

# Formation Process of Si-Coated C<sub>60</sub>

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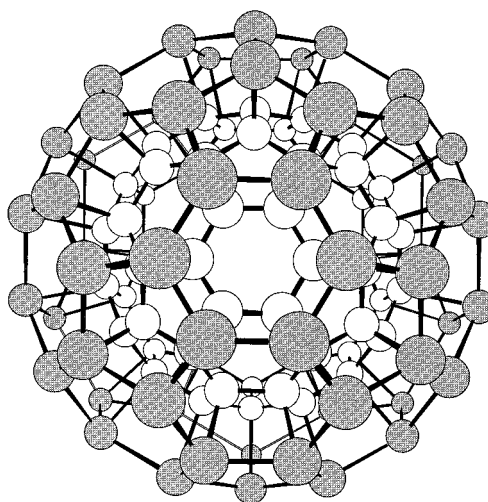
The formation process of Si-coated C<sub>60</sub>, C<sub>60</sub>Si<sub>n</sub> ( $n = 1-60$ ), was theoretically investigated by examining both the geometric structure and standard heat of formation ( $\Delta H_f^0$ ) for individual C<sub>60</sub>Si<sub>n</sub> clusters using a semiempirical molecular orbital method. For a small number of Si atoms ( $n < 3$ ), it was found that each Si atom is preferentially bound to the 6/6 bonds (double bond between adjacent hexagon rings) of the C<sub>60</sub> substrate independently. On the other hand, for a large number of Si atoms ( $n \geq 3$ ), besides the bond formation between Si atoms and the C<sub>60</sub>, the adjacent Si atoms tend to form chemical bonds with each other. The  $n$ -dependence of  $\Delta H_f^0$  for the C<sub>60</sub>Si<sub>n</sub> was quantitatively interpreted by the number of Si atoms with dangling bonds in the framework of the isolated pentagon rule (IPR). It was revealed that the Si–Si bond formation is an essential process to successfully synthesize the C<sub>60</sub>Si<sub>60</sub>.

## Introduction

C<sub>60</sub>Si<sub>60</sub>, in which C<sub>60</sub> is fully coated by Si atoms as shown in Figure 1, is fascinating because it can be regarded as a single-sized Si cluster which has the potential for use in new optical and electrical nanodevices due to its electronic structure.<sup>1–12</sup> In fact, Ōsawa and co-workers<sup>1,2</sup> theoretically predicted that the C<sub>60</sub>Si<sub>60</sub> is more stable than isolated C<sub>60</sub> and Si<sub>60</sub> and that its energy levels of the frontier orbitals are similar to those of Si<sub>60</sub>.

Experimental studies in order to synthesize C<sub>60</sub>Si<sub>60</sub> have been extensively reported.<sup>3–12</sup> Moriarty et al.<sup>3</sup> examined the C<sub>60</sub> molecules deposited on a Si surface at room temperature and only found the formation of a charge-transfer complex between the surface and the molecules. Hunt et al.<sup>4</sup> studied the electron-beam irradiation of C<sub>60</sub> films on a Si surface and confirmed the formation of Si–C bonds in the film by high-resolution electron energy-loss spectroscopy (HREELS). This indicates that a C<sub>60</sub> itself or a C<sub>60</sub> destroyed by the electron-beam irradiation can stick to the Si surface. It is well-known that mixed clusters composed of carbon and Si atoms are effectively produced from a silicon carbide substrate irradiated by a laser.<sup>5–12</sup> Pellarin et al.<sup>5</sup> applied this method to synthesize the C<sub>60</sub>Si<sub>60</sub>. While they successfully observed a mass distribution at around  $m/z \approx 2400$  corresponding to the C<sub>60</sub>Si<sub>60</sub>, they could not find any “magic number” for a cluster that may have a highly symmetrical and stable structure such as the C<sub>60</sub>Si<sub>60</sub> shown in Figure 1. Consequently, these previous experimental results suggest that the formation of the C<sub>60</sub>Si<sub>60</sub> is quite difficult, though a small number of Si atoms can easily stick to or exchange with the constituent carbon atoms of the C<sub>60</sub>. This difficulty may arise from the presence of a bottleneck in the formation of the C<sub>60</sub>Si<sub>60</sub>.

Understanding the stability of individual C<sub>60</sub>Si<sub>n</sub> is very important for developing a promising way to synthesize the C<sub>60</sub>Si<sub>60</sub>. The aim of the present work is to study the stability of the intermediate complex, C<sub>60</sub>Si<sub>n</sub>, during the formation process



**Figure 1.** Geometric structure of C<sub>60</sub>Si<sub>60</sub> made of an  $I_h$  Si<sub>60</sub> cage bound to a C<sub>60</sub> substrate. The open and closed circles represent carbon and silicon atoms, respectively.

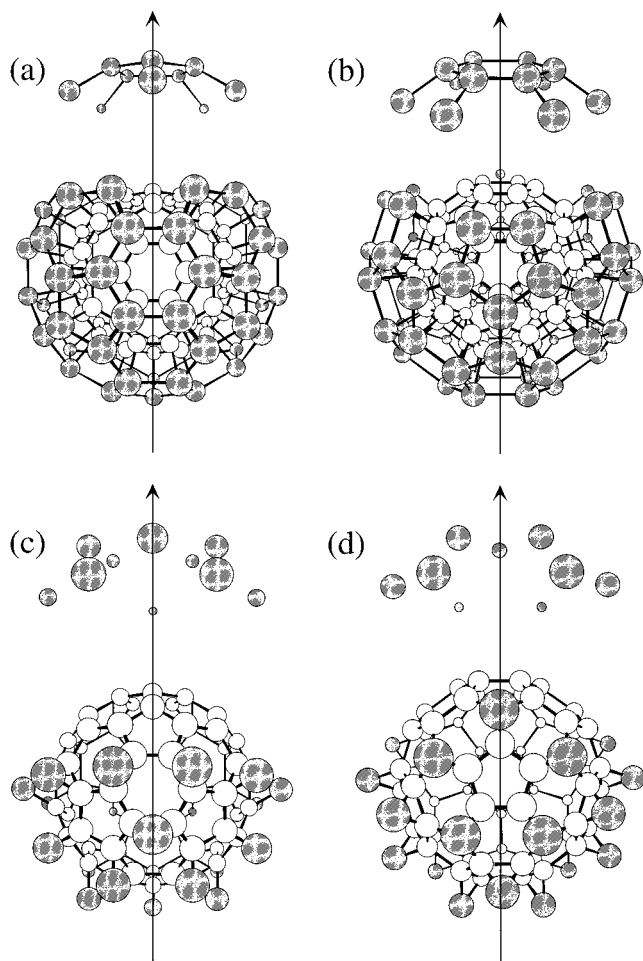
of the C<sub>60</sub>Si<sub>60</sub> by a systematic investigation of the geometric structure and energetics for the C<sub>60</sub>Si<sub>n</sub> using a semiempirical molecular orbital method. The standard heat of formation ( $\Delta H_f^0$ ), average bond length of adjacent Si atoms ( $L_{Si}$ ), and average bond energy of the Si–Si bonding ( $E_{Si}$ ) for the C<sub>60</sub>Si<sub>n</sub> are presented, and the  $n$ -dependencies ( $n = 1-60$ ) of these parameters are examined and discussed based on the isolated pentagon rule (IPR).

## Computational Method

To elucidate the formation process of the C<sub>60</sub>Si<sub>60</sub> shown in Figure 1, several isomers of the Si-coated fullerene C<sub>60</sub>Si<sub>n</sub> ( $n = 1-60$ ) were examined as an intermediate for the C<sub>60</sub>Si<sub>60</sub> formation. In the small size range ( $n = 1-5$ ), the possible isomers for the C<sub>60</sub>Si<sub>n</sub> were extensively treated. On the other hand, in the large size range ( $n > 5$ ), the structures of the C<sub>60</sub>Si<sub>n</sub> were systematically constructed by removal of Si atoms from the C<sub>60</sub>Si<sub>60</sub>. Parts a and b of Figure 2 show the schematic procedure to construct the structure of the C<sub>60</sub>Si<sub>n</sub> derived from

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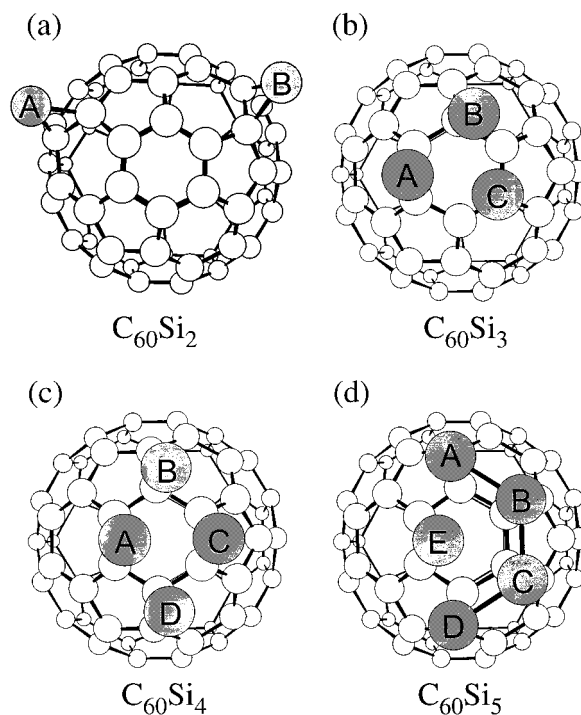
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**Figure 2.** Schematic procedure to construct the structures of  $C_{60}Si_n$ . Derivatives made from the  $C_{60}Si_{60}$  by removal of Si atoms along the arrow perpendicular to (a) a five-membered ring and (b) a six-membered ring and derivatives made from the  $C_{60}Si_{30}$  by removal of Si atoms along the arrow perpendicular to (c) a five-membered ring and (d) a six-membered ring.

the  $C_{60}Si_{60}$  by removal of Si atoms along the arrow perpendicular to a pentagon ring and a hexagon ring, respectively. The open and closed circles represent the carbon and silicon atom, respectively. The  $C_{60}Si_n$  with incremental  $Si_2$  releases from the  $C_{60}Si_{60}$  was examined as a candidate for the most stable isomer since the  $C_{60}Si_{60}$  is analogous to the  $C_{60}$  featured by  $C_2$  releases. To estimate the effects of the Si–Si bonding on the stability of the  $C_{60}Si_n$ ,  $C_{60}Si_{30}$ , in which Si atoms are independently bound to the 6/6 bonds of the  $C_{60}$ , was used as the starting molecule. Parts c and d of Figure 2 show the schematic procedure to construct the structure of the  $C_{60}Si_n$  derived from the  $C_{60}Si_{30}$  by removal of Si atoms along the arrow perpendicular to a pentagon ring and a hexagon ring, respectively.

The geometric structure for a given cluster was energetically optimized by using the semiempirical PM3 Hamiltonian in the MOPAC93 package.<sup>13–15</sup> In practice, the optimization of the structure for  $C_{60}Si_n$  was accomplished via two steps: (1) rough optimization using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) routine and (2) subsequent careful optimization using the eigenvector following (EF) routine. The final convergence criteria was fulfilled within an accuracy of  $4 \times 10^{-4}$  kJ mol<sup>-1</sup>Å<sup>-1</sup> for the geometric optimization and within  $4 \times 10^{-6}$  kJ mol<sup>-1</sup>Å<sup>-1</sup> for the SCF iteration by these procedures. It is well-known that this method gives a reliable  $\Delta H_f^0$  value for fullerene derivatives relative to that for the  $C_{60}$ .<sup>1,2</sup> The calculation was performed both under nonsymmetry for the geometric



**Figure 3.** Geometric structure giving the lowest value of  $\Delta H_f^0$  among the possible structures of (a)  $C_{60}Si_2$ , (b)  $C_{60}Si_3$ , (c)  $C_{60}Si_4$ , and (d)  $C_{60}Si_5$  examined in this study.

structure and under a singlet ground state for the cluster. All calculations were carried out using DEC3000 workstations.

## Results and Discussion

**Geometric Structure of  $C_{60}Si_n$  ( $n \leq 5$ ).** Figure 3 shows the optimized geometric structures of  $C_{60}Si_n$  ( $n = 2–5$ ) that give the lowest  $\Delta H_f^0$  value among the isomers examined in this study. The open and closed circles represent the carbon and silicon atoms, respectively. Chemical bonding shown as the solid line is assumed to be formed when the distance between the two circles is shorter than the bond length obtained from the sum of the covalent radii of the corresponding atoms.

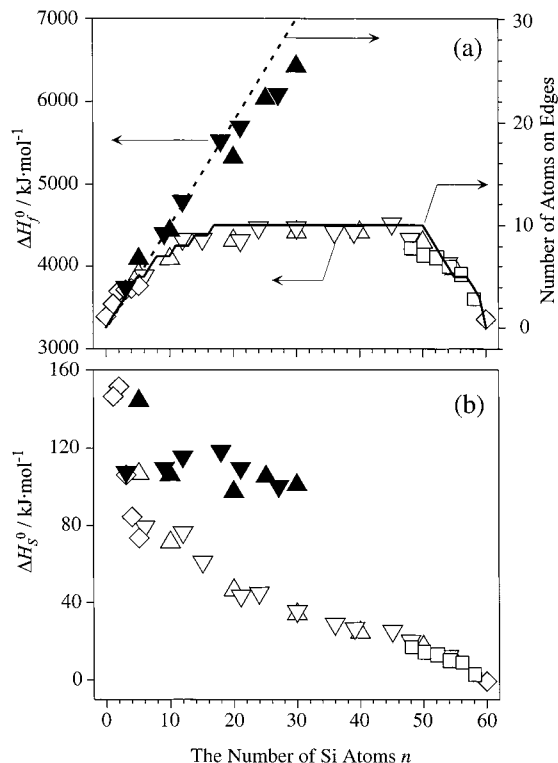
As shown in Figure 3a, each Si atom on  $C_{60}Si_2$  is chemically bound to two adjacent carbon atoms forming the 6/6 bond separately. This tendency was observed even for the other isomers of the  $C_{60}Si_n$ . The  $C_{60}Si_2$  became more stabilized as the two Si atoms (A, B) were located as far apart as possible. On the other hand, the Si atoms of  $C_{60}Si_3$  shown in Figure 3b are perpendicular bound to a 6/6 bond (A), a 5/6 bond (B), and a carbon atom (C). They form a triangle shape on the hexagon ring of the  $C_{60}$ . For  $C_{60}Si_4$ , shown in Figure 3c, Si atoms are perpendicular bound to a 6/6 bond (A), a 5/6 bond (C), and two carbon atoms (B, D). In this case, they form a diamond shape on the hexagon ring of the  $C_{60}$ . For  $C_{60}Si_5$ , shown in Figure 3d, four Si atoms are perpendicular bound to carbon atoms (A–D) and the other Si atom is perpendicular bound to a 6/6 bond (E). They form a pentagon shape on the hexagon ring of the  $C_{60}$ . The preferential formation of both the Si–Si bonding and the Si–C bonding perpendicular to the  $C_{60}$  is apparently present in the larger  $C_{60}Si_n$  ( $n > 2$ ).

Table 1 shows the values of  $\Delta H_f^0$ ,  $L_{Si}$ , and  $E_{Si}$  for the optimized structure of the  $C_{60}Si_n$  ( $n = 0–5, 60$ ).  $\Delta H_f^0$  increases with the number of Si atoms up to  $n = 5$ , while  $\Delta H_f^0$  at  $n = 60$  shows the lowest value. The  $L_{Si}$  gradually decreases and seems to converge to the value for the  $C_{60}Si_{60}$  as the number of Si atoms increases. The  $E_{Si}$  gradually decreases as the number of

**TABLE 1: Standard Heat of Formation ( $\Delta H_f^0$ ), Average Bond Length for Adjacent Si Atoms ( $L_{Si}$ ), and Average Bond Energy for Adjacent Si Atoms ( $E_{Si}$ ) for C<sub>60</sub>Si<sub>n</sub>, Which Gives the Lowest Value of  $\Delta H_f^0$  among Isomers Examined in This Study<sup>a</sup>**

n	$\Delta H_f^0$ (kJ mol <sup>-1</sup> )	$L_{Si}$ (Å)	$E_{Si}$ (eV)
0	3393		
1	3540		
2	3690	7.58	+0.9
3	3711	2.61	-3.3
4	3729	2.53	-4.0
5	3759	2.46	-4.7
60	3350	2.31	-6.3

<sup>a</sup> The geometric structure corresponding to the number of Si atoms,  $n = 2-5$ , is shown in Figure 3.



**Figure 4.** (a) The  $n$ -dependence of  $\Delta H_f^0$  for optimized geometric structure of the C<sub>60</sub>Si<sub>n</sub>. Open and closed plots show the  $\Delta H_f^0$  for the C<sub>60</sub>Si<sub>n</sub> derived from the C<sub>60</sub>Si<sub>60</sub> and the C<sub>60</sub>Si<sub>30</sub>, respectively. Triangles ( $\Delta$ ,  $\nabla$ ,  $\blacktriangle$ , and  $\blacktriangledown$ ) represent the  $\Delta H_f^0$  for the structure constructed by the procedure shown in parts a, b, c, and d of Figure 2, respectively. Squares ( $\square$ ) represent the  $\Delta H_f^0$  for the C<sub>60</sub>Si<sub>n</sub> with incremental Si<sub>2</sub> releases from the C<sub>60</sub>Si<sub>60</sub>. Diamonds ( $\diamond$ ) represent the  $\Delta H_f^0$  for the structure with the lowest value of the  $\Delta H_f^0$  among the isomers shown in Figure 3. Solid and dotted lines with the scale shown on the right side denote the number of Si atoms on edges for the C<sub>60</sub>Si<sub>n</sub>.<sup>16</sup> (b) The  $n$ -dependence of the average binding energy of Si atoms to the C<sub>60</sub> for the production of the C<sub>60</sub>Si<sub>n</sub>.

Si atoms increases. While the interaction between adjacent Si atoms observed in both the  $L_{Si}$  and the  $E_{Si}$  becomes monotonically larger with the number of Si atoms, the stability of the C<sub>60</sub>Si<sub>n</sub> seems to decrease for a small number of Si atoms. The change in the  $\Delta H_f^0$  with regard to the number of Si atoms may provide important information about the difficulty of the synthesis of the C<sub>60</sub>Si<sub>60</sub>.

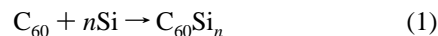
**Energetics of C<sub>60</sub>Si<sub>n</sub> ( $n = 1-60$ ).** We next systematically examined the  $n$ -dependence of  $\Delta H_f^0$  for C<sub>60</sub>Si<sub>n</sub>. Figure 4a shows the plot of  $\Delta H_f^0$  for the optimized C<sub>60</sub>Si<sub>n</sub> as a function of the number of Si atoms ( $n$ ). The open and closed plots show  $\Delta H_f^0$  for C<sub>60</sub>Si<sub>n</sub> calculated using C<sub>60</sub>Si<sub>60</sub> and C<sub>60</sub>Si<sub>30</sub> as the starting molecules, respectively. The triangles ( $\Delta$  and  $\blacktriangle$ ) represent  $\Delta H_f^0$

for the structure constructed by the procedure shown in parts a and c of Figure 2, respectively. The reversed-triangles ( $\nabla$  and  $\blacktriangledown$ ) represent  $\Delta H_f^0$  for the structure constructed by the procedure shown in parts b and d of Figure 2, respectively. The squares ( $\square$ ) represent  $\Delta H_f^0$  for C<sub>60</sub>Si<sub>n</sub> with incremental Si<sub>2</sub> releases from the C<sub>60</sub>Si<sub>60</sub>. The diamonds ( $\diamond$ ) represent  $\Delta H_f^0$  for the structure with the lowest  $\Delta H_f^0$  value among the isomers shown in Figure 3. Since the four open plots ( $\Delta$ ,  $\nabla$ ,  $\square$ , and  $\diamond$ ) show similar tendencies, they can be treated as one group. Similarly, the two closed plots ( $\blacktriangle$  and  $\blacktriangledown$ ) can also be treated as another single group. As the number of Si atoms increases,  $\Delta H_f^0$  for the open plots increases and reaches a plateau at around  $n = 10$  and then starts to decrease at  $n = 50$ . On the other hand,  $\Delta H_f^0$  for the closed plots monotonically increases with the number of Si atoms.

We next discuss the discrepancy in the  $n$ -dependence of  $\Delta H_f^0$  between the open and the closed plots. In the previous section, it was found that the adjacent Si atoms tend to form bonds with an increasing number of Si atoms. In other words, Si atoms tend to form an island resulting from this bond formation in the larger C<sub>60</sub>Si<sub>n</sub>. Since the Si atoms located on the edges of the island have unstable dangling bonds, the number of the Si atoms located on the edges of the island may affect the stability of the C<sub>60</sub>Si<sub>n</sub>. The number of the Si atoms located on the edges of the C<sub>60</sub>Si<sub>n</sub> can be quantitatively estimated using Smalley's method,<sup>16</sup> which has been applied to explain the stability of C<sub>60</sub> because the Si atoms of the island align along the lattice of the C<sub>60</sub>. According to the method, the most stable isomer among those of C<sub>60</sub>Si<sub>n</sub> is predicted as the C<sub>60</sub>Si<sub>n</sub> constructed by removal of Si atoms from C<sub>60</sub>Si<sub>60</sub> along with the isolated pentagon rule (IPR), which gives a structure having as many pentagons as possible such that no two are adjacent.

In Figure 4a, the solid line (units are given at the right side) shows the number of Si atoms located on the edges for the C<sub>60</sub>Si<sub>n</sub> constructed by Smalley's method as a function of  $n$  and the dotted line simply shows the number of constituent Si atoms of the C<sub>60</sub>Si<sub>n</sub> as a function of  $n$ . The  $n$ -dependence of the  $\Delta H_f^0$ , shown as the open plots, is well correlated with the solid line, while that of the  $\Delta H_f^0$ , shown as the closed plots, is well correlated with the dotted line. This implies that the formation of the Si-Si bond network in order to reduce the number of the Si atoms with the dangling bonds is an essential process for the stabilization of the C<sub>60</sub>Si<sub>n</sub>.

To understand the role of the Si-Si bond formation in the synthesis of the C<sub>60</sub>Si<sub>60</sub> more clearly, we replotted the  $n$ -dependence of the average binding energy of Si atoms, as shown in Figure 4b. The formation of C<sub>60</sub>Si<sub>n</sub> from C<sub>60</sub> and Si atoms can be expressed as



From this scheme, the average binding energy of one Si atom to the C<sub>60</sub>,  $\Delta H_S^0(C_{60}Si_n)$ , is written as

$$\Delta H_S^0(C_{60}Si_n) = \frac{\Delta H_f^0(C_{60}Si_n) - \Delta H_f^0(C_{60})}{n} \quad (2)$$

where  $\Delta H_f^0(C_{60})$  and  $\Delta H_f^0(C_{60}Si_n)$  represent the standard heat of formation for the C<sub>60</sub> and the C<sub>60</sub>Si<sub>n</sub>, respectively. Figure 4b shows the plot of  $\Delta H_S^0(C_{60}Si_n)$  as a function of  $n$ . The  $\Delta H_S^0(C_{60}Si_n)$  for the open plots rapidly decreases with increasing  $n$ , while that for the closed plots levels off. On the basis of the results shown in Figure 4b, the presence of the Si-Si bond formation allows the Si atoms to bind to the C<sub>60</sub>Si<sub>n</sub> more easily for the larger  $n$ .

## Conclusions

We theoretically investigated the formation process of the  $C_{60}Si_{60}$  by examining the  $n$ -dependencies of the geometric structure and the energetics of the  $C_{60}Si_n$  using the semiempirical PM3 Hamiltonian in the MOPAC93 package. The conclusions obtained in the present study are as follows. (1) For a small number of Si atoms ( $n < 3$ ), it was found that each Si atom is preferentially bound to the 6/6 bonds of the  $C_{60}$  independently. On the other hand, for a large number of Si atoms ( $n \geq 3$ ), the adjacent Si atoms tend to form chemical bonds and they form an island with a network of Si–Si bonds analogous to that of the substrate  $C_{60}$ . (2) The  $n$ -dependence of  $\Delta H_f^0$  for the  $C_{60}Si_n$  was quantitatively explained by the number of Si atoms with dangling bonds. (3) It was found that the presence of the Si–Si bond formation makes the Si atoms bind to  $C_{60}Si_n$  more easily for the larger  $n$ . This indicates that the Si–Si bond formation is an essential process to successfully synthesize the  $C_{60}Si_{60}$ .

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