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Synthesis of selenylfullerene with selenium-containing dibenzo[*b*,*g*]cyclooctane moiety

Tsukasa Nakahodo[a], Kensaku Takahashi[b], Midori O. Ishitsuka[b], Takahiro Tsuchiya[b], Yutaka Maeda[c,d], Hisashi Fujihara[a], Shigeru Nagase[e], Takeshi Akasaka[b,*]

[a] *Department of Applied Chemistry, Kinki University, Kowakae, Higashi-Osaka 577-8502, Japan*
[b] *Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan*
[c] *Department of Chemistry, Tokyo Gakugei University, Koganei, Tokyo 184-8501, Japan*
[d] *PRESTO, Japan Science and Technology Agency, Tokyo 102-0075, Japan*
[e] *Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan*

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Abstract

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

Keywords: Selenylfullerene; Chalcogen; Dibenzocyclooctane; Photochemical reaction; C_{60}

Chemical functionalization of fullerenes has attracted much attention for application in material science and biochemistry.[1] A chalcogen atom shows its unique characters such as various oxidation states, specific reactivity, neighboring-group assistance, and so forth.[2–4] Although chalcogen-containing C_{60} derivatives were reported so far,[5–9] only few derivatives in which a chalcogen atom is directly connected with a fullerene skeleton has 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] 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.

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 plays an important role.[2] A variety of chalcogen species can be easily incorporated into 1- and 5-positions of a cyclooctane skeleton. We have utilized the chalcogen-containing dibenzo[*b*,*g*]cyclooctane as a reactant to synthesize the corresponding chalcogenylfullerene.[7] 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 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 (Scheme 1). Their structures and redox properties were also well characterized.

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 **2** in 30% yield (Scheme 1).[12] The derivative **2** was easily isolated from the reaction

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[*] Corresponding author. Tel./fax: +81 29 853 6409.
E-mail address: akasaka@tara.tsukuba.ac.jp (T. Akasaka).

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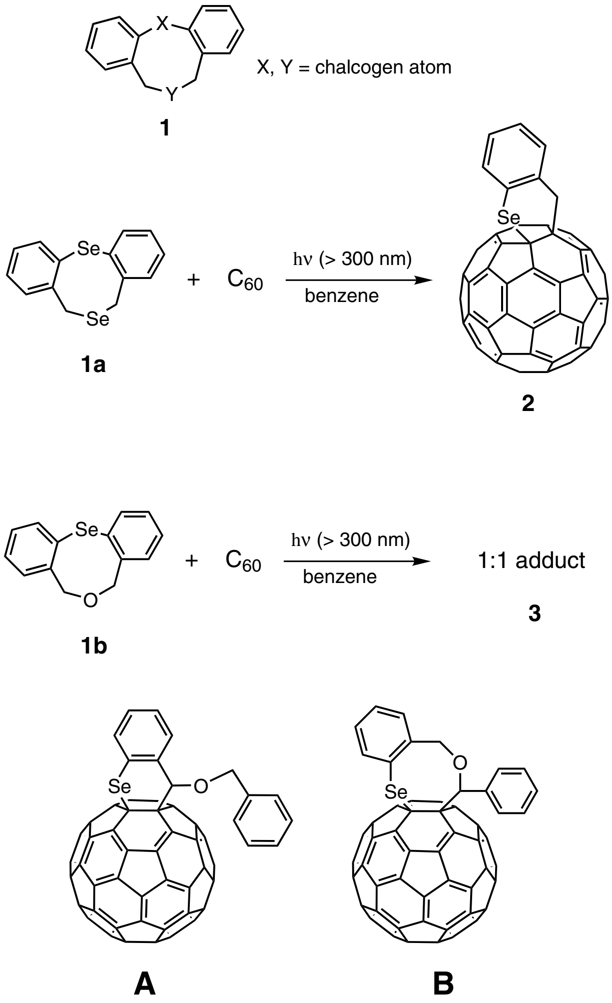


Scheme 1.

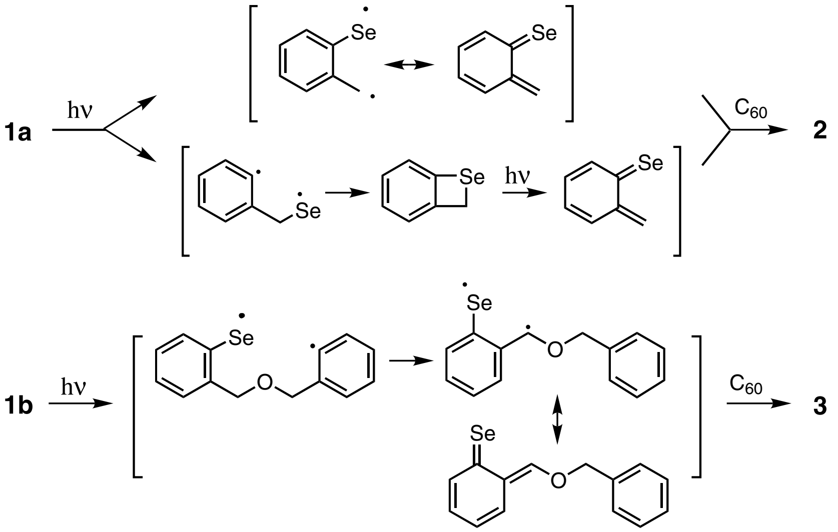
mixture by preparative HPLC using a Buckyprep column (Nacalai Tesque Inc). The color of the reaction mixture changed from purple to brownish-red. Meanwhile, the irradiation with a halogen–tungsten lamp using a filter solution (cutoff <400 nm) for 3 h gave no change monitored by analytical HPLC. This suggests that the photochemical reaction may proceed via the excitation of **1a**, not that of C_{60}.[13]

The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of **2** displays a molecular ion peak at *m*/*z* 890 corresponding to the molecular formula of $C_{67}H_6Se$ as well 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 peak. The visible absorption spectrum of **2** shows an shoulder-like absorption maximum at 450 nm, which is characterized as the result of 6,6-addition on C_{60}.[14] The ^1H and ^{13}C NMR spectra of **2** clearly display 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. These data are very similar to the sulfur analog of **2** reported by Ohno et al.[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 the sp^2 carbon signals (64 carbons (8 signals overlapped)) in the range of 130–156 ppm assignable for a benzene ring (6C) and C_{60} (58C). If **2** 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 the phenyl carbon. The ^{13}C NMR spectrum reveals that **2** has two conformers with C_1 symmetry inversing slower than NMR time scale, which is also observed in the case of the sulfur analog of **2**. To confirm the structure of **2**, 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. ^{77}Se NMR spectrum of **2** shows a singlet signal at 580 ppm (Me_2Se used as external standard). These results confirm that **2** has the structure shown in Scheme 1. This is the first fullerene derivative with the carbon–selenium bond directly on 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 2).

The photochemical reaction of C_{60} with **1b** was also conducted in the same way for **1a** (Scheme 1), resulting in the formation of **3** in 53% yield.[15] Compound **3** was isolated from the reaction mixture by preparative HPLC. Irradiation at over 400 nm gave no product, similar to the reaction of **1a** with C_{60}.[13]

The MALDI-TOF mass spectrum of **3** 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. The absorption maximum at 450 nm in the visible absorption spectrum also suggests the 6,6-addition on C_{60}.[14] The ^1H and ^{13}C NMR spectra of **3** display two methylene proton signals at 4.36 (1H, d, $J = 12$ Hz) and 4.50 (1H, d, $J = 12$ Hz) and the carbon signal 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, that is, one is mono-substituted and another is 1,2-substituted. In addition, the ^{13}C NMR spectrum of **3** shows 53 peaks due to the overlapping of 5 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 **3** shows a signal at 550 ppm. These results suggest that the structure of **A** or **B** may be conceivable for **3**. The 2D HMBC spectrum displays the long-range correlation peaks between the methylene proton and the *ortho*-carbon in the phenyl 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. From these results, the structure of **A** may be concluded to be **3**.

Finally, the X-ray crystallographic analysis of **3** unambiguously revealed the molecular structure of **A** for **3**



Scheme 2.

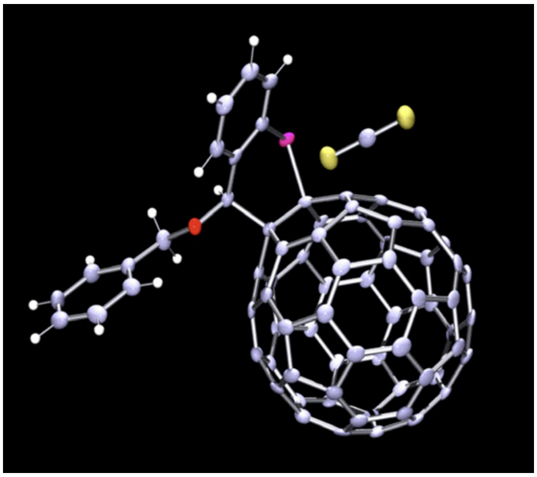


Fig. 1. ORTEP drawing of **3** with CS_2. Thermal ellipsoids are shown at 50% probability. CS_2 molecules are included as crystal solvent.

(Fig. 1).[16] On the basis of these observations, the formation of the 1:1 adduct **3** of C_{60} and the selenium-containing cyclooctane **1b** has been evidenced. 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 **3** (Scheme 2).

The redox potentials of **2** and **3** 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 are summarized in Table 1, together with those of C_{60} as a reference. This result reveals that the introduction of a selenyl group on the C_{60} cage lowers the oxidation potential of C_{60}.

In conclusion, we have for the first time succeeded in the syntheses of the selenylfullerenes, **2** and **3**, by the photochemical reaction of C_{60} with selenium-containing dibenzo[*b*,*g*]cyclooctane, **1a** and **1b**, and characterized their structures and electronic properties. Selenylfullerene **2** 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 analog. The photochemical reaction with dibenzo[*b*,*g*][1,5]oxaselenacin (**1b**), however, afforded the unexpected and unique compound **3** and its structure was determined by X-ray crystallographic analysis. The reaction mechanisms have also been presented in Scheme 2. Successful chemical functionalization of fullerene with chalcogen atom may promise application of the derivatized fullerene in material science and biochemistry.

Table 1
Redox potentials[a] in V of **2**, **3** and C_{60}

Compounds	${}^{ox}E_1{}^{b}$	${}^{red}E_1$	${}^{red}E_2$	${}^{red}E_3$
2	+1.06	−1.20	−1.49	−1.64
3	+1.05	−1.18	−1.45	−1.62
C_{60}[c]	+1.26	−1.13	−1.50	−1.95

[a] Values are relative to Fc/Fc^+ in *o*-dichlorobenzene.
[b] Values are irreversible and obtained by DPV.
[c] Ref. 17.

Acknowledgments

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Supplementary data

HPLC profiles, MALDI-TOF-MS, ^{1}H NMR, ^{13}C NMR, ^{77}Se NMR, 2D NMR, CV and DPV spectra for **2** and **3**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.02.017.

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12. Compound **2**: ^{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 580.0 (relative to Me_2Se). MALDI–TOF MS (m/z) 890 (M^-). UV–vis absorption λ_{sh} 450 nm.
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15. Compound **3**: ^{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.
16. *Crystal data for* **3**: $C_{75}H_{12}OS_2Se$, $FW = 1072.00$, black crystals, $0.20 \times 0.20 \times 0.15$ mm^3, triclinic, $P\bar{1}$ (#2), $a = 10.0056(6)$ Å, $b = 21.4859(18)$ Å, $c = 9.9009(7)$ Å, $\alpha = 101.741(3)°$, $\beta = 102.084(2)°$, $\gamma = 82.923(3)°$, $V = 2030.5(3)$ Å^3, $Z = 2$, $D_c = 1.753$ mg/m^3, $T = 100$ K, 17,691 reflections, 8081 unique reflections, $R_1 = 0.0633$, $wR_2 = 0.1911$, GOF = 1.055. The maximum and minimum residual electron density is equal to 1.51 and −0.98 e Å^{-3}. CCDC No. 672026 contains the supplementary crystallographic data for this Letter. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing 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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