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Expansion of Orifices of Open C_{60} Derivatives and Formation of an Open $C_{59}S$ Derivative by Reaction with Sulfur

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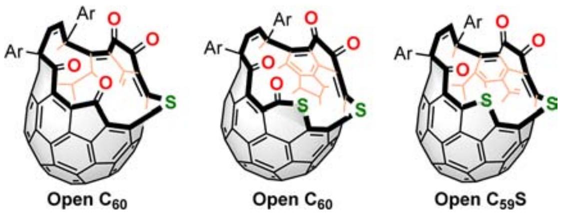
ABSTRACT



The reaction of a tetraketo-open-cage C_{60} derivative with elemental sulfur in the presence of tetrakis(dimethylamino)ethylene afforded novel open C_{60} derivatives containing sulfur atom(s) in the rim of the orifice and the first example of an open $C_{59}S$ derivative. The single crystal X-ray analyses clearly determined these structures and demonstrated that a water molecule was encapsulated inside the cages. The orifice sizes and electronic properties of these fullerene derivatives were revealed.

Developments for open-cage fullerenes[1−5] have been attracting considerable attention from the viewpoints of host−guest chemistry and usage as precursors for a heterofullerene such as a $C_{59}N$ derivative[6] as well as novel endohedral fullerenes when closing of the opening is successful, keeping the encapsulated species inside fullerenes.[1−5] After the pioneering report of an open-cage C_{60} derivative by Wudl et al. in 1995,[7] several derivatives were developed so that small molecules, including a helium atom[8−10] and a hydrogen molecule,[8,11−14] can go inside through the opening. Furthermore, a water molecule was encapsulated into an open-cage C_{60} synthesized by Iwamatsu et al. in 2004 for the first time[15] and later into open C_{60} and open $C_{59}O$ derivatives reported by Gan et al., whose structures were determined by single crystal X-ray analysis.[16−19] The synthesis of $H_2O@C_{60}$ was recently achieved through quantitative encapsulation of

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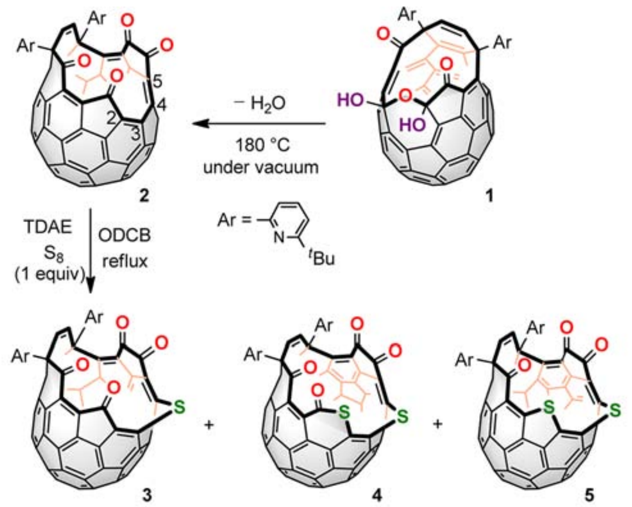
a water molecule under high-pressure conditions into an open-cage C_{60} having ketal moieties followed by subsequent closure of the opening.[20] In the case that a large opening was constructed on the C_{60} cage, other small molecules including CO,[21,22] N_2,[22] NH_3,[23] and CH_4[24] can be encapsulated inside the cage. Since examples of open-cage fullerenes are still limited, synthetic methods should be developed to give novel open-cage fullerene derivatives with a large opening, giving rise to realizing the encapsulation of a variety of molecules as well as heteroatom embedded carbon cages.

Sulfur insertion into the rim of the opening on the C_{60} and C_{70} cage is a powerful method to construct a large opening.[25,26] The reaction of an open-cage C_{60} derivative having a 12-membered ring opening with sulfur in the presence of tetrakis(dimethylamino)ethylene (TDAE) as a π-donor was reported to give the sulfur-inserted products with a 13-membered ring opening in a good yield.[25] Here we report application of this reaction to an open-cage C_{60} having a 16-membered ring opening,[20] leading to the construction of larger openings. The structure, encapsulation of a small molecule, and electronic properties of the novel open-cage derivatives were studied in detail.

Open-cage C_{60} derivative **2** with a tetraketone moiety was generated from its precursor **1**[20] with diketone and diketal moieties by dehydration at 180 °C under vacuum as shown in Scheme 1. Although generation of **2** occurred smoothly in solution,[20] formation of **2** in the solid state required several hours at higher temperature. It was found that **2** is stable as powder and in a dry solution and that **2** gradually goes back to **1** by hydration under ambient conditions in solution.

The reaction of **2** with 1 equiv of S_8 in 1,2-dichlorobenzene (ODCB) at 180 °C in the presence of TDAE was conducted as shown in Scheme 1. It was found that the reaction using 0.2 equiv of TDAE for 15 min afforded sulfide **3** having a 17-membered ring opening as a nearly single product in 60% isolated yield (entry 1) as expected. However when the amount of TDAE was increased to 0.5 equiv (entry 2), two unprecedented products, sulfide thioester **4** (16%) and open-cage $C_{59}S$ derivative **5** (31%), were found to be obtained in addition to sulfide **3** (24%). Furthermore, the reaction using 2.0 equiv of TDAE for 14 h afforded **5** selectively in 68% yield (entry 3). It should be noted that the sulfur insertion reaction using **3** as the starting material in the presence of 1.0 equiv of TDAE for 15 min afforded **4** and **5**, indicating the stepwise insertion of the second sulfur atom to the opening containing the first sulfur atom. In these reactions, we selectively used argon or nitrogen for the inert gas because it was found that a nitrogen molecule was encapsulated in **4** and **5** (*vide infra*).

Scheme 1. Synthesis of Novel Open C_{60} Derivatives **3**–**4** and Open $C_{59}S$ Derivative **5**



entry	TDAE (equiv)	time (h)	isolated yield[a]		
			3	4	5
1[b]	0.2	0.25	60	0	0
2[b]	0.5	0.25	24	16	31
3[c]	2.0	14	0	0	68

[a] Isolated yields were estimated using the encapsulated ratio of H_2O and N_2, determined by the X-ray and ^1H NMR analyses. [b] Reactions were conducted under an argon atmosphere. [c] Reaction was conducted under a nitrogen atmosphere.

The structures of **3**–**5** were determined unambiguously by single crystal X-ray analyses. As shown in Figure 1a, a sulfur atom was actually inserted into the conjugated butadiene unit C2═C3—C4═C5 in **2** to give **3** (the numbering system shown in Scheme 1). The DFT calculations (B3LYP/6-31G*)[27] demonstrated that the LUMO of **2** is relatively localized on the butadiene unit. This position is considered to be activated by electron transfer from TDAE, followed by the reaction with elemental sulfur[25] to form sulfide **3**. The X-ray structures of **4** and **5** are shown in Figure 1b and 1c, respectively. It is clearly seen that **4** has the thioester C1(O)—S2—C2 in addition to the sulfide C2═C3—S1—C4═C5 moieties, resulting in the formation of the 18-membered ring opening. Surprisingly, the carbonyl group C1(O) of **4** is lost in **5**, resulting in the construction of the 17-membered ring opening with two sulfide moieties. This compound **5** is the first example of a fullerene derivative having a $C_{59}S$ skeleton.

The shapes of the opening in **3**–**5** are rather ellipsoid as shown in the top views of the X-ray structures. The lengths of the longer axes of the openings in **3**–**5** are in the order **3** < **4** < **5**; C11−S1 distances are 6.804(3), 7.101(4), and 7.165(4) Å, for **3**, **4**, and **5**, respectively. These values are close to the diameter of pristine C_{60} (7.10 Å),[28] with the size

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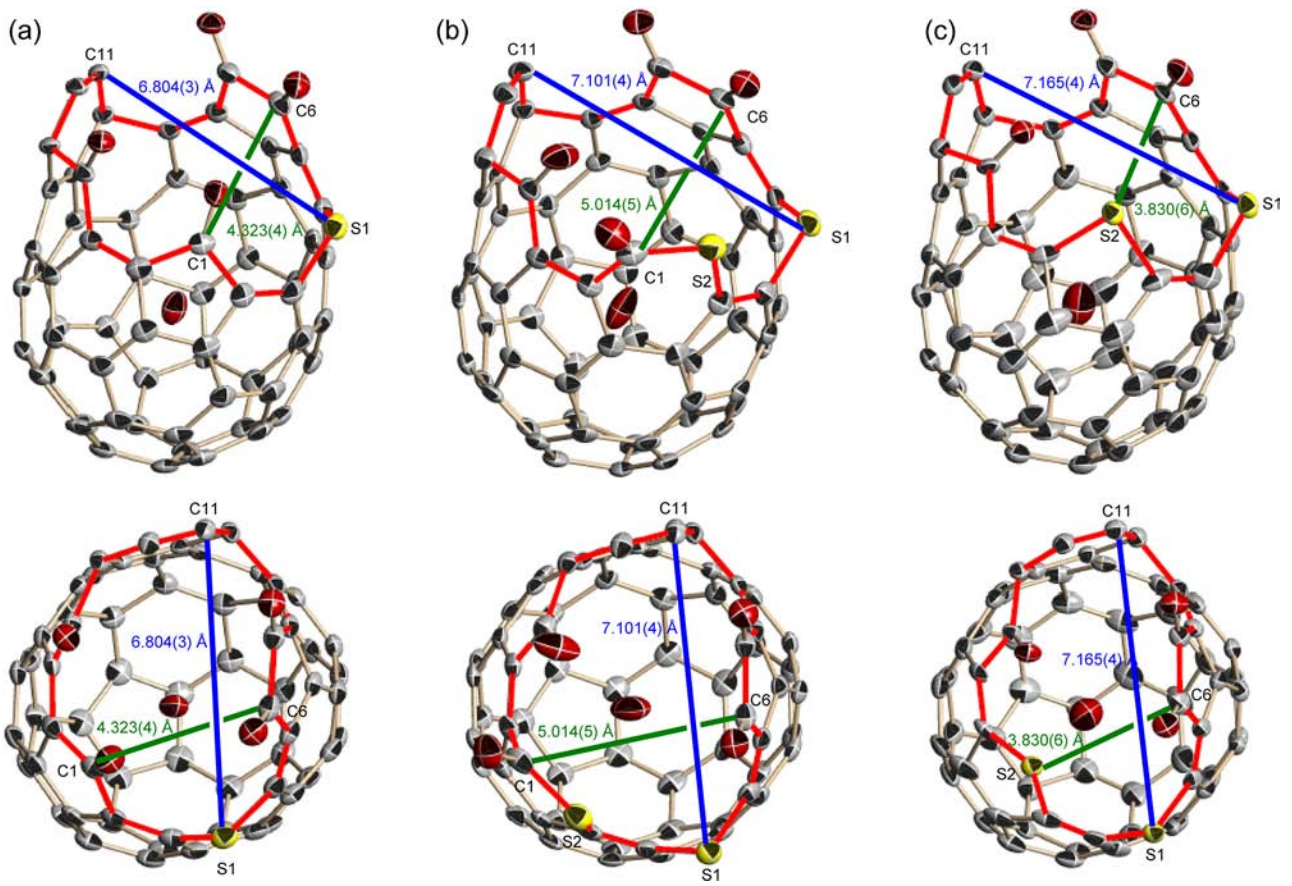

Figure 1. Side and top views of the X-ray structures of (a) **3**, (b) **4**, and (c) **5**. Ellipsoids were shown at 50% probability levels. Color scheme: gray, C; red, O; yellow, S; red-highlighted bonds, structure of the opening. Nickel octaethylporphyrin, aryl groups, hydrogen atoms, encapsulated nitrogen molecule in minor occupancies, and solvent molecules were omitted for clarity.

of the opening being almost the same as that of its body. On the other hand, the lengths of the shorter axes changed sensitively with the structures of the openings. The opening of **4** is the largest, judging from the length of the shorter axis of the opening in **4** (C1(O)−C6(O), 5.014(5) Å), which is longer than those of **3** (C1(O)−C6(O), 4.323(4) Å) and **5** (S2−C6(O), 3.830(6) Å), respectively. The opening of **5** seems smaller than that of **3**, despite the fact that the openings of these compounds consisted of a similar 17-membered ring, with the only difference being that the carbonyl group C1(O) in **3** was replaced by a sulfide moiety (S2) in **5**.

In order to gain further insights into the opening sizes, DFT calculations were conducted to estimate the required energies for the insertion of a nitrogen molecule into **3′**−**5′** at the M06-2X/3-21G level of theory, with the *tert*-butyl groups replaced by the methyl groups. The calculated energies are 17.0, 9.7, and 23.5 kcal/mol for **3′**, **4′**, and **5′**, respectively, indicating that the size of the openings is in the order **5** < **3** < **4**, which is the same order of the length of the shorter axes of the openings. It is interesting to mention that the reason for the apparently smaller size of the opening of **5** with reference to that of **3** is the larger van der Waals radius of the sulfur atom (1.80 Å)[29] in **5** than that of the carbon (1.70 Å)[29] in **3**.

The encapsulation behavior of a water molecule inside **3**−**5** was reflected by the size of the openings. A sharp signal corresponding to the encapsulated water molecule inside **5** appeared at δ −10.96 ppm, and a broad signal was detected for that inside **3** at δ −11.48 ppm in $CDCl_3$ at room temperature. Although the signal for that inside **4** was not seen at room temperature, a broad signal was observed at δ −10.95 ppm in 1,1,2,2-tetrachloroethane at −25 °C, likely due to the rapid exchange of water between the inside and outside of the C_{60} cage.[30] The encapsulation ratios in solution were ca. 70%[31] and 40% for **5** and **3** at room temperature and ca. 30% for **4** at −25 °C, respectively.

Interestingly, it was found that open-cage $C_{59}S$ derivative **5** synthesized under a nitrogen atmosphere (Scheme 1, entry 3) encapsulates even a nitrogen molecule (35%) in addition to a water molecule (55%) as judged from the APCI MS and ^{1}H NMR analyses. The ^{1}H NMR showed

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(31) The sample of **5** for the ^{1}H NMR and the X-ray analysis in this study was prepared from a mixture of $H_2O@$**5** and empty **5** without contamination of $N_2@$**5**.

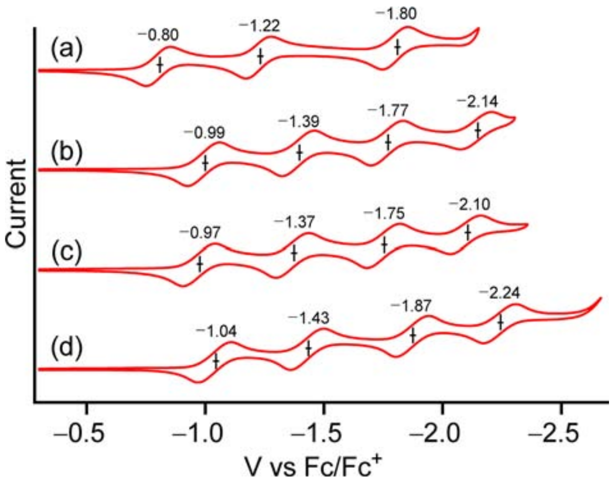

Figure 2. Cyclic voltammograms of (a) **2**, (b) **3**, (c) **4**, and (d) **5**. Conditions: 1 mM sample with 0.1 M n-Bu_4NBF_4 in ODCB at a scan rate of 20 mV s^{-1}.

the signals corresponding to one of the olefinic protons separately at δ 6.57 ppm for H_2O@**5**, δ 6.56 ppm for empty **5**, and δ 6.55 ppm for N_2@**5**. Separation of N_2@**5** from a mixture of H_2O@**5** and empty **5** was possible by the use of recycling HPLC equipped with Buckyprep columns, presumably owing to greater interaction of the fullerene cage with N_2 compared with H_2O.

The X-ray analyses of sulfide **3**, thioester **4**, and open $C_{59}S$ **5** revealed that a water molecule is encapsulated in the solid state at encapsulation ratios of 100%, 52%, and 75% for **3**, **4**, and **5**,[31] respectively. The larger encapsulation ratios of H_2O for **3**−**5** in the solid state than those observed in solution can be ascribed to enrichment of the encapsulated H_2O during the recrystallization as reported.[16] It should be mentioned that the X-ray analysis of **4**, which has the largest opening, indicates the encapsulation of not only H_2O (52%) but also N_2 (48%). The molecular ion peak of N_2@**4** was detected in the APCI-MS analysis, and N_2 was likely encapsulated during the course of the crystallization through slow evaporation of an air saturated benzene solution of **4**.

Since all carbons derived from the pristine C_{60} cage retain sp^2-hybridization including carbonyl carbons and divinyl sulfides, **2**−**4** still have spherical 60π systems with the functional groups directly introduced at the rim of the opening. To examine the electronic properties of these compounds, the redox behaviors were studied by cyclic voltammetry (CV) in ODCB (Figure 2). All derivatives **2**−**5** exhibited pseudo-reversible three- or four-step reduction waves. The first reduction potential of tetraketone **2** appeared at −0.80 V (vs Fc/Fc^+ couple), which is anodically shifted by 0.29 V with reference to that of C_{60} (−1.09 V).[26] Those of the sulfur-containing compounds **3**−**5** were observed at −0.99, −0.97, and −1.04 V, respectively, which are still less negative than that of C_{60} due to three or four carbonyl groups. These electron-accepting characters were in good agreement with the LUMO levels calculated at B3LYP/6-31G* level of theory: −3.43 eV for **2**, −3.30 eV for **3**, −3.35 eV for **4**, and −3.26 eV for **5**, respectively. The carbonyl groups directly connected to the π-system of the fullerene cage lower the LUMO levels, whereas the sulfide moieties raise them.[25] No oxidation waves were observed for **2**−**5** within the potential window up to +1.33 V vs Fc/Fc^+.

In summary, the reaction of **2** with elemental sulfur in the presence of TDAE afforded novel open-cage C_{60} derivatives **3** and **4** as well as open-cage $C_{59}S$ derivative **5** with a loss of one carbon atom from the C_{60} cage, by simply changing the reaction conditions. The structures of **3**−**5** were determined by single crystal X-ray analyses which showed the encapsulation of a water molecule inside the fullerenes. The reduction potentials of these compounds can be tuned by the sulfide moieties in addition to at most four carbonyl groups. These fullerene derivatives would be good host compounds for other small molecules as well as potential precursors for novel endohedral fullerenes in the near future.

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Supporting Information Available. Experimental procedure and spectroscopic data for all new compounds, calculated geometries, and cif files for compounds **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.