = 0.0$). Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) in ODCB were recorded on a BAS 50W electrochemical analyzer. A conventional three-electrode cell for CV and DPV measurements consists of platinum working electrode, a platinum counter electrode, and a saturated calomel reference electrode (SCE). $(n\text{-Bu})_4NPF_6$ was used as supporting electrolyte. All potentials were recorded against SCE reference electrode and corrected against Fc/Fc^+ . DPV and CV were measured at a scan rate of 10$\sim$ 30 mVs^{-1} and 100 mVs^{-1}, respectively.

Dibenzo[*b,g*][1,5]cyclooctane Dichalcogenides (1a,[10] 1b,[11] 1c,[16] 1d,[16] 1e[17])

Those compounds were synthesized by using the procedures described in the references.

Photoreaction of C_{60} with Dibenzo[*b,g*][1,5]cyclooctane Dichalcogenides

An equivalent amount of C_{60} (10.0 mg, 5.6×10^{-4} M) and dibenzo[b, g][1,5]cyclooctane dichalcogenides (5.6×10^{-4} M) in dry benzene was placed in a ϕ 20 mm PYREX tube, degassed by freeze-thaw cycles under reduced pressure, and then irradiated by a high-pressure mercury lamp (>300 nm) at 20°C for 2 h. The reaction mixture was analyzed with HPLC; column; Buckyprep ϕ 4.6 × 250 mm; eluent, toluene; flow rate, 1.0 mL/min; temperature, 40 °C; detector, UV 284 nm. The product was purified by HPLC; column; Buckyprep ϕ 20 × 250 mm; eluent, toluene; flow rate, 9.9 mL/min.

Control Experiment of the Photoreaction of C_{60} with Dibenzo[*b,g*][1,5]cyclooctane Dichalcogenides

An equivalent amount of C_{60} (2.0 mg, 5.6×10^{-4} M) and dibenzo[b, g][1,5]cyclooctane dichalcogenides (5.6×10^{-4} M) in dry benzene was placed in a ϕ 5 mm PYREX tube, degassed by freeze-thaw cycles under reduced pressure, and then irradiated by a halogen-tungsten lamp using a filter solution (cut-off < 400 nm, prepared from $NaNO_2$ 30 g, 25% NH_3 aq., H_2O 1L) at 20 °C for 3 h. The reaction mixture was analyzed with HPLC; column, Buckyprep ϕ 4.6 × 250 mm; eluent, toluene; flow rate, 1.0 mL/min; temperature, 40 °C; detector, UV 284 nm.

Compound 3

^{1}H-NMR (500 MHz, acetone-d_6 capillary in CS_2) δ 3.91, 4.41 (ABq, each 1H, $J = 13$ Hz, CH_2), 6.86, 7.04, and 7.31 (2H, 1H, and 1H, respectively, C_6H_4). ^{13}C-NMR (125 MHz, acetone-d_6 capillary in CS_2) δ 54.92, 66.30, 69.48, 130.05, 130.54, 130.78, 134.20, 134.81, 136.63, 137.07, 137.22, 137.49, 140.97, 141.53 (2C), 141.87, 142.59, 142.87, 142.88, 143.17 (2C), 143.22, 143.26, 143.30, 143.66, 143.37, 143.43, 143.59 (2C), 143.65, 143.78, 143.84 (2C), 143.85, 143.98, 144.32, 144.47, 144.83, 145.68, 145.76, 145.87, 145.93, 145.96, 146.01, 146.10, 146.73, 146.74 (2C), 146.79, 146.81, 146.86, 146.96, 147.12, 147.22, 147.42 (2C), 147.64 (2C), 147.66, 147.81 (2C), 148.98, 148.99, 152.90, 154.27, 156.33, 157.82. ^{77}Se-NMR (57.2 MHz, acetone-d_6 capillary in CS_2) δ 80.0 (relative to Me_2Se). MALDI–TOF MS (m/z) 890 (M^-). UV-vis absorption λ_{sh} 450 nm.

Compound 4

^{1}H-NMR (500 MHz, acetone-d_6 capillary in CS_2) δ 4.36, 4.50 (ABq, each 1H, $J = 12$ Hz, CH_2), 5.62 (s, 1H, CH), 6.58 (m, 3H, ArH), 6.67 (m, 2H, ArH), 6.90 (t, $J = 8$ Hz, 1H, ArH), 6.94 (t, $J = 8$ Hz, 1H, ArH), 7.26 (t, $J = 8$ Hz, 2H, ArH). ^{13}C-NMR (125 MHz, acetone-d_6 capillary in CS_2) δ 64.52, 72.96, 73.88, 85.49, 126.37, 127.65 (2C), 127.99, 128.46 (2C), 128.82, 128.96, 131.97, 132.61, 133.60, 135.08, 135.68, 135.75, 136.85, 138.71, 139.28, 140.14, 140.29, 140.70, 141.03, 141.33, 141.52, 141.75, 141.85, 141.89 (2C), 141.93, 141.94, 142.04, 142.15, 142.25, 142.42 (2C), 142.46, 142.58, 142.79, 142.89 (2C), 142.91, 143.51, 144.19, 144.33, 144.46 (2C), 144.47, 144.54, 145.18, 145.19, 145.32, 145.39, 145.44, 145.57, 145.60, 145.74, 145.90, 146.01, 146.11, 146.19, 146.22, 146.39 (2C), 146.40, 147.40, 147.49, 148.19, 150.00, 151.13, 151.74, 155.25. ^{77}Se-NMR (57.2 MHz, acetone-d_6 capillary in CS_2) δ 549.9 (relative to Me_2Se). MALDI–TOF MS (*m/z*) 996 (M^-), UV-vis absorption λ_{sh} 450 nm.

Crystallization of 4

Black crystal of **4** was obtained by slow evaporation of a solution of **4** in CS_2 at 0 °C.

Crystal Data for 4

$C_{75}H_{12}OS_2Se$, FW = 1072.00, black crystals, 0.20 × 0.20 × 0.15 mm^3, triclinic, P-1 (#2), a = 10.0056(6) Å, b = 21.4859(18) Å, c = 9.9009(7) Å, $\alpha = 101.741(3)^\circ$, $\beta = 102.084(2)^\circ$, $\gamma = 82.923(3)^\circ$, V = 2030.5(3) Å^3, Z = 2, Dc = 1.753 Mg/m^3, T = 100 K, 17691 reflections, 8081 unique reflections, R1 = 0.0633, wR2 = 0.1911, GOF = 1.055. The maximum and minimum residual electron density is equal to 1.51 and –0.98 eÅ^{-3}. CCDC No.672026 contains the supplementary crystallographic data for this article. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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