

# Addition of S-Heterocyclic Carbenes to Fullerenes: Formation and Characterization of Dithiomethano-Bridged Derivatives

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Dedicated to Professor François Diederich

The reactions of novel S-heterocyclic carbenes (SHCs), which were prepared by the cycloaddition of disilenes and digermenes to CS<sub>2</sub>, with C<sub>60</sub> and Sc<sub>3</sub>N@*I*<sub>h</sub>-C<sub>80</sub> afforded the corresponding methano-bridged fullerenes. The [6,6]-closed and [6,6]-open structures were characterized for the SHC adducts of C<sub>60</sub> and Sc<sub>3</sub>N@*I*<sub>h</sub>-C<sub>80</sub>, respectively. These derivatives exhibited relatively low oxidation potentials, indicative of the electron-donating effects of the SHC addends. The electronic properties of the SHC derivatives were clarified by the density functional theory calculations.

Keywords: fullerenes, cluster compounds, sulfur heterocycles, S-heterocyclic carbenes, disilenes, digermenes.

# Introduction

Endohedral metallofullerenes (EMFs)<sup>[1-14]</sup> are of great interest because of their remarkable structures and properties based on the encapsulated metal atoms and metallic clusters inside the carbon cages. Thus far, many EMFs with various cage structures and endohedral species have been extensively investigated, stimulating their potential applications in biochemistry, nanomaterial science, and molecular electronics.<sup>[1-14]</sup> To develop their applications to functional materials, exohedral derivatization plays an indispensable role via the modification of the fundamental properties of EMFs, such as their solubilities and redox potentials.

Among the several functionalization methods for EMFs, the methano-bridge formation<sup>[7]</sup> is one of the

most frequently employed reactions. Hitherto, the radical malonate addition, the Bingel-Hirsch reaction, reactions of carbenes and diazoalkanes, electrochemical synthesis, and zwitterion addition have been reported for the synthesis of methano-bridged EMFs.<sup>[7]</sup> For example, the addition of carbenes to  $M_3N@I_b-C_{80}$ (M=Sc, Y, and Lu),  $I_{h}$ -C<sub>80</sub>-based trimetallic nitride template (TNT) EMFs, afforded two regioisomeric methanofullerenes at the [6,6] (two hexagons) and [5,6] (a pentagon and a hexagon) ring junctions.<sup>[15–23]</sup> In these cases, methano-bridged EMF derivatives have 'open' structures (also known as fulleroids), in which the C-C bonds of the addition sites are cleaved. One of the most practical uses of methano-bridged fullerenes is the acceptor materials in organic photovoltaic (OPV) devices.<sup>[24]</sup> For example, phenyl-C<sub>61</sub>butyric acid methyl ester  $(PC_{61}BM)^{[25]}$  and the corresponding  $C_{70}$  derivative  $(PC_{71}BM)^{[26,27]}$  are well known to be excellent electron acceptor materials for organic

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solar cells. For EMFs, similar Lu<sub>3</sub>N@*l*<sub>h</sub>-C<sub>80</sub> derivatives were reported as promising materials for OPV devices.<sup>[28-30]</sup> As the lowest unoccupied molecular orbital (LUMO) of Lu<sub>3</sub>N@*l*<sub>h</sub>-C<sub>80</sub> is higher than that of C<sub>60</sub>, the OPV devices fabricated using Lu<sub>3</sub>N@*l*<sub>h</sub>-C<sub>80</sub> derivatives exhibited an increase in the open-circuit voltage, affording higher power conversion efficiencies.

In our ongoing study on the derivatization of fullerenes with carbenes,<sup>[7]</sup> the formation of *S*-heterocyclic carbene (SHC)  $\mathbf{3}^{[31]}$  was previously reported in the photoreaction of tricyclic octasilane  $\mathbf{1}^{[32]}$  and CS<sub>2</sub> (*Scheme 1*). The subsequent addition of



Scheme 1. Reaction of S-heterocyclic carbene 3 with C<sub>60</sub>.

**3** to  $C_{60}$  produced the corresponding [6,6]-closed methanofullerene **4**.<sup>[31]</sup> The formation of **3** was easily rationalized by the [2+3] cycloaddition of *in situ* generated cyclic disilene **2** with CS<sub>2</sub> as reported for an isolable disilene reported by *Wiberg* and co-workers.<sup>[33]</sup> However, the synthetic yield of **1** was not sufficient to perform studies on **3** because the preparation of **1** requires multiple step syntheses and subsequent separation by high-performance liquid chromatography (HPLC).<sup>[32]</sup>

Since the discovery of a stable carbene, 1,3-di-1adamantylimidazol-2-ylidene,<sup>[34]</sup> *N*-heterocyclic carbenes (NHCs) have been extensively studied from fundamental viewpoints as well as with respect to the application to catalysts or ligands for metallic complexes.<sup>[34-36]</sup> In fullerene chemistry, the NHC adducts as the *Lewis* donor–acceptor complexes have been studied for  $C_{60}$ ,<sup>[37]</sup>  $C_{70}$ ,<sup>[37]</sup> and a few EMFs.<sup>[38-41]</sup> Nevertheless, examples of cyclic carbenes containing other heteroatoms such as phosphorus and sulfur are extremely sparse compared with those of NHCs.<sup>[42,43]</sup> As compounds related to SHCs, the studies of 1,3dithiocarbenes (RS–C–SR) also have been limited in few studies based on chemical trapping experiments, spectroscopic observation, and theoretical calculations.<sup>[44,45]</sup>

Herein we report the reactions of  $Sc_3N@l_h-C_{80}$ , <sup>[46][47]</sup> the third most abundant fullerene after  $C_{60}$  and  $C_{70}$ , with novel SHCs, which are generated using synthetically more accessible precursors. The SHC adducts of  $Sc_3N@l_h-C_{80}$  as well as those of  $C_{60}$  are characterized on the basis of spectroscopic, electrochemical, and theoretical studies. These results provided a basis for understanding the electronic properties of these compounds, revealing the electronic effects of SHCs as nucleophilic carbenes.

## **Results and Discussion**

#### Syntheses of SHC Adducts of Fullerenes

Novel SHCs **7**, **10a**, and **10b** were synthesized using disilene **6**<sup>[48]</sup> and digermenes **9a**<sup>[49]</sup> and **9b**,<sup>[50]</sup> respectively (*Scheme 2*). To prepare compound **6**, trisilane



Scheme 2. Formation of SHCs 7, 10a, and 10b.

 $5^{[48]}$  was employed as the disilene precursor. Because the photolysis of **5** requires short-wavelength ultraviolet (UV) irradiation, we conducted the following stepwise procedure involving the photolytic synthesis of **6** and subsequent formation of **7**. Thus, a benzene solution of **5** was subjected to photolysis in a quartz tube by a low-pressure mercury arc lamp for 4 h. Then, the resultant solution containing **6** was added to a benzene solution of  $C_{60}$  and  $CS_2$  (*Scheme 3*). The subsequent preparative HPLC separation of the reaction mixture afforded **11** in 36% yield. The matrixassisted laser desorption ionization time-of-flight



Scheme 3. Reactions of  $C_{60}$  with SHCs 7 and 10a.



Figure 1. UV/Visible absorption spectra of 11 and 12 in CH<sub>2</sub>Cl<sub>2</sub>.

photolysis for 2 h, the mixture was separated by preparative HPLC to afford the corresponding adduct **12** in 22% yield. As described above for **11**, the [6,6]-closed structure of **12** was confirmed by the MALDI-TOF, UV/Visible (*Figure 1*), and <sup>13</sup>C-NMR spectra (*Figure S12*). Selective formation of **11** and **12** as the [6,6]-closed adducts was consistent with the result obtained previously for the addition of **3** to C<sub>60</sub>.<sup>[6]</sup>

Subsequently, these synthetic procedures for the derivatization with SHCs were applied to  $Sc_3N@I_h-C_{80}$ . After the addition of **6** into a solution of  $CS_2$  and  $Sc_3N@I_h-C_{80}$ , the mixture was separated by preparative HPLC to give **13** (*Scheme 4*). For derivatization using



**Scheme 4.** Reactions of  $Sc_3N@l_h-C_{80}$  with SHCs **7** and **10b**.

(MALDI-TOF) mass spectrum and the UV-visible spectrum (*Figure 1*) of **11** confirmed the formation of a [6,6]-closed adduct of  $C_{60}$  and **7**. The <sup>13</sup>C-NMR spectrum of **11** (*Figure S10* in the *Supporting Information*) showed 17 peaks for sp<sup>2</sup> carbon atoms of the  $C_{60}$ cage, 13 signals of which exhibited doubled intensities, indicative of the  $C_{2v}$  symmetry of the  $C_{60}$  cage by assuming the inversion of the SHC ring and rotation of the mesityl (Mes) groups within the NMR timescale. In addition, signals corresponding to the sp<sup>3</sup> carbon atom of the  $C_{60}$  cage, and to the spirocarbon atom of the SHC addend were also observed at 80.19 ppm and 50.83 ppm, respectively. These chemical shifts are similar to those of **4**,<sup>[31]</sup> confirming the [6,6]-closed structure of **11**.

In the case of **10a** and **10b**, cyclotrigermanes **8a**<sup>[49]</sup> and **8b**<sup>[50]</sup> were photolyzed in the presence of  $C_{60}$  and  $CS_2$  because **8a** and **8b** are reactive for the extrusion of **9a** and **9b**, respectively, under long-wavelength UV irradiation (*Scheme 2*). Hence, it is feasible to conduct the derivatization of fullerenes with SHCs **10a** and **10b** for one-pot syntheses. For this purpose, a toluene solution of  $C_{60}$ ,  $CS_2$ , and **8b** was irradiated in a *Pyrex* tube using a medium-pressure mercury arc lamp (*Scheme 3*). After the

**10b**, the photolysis of a toluene solution of  $Sc_3N@l_h^-C_{80}$ , **8b**, and  $CS_2$  using a medium-pressure mercury arc lamp for 1 h afforded the corresponding adduct **14**. The MALDI-TOF mass spectra of **13** and **14** show molecular ion peaks for the SHC adduct of  $Sc_3N@l_h^-C_{80}$ , with the fragment ion peak for  $Sc_3N@l_h^-C_{80}$ . In the Vis/NIR spectra, gentle curves with absorption shoulders around 760 nm were observed, which was similar to those of pristine  $Sc_3N@l_h^-C_{80}$ , as well as its [6,6]- and [5,6]-open methano-derivatives,<sup>[17-19,21-23]</sup> suggesting fulleroid structures of **13** and **14** (*Figure 2*). It is well known that fulleroid structures exhibit absorption spectra that resemble to those of the corresponding parent fullerenes due to the preservation of  $\pi$ -electronic systems.

In the <sup>13</sup>C-NMR spectrum, **14** showed 44 sp<sup>2</sup> carbon signals corresponding to the  $l_h$ - $C_{80}$  cage, in which eight signals were observed in half-intensities (*Figure S16*). Among the signals, two signals observed at 123.88 ppm and 122.10 ppm were assigned to those of bridgehead carbon atoms of the methano-addition site. In the upfield region, one quaternary carbon signal (56.82 ppm) was observed for the dithiocarbon atom. These results are consistent with the [6,6]-open structure of **14** with  $C_2$  symmetry by assuming that





Figure 2. Vis/NIR absorption spectra of 13, 14, and Sc<sub>3</sub>N@/ $_h$ -C<sub>80</sub> in CS<sub>2</sub>.

the Sc<sub>3</sub>N cluster possibly does not affect the molecular symmetry on the NMR timescale by its rotation inside the C<sub>80</sub> cage. In addition, methyl and aromatic carbon signals of the Mes groups were observed as broadened peaks probably due to the restricted ring rotation by their steric congestion. In contrast, no [5,6]-open SHC adduct was obtained in these results, which may be attributed to its low yield. In fact, the reactions of adamantylidene carbene to Sc<sub>3</sub>N@*l*<sub>*h*</sub>-C<sub>80</sub> afforded low yields of the [5,6]-open adduct along with the [6,6]-open adduct as the predominant product, respectively.<sup>[23]</sup> The <sup>13</sup>C-NMR spectrum of **13** also shows similar results indicating the [6,6]-open structure of **13**.

#### Theoretical Calculations

Structural and electronic properties of the SHC adducts were investigated by the density functional theory calculations. The optimized structures of **11** and **12** were obtained as **11**-I and **12**-I, respectively, by the B3LYP<sup>[51-53]</sup> method (*Figures 3* and *518*). The corresponding [5,6]-open adducts were also calculated as **11**-II and **12**-II, respectively. As a result, **11**-I is lower in energy than **11**-II by 10.87 kcal/mol, **12**-I is also



Figure 3. Structures of 11-I, 11-II, 12-I, and 12-II.

lower than **12**-II by 5.43 kcal/mol, supporting the selective formation of **11** and **12** as the [6,6]-open adduct.

In the case of **14**, optimized structures were calculated for the [6,6]-open adducts **14**-I-VII and the [5,6]-open adducts **14**-VIII-XI, by the M06- $2X^{[54]}$  methods (*Figures 4*, *S19*, and *S20*). In addition, the







**Figure 4.** Representation of 14-I–XI and the orientations of Sc<sub>3</sub>N cluster. Values in the parentheses are the relative energies in kcal/mol compared to that of 14-III.

orientations of the Sc<sub>3</sub>N cluster were changed in these isomers to examine the dependence of the relative energies on the orientations of the Sc<sub>3</sub>N cluster. *Figure 4* shows partial structures of **14**-I–XI in addition to their relative energies [kcal/mol] in parentheses. The results revealed that the **14**-I–V, in which one of the Sc atoms is oriented to the addition sites, respectively, are lower in energy than **4**-VI–VII that exhibit the



**Figure 5.** Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) of *a*) **11**, *b*) **12**, *c*) **13**, and *d*) **14** in ODCB containing 0.1  $\bowtie$  (Bu)<sub>4</sub>NPF<sub>6</sub>. In DPVs, peaks of the adducts and pristine EMFs are indicated by circles and squares, respectively. Conditions: working electrode, a glassy carbon electrode; counter-electrode, Pt wire; reference electrode, SCE; scan rate, 50 mV/s.

slantwise and horizontal orientations of the Sc<sub>3</sub>N clusters. Furthermore, the relative energies of 4-I-V fall within the range of 3.12 kcal/mol, suggesting that the Sc<sub>3</sub>N cluster possibly rotates around an axis pointing to the addition sites. Similar results were obtained for the [5,6]-adducts 14-VIII-XI. Such orientations of the Sc<sub>3</sub>N clusters have been reported commonly for the [6,6]-open and [5,6]-open methanobridged  $M_3N@I_h-C_{80}$  (M=Sc, Y) structurally determined by X-ray crystallography.<sup>[16,18,22,23]</sup> By the comparison of the adducts with the vertical orientations of the Sc<sub>3</sub>N cluster, the [6,6]-adducts 14-I-V are energetically lower than the [5,6]-adducts 14-VIII-X. This result may support the experimentally observed predominant production of the [6,6]-open adducts although low yield formation of the [5,6]-open adducts cannot be excluded. On the basis of these results, the most stable structure, 14-III is employed for the theoretical consideration of the electronic properties of 14.

## Electronic Effects of SHC Addends on Fullerenes

To obtain insight into the electronic properties of 11-14, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were conducted in o-dichlorobenzene (ODCB) as shown in Figure 5. Their redox potentials are summarized in Table 1 with those of the corresponding parent fullerenes. Both the reduction  $(E^{\text{red}})$  and the oxidation  $(E^{\text{ox}})$  potentials of **11–14** shifted to more negative values relative to those of pristine fullerenes, respectively, indicative of the electron-donating effects of SHCs as nucleophilic carbenes. In particular, the  $E^{ox}$  potentials of **13** and **14** are slightly lower than those of the related methanobridaed  $Sc_3N@l_h-C_{80}$ derivatives 15 - 19(Fiaure 6).<sup>[19,21,22]</sup> It is also noteworthy that **12** and **14** exhibited slightly lower  $E^{ox}_{1}$  potentials than **11** and **13**, respectively, suggesting that the energetically lower molecular orbitals of Ge-Ge bonds contribute more than those of Si-Si bonds. Previously, the similar slight cathodic shift of the  $E^{ox}_{1}$  potential has been reported



**Table 1.** Redox potentials [V] of **11**–**14**<sup>[a]</sup> and related compounds.

E <sup>ox</sup> 1	E <sup>red</sup> 1	E <sup>red</sup> <sub>2</sub>
+1.21	-1.12	-1.50
+0.90	-1.24	-1.66
+0.76	-1.23	-1.64
+0.59	-1.26	-1.62
+0.48	-1.35	-1.77
+0.45	-1.34	-1.74
+0.52	-1.24	-1.96
+0.56	-1.34	-1.90
+0.52	-1.37	-1.93
+0.50	-1.48	-2.01
+0.52	-1.51	-1.61
	$     E^{ox}{}_{1} + 1.21 + 0.90 + 0.76 + 0.59 + 0.48 + 0.45 + 0.52 + 0.56 + 0.52 + 0.56 + 0.52 + 0.50 + 0.52 $	$\begin{array}{c c} E^{\text{ox}} & E^{\text{red}} \\ & + 1.21 & -1.12 \\ & + 0.90 & -1.24 \\ & + 0.76 & -1.23 \\ & + 0.59 & -1.26 \\ & + 0.48 & -1.35 \\ & + 0.45 & -1.34 \\ & + 0.52 & -1.24 \\ & + 0.56 & -1.34 \\ & + 0.52 & -1.37 \\ & + 0.50 & -1.48 \\ & + 0.52 & -1.51 \end{array}$

<sup>[a]</sup> Values obtained by DPV are in volts relative to the ferrocene/ ferrocenium couple. <sup>[b]</sup> Data from ref. [31]. <sup>[c]</sup> Data from ref. [19]. <sup>[d]</sup> Data from ref. [21]. <sup>[e]</sup> Data from ref. [22].



**Figure 6.** Partial structures of  $Sc_3N@l_h-C_{80}$ -based methanofullerenes **15–19**.

Table 2. Calculated HOMO/LUMO Levels [eV].

Compound	НОМО	LUMO	
C <sub>60</sub> <sup>[a]</sup>	-5.99	-3.23	
<b>11</b> -I <sup>[a]</sup>	-5.57	-3.02	
<b>12-I</b> <sup>[a]</sup>	-5.52	-2.96	
Sc <sub>3</sub> N@ <i>I<sub>h</sub></i> -C <sub>80</sub> <sup>[b]</sup>	-6.44	-2.78	
<b>14</b> -III <sup>[b]</sup>	-6.14	-2.15	
<sup>[a]</sup> B3LYP/6-31G(d). <sup>[b]</sup> M06-2X/LanL2DZ[Sc, Ge], 6-31G(d)[C, H, N,			

S].

for the digermirane adduct of  $Lu_3N@l_h-C_{80}$  compared to the corresponding silicon analog.<sup>[55]</sup>

Furthermore, the electronic properties of **11–14** were evaluated by the theoretical calculations. *Table 2* summarizes the energies of the highest occupied molecular orbitals (HOMOs) and the LUMOs of **11-**I,

**12**-I, and **14**-III. The HOMO and LUMO levels of **11**-I are higher than those of  $C_{60}$  by +0.42 eV and +0.21 eV, respectively. Similarly, **12**-I, and **14**-III also exhibited shifts of the HOMOs and LUMOs to more positive values compared with those of the corresponding pristine fullerenes. These shifts in the MO levels are qualitatively consistent with the experimental cathodic shifts of the redox potentials, thereby confirming the electron-donating effects of SHCs.

## Conclusions

The preparation of SHCs was established by the cycloaddition of synthetically more accessible disilenes and digermenes to  $CS_2$ . The reactions of SHCs with  $C_{60}$ and  $Sc_3N@l_h-C_{80}$  produced the corresponding [6,6]methanofullerenes 11-14, which were characterized using spectroscopic, electrochemical, and theoretical studies. The preferential formation of the [6,6]-methanofullerenes over the [5,6]-isomers is consistent with the previous examples of carbene addition to C<sub>60</sub> and Sc<sub>3</sub>N@l<sub>h</sub>-C<sub>80</sub>, and supported by relative stabilities of optimized structures of the [6,6]-isomers. The electrondonating effect of the SHC addends was also indicated for 11-14, for which relatively low oxidation potentials were obtained. The cathodic shifts of redox potentials of 11, 12, and 14 were verified by the calculated energies of HOMOs and LUMOs with those of  $C_{60}$  and  $Sc_3N@l_h-C_{80}$ .

# **Experimental Section**

## Materials and General Method

All chemicals were reagent grade, purchased from Wako Pure Chemical Industries Ltd. Sc<sub>3</sub>N@l<sub>h</sub>-C<sub>80</sub> was purchased from Luna Innovations Inc. o-Dichlorobenzene (ODCB) was distilled from P<sub>2</sub>O<sub>5</sub> under vacuum before use. Toluene was distilled from benzophenone sodium ketyl under dry N<sub>2</sub> prior to use. Reagents were used as purchased unless otherwise specified. HPLC was performed on an LC-908 apparatus (Japan Analytical Industry Co. Ltd.) monitored using a UV3702 detector. Analytical HPLC was performed on a PU-1586 pump with a UV-1575 detector (JASCO Corp.). Buckyprep-M and 5PBB(Nacalai,  $\phi$  10 mm  $\times$  250 mm,  $\phi$ 4.6 mm × 250 mm) columns were used for HPLC separation. Toluene was used as the eluent for HPLC. The <sup>1</sup>H- and <sup>13</sup>C-NMR measurements were conducted on a JEOL ECA-500 spectrometer (JEOL Ltd.). MALDI-TOF mass experiments were performed on an Autoflex III

Smartbeam mass spectrometer (Bruker Daltonics) with 1,1,4,4-tetraphenyl-1,3-butadiene (TPB) as the matrix in both positive and negative ion modes. Absorption spectra were measured using a UV-3150 spectrophotometer (Shimadzu Corp.). IR Spectra were obtained by an FT-730 spectrometer (HORIBA, Ltd.). Cyclic voltammograms and differential pulse voltammograms were recorded on a BAS CV50W electrochemical analyzer (BAS Inc.). The reference electrode was a saturated calomel reference electrode (SCE). The glassy carbon electrode was used as the working electrode, and a platinum wire was used as the counter electrode. All potentials are referenced to the ferrocene/ferrocenium couple (Fc/Fc<sup>+</sup>) as the standard. (Bu)<sub>4</sub>NPF<sub>6</sub> (0.1  $\mu$ ) in ODCB was used as the supporting electrolyte solution. The cyclic voltammograms were recorded using a scan rate of 50 mV/s. The differential pulse voltammograms were obtained using a pulse amplitude of 50 mV, a pulse width of 50 ms, a pulse period of 200 ms, and a scan rate of 50 mV/s.

Synthesis of 11. A solution of 5<sup>[48]</sup> (400 mg, 0.97 mmol) in benzene (3 ml) in a guartz tube was degassed using freeze-pump-thaw cycles under reduced pressure, and irradiated by a 125 W lowpressure mercury lamp for 20 h. Subsequently, the resultant solution containing 6 was added to a benzene solution of  $C_{60}$  (10 mg,  $1.4 \times 10^{-2}$  mmol) and CS<sub>2</sub> (0.8 ml) under an argon atmosphere in the dark. After stirring the solution for 12 h, preparative HPLC separation of the reaction mixture with a 5PBB column ( $\phi$  10×250 mm) afforded **11** in 36% yield. UV/Vis (CS<sub>2</sub>): 430. IR (KBr) 1026. <sup>1</sup>H-NMR (CDCl<sub>3</sub>/CS<sub>2</sub> 1:1): 6.78-6.56 (m, 8 H); 2.75-2.41 (br. s, 12 H); 2.33-2.01 (m, 24 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>/CS<sub>2</sub> 1:1): 148.13 (4 C); 147.52 (4 C); 145.90 (8 C); 145.29 (4 C); 145.21 (4 C); 144.95 (2 C); 144.84 (4 C); 144.73 (6 C); 144.33 (4 C); 143.95 (4 C); 143.03 (4 C); 142.99 (4 C); 142.84 (2 C); 142.25 (4 C); 142.19 (4 C); 140.20 (4 C); 139.63 (8 C); 130.43 (8 C); 80.14 (2 C); 50.83 (1 C); 27.30 (4 C); 25.14 (8 C). MALDI-TOF MS (TPB): 1329 (*M*<sup>-</sup>), 720 (C<sub>60</sub><sup>-</sup>).

Synthesis of **12**. A toluene solution (25 ml) of **8b**<sup>[50]</sup> (99.0 mg,  $9.7 \times 10^{-2}$  mmol), C<sub>60</sub> (10.0 mg,  $1.4 \times 10^{-2}$  mmol), and CS<sub>2</sub> (3.2 ml) in a *Pyrex* tube was degassed using freeze-pump-thaw cycles under reduced pressure, and irradiated by a 125 W medium-pressure mercury lamp for 2.5 h. Preparative HPLC separation of the reaction mixture with a 5PBB column ( $\phi$  10×250 mm) afforded **12** in 22% yield. UV/Vis (CS<sub>2</sub>): 437. IR (KBr) 1072. <sup>1</sup>H-NMR (CDCl<sub>3</sub>/CS<sub>2</sub> 1:1): 7.23 (*t*, *J*=7.5, 4 H); 7.05 (*d*, *J*=7.5, 8 H); 3.19–2.71 (br. *s*,

16 H); 0.97 (br. s, 24 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>/CS<sub>2</sub> 1:1): 148.58 (8 C); 148.02 (4 C); 145.85 (4 C); 145.28 (4 C); 145.19 (4 C); 144.96 (2 C); 144.73 (4 C); 144.70 (2 C); 144.32 (4 C); 143.97 (4 C); 143.06 (4 C); 143.01 (4 C); 142.84 (2 C); 142.21 (4 C); 142.14 (4 C); 140.42 (4 C); 139.22 (4 C); 138.40 (4 C); 129.99 (4 C); 126.38 (8 C); 80.96 (2 C); 51.62 (1 C); 30.48 (8 C); 15.13 (8 C). MALDI-TOF MS (TPB): 1474 ( $M^+$ ), 720 ( $C_{60}^+$ ).

Synthesis of 13. The procedure was similar to that for **11**. A solution containing **6** prepared from **5**<sup>[48]</sup> (200 mg, 0.49 mmol) in benzene (4 ml) was added to a benzene solution of  $Sc_3N@l_h-C_{80}$  (0.6 mg, 5.4×  $10^{-4}$  mmol) and CS<sub>2</sub> (0.4 ml), and stirred for 12 h under an argon atmosphere in the dark. Preparative HPLC separation of the mixture with a Buckyprep-M column ( $\phi$  10×250 mm) afforded **11** in 36% yield. Vis/NIR (CS<sub>2</sub>): 750. IR (KBr) 1026. <sup>1</sup>H-NMR (CDCl<sub>3</sub>/CS<sub>2</sub> 1:1): 6.76– 6.46 (m, 8 H); 3.08-2.58 (m, 24 H); 2.34-2.14 (m, 12 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>/CS<sub>2</sub> 1:1): 153.04 (2 C); 151.96 (2 C); 149.86 (2 C); 147.84 (8 C); 146.81 (2 C); 146.77 (2 C); 146.56 (2 C); 144.97 (2 C); 144.82 (2 C); 144.80 (2 C); 144.48 (2 C); 144.20 (1 C); 144.10 (1 C); 143.86 (4 C); 143.59 (2 C); 143.25 (2 C); 142.99 (2 C); 142.57 (4 C); 142.32 (1 C); 141.53 (2 C); 141.22 (2 C); 140.97 (2 C); 140.89 (2 C); 140.23 (4 C); 140.03 (4 C); 139.78 (4 C); 139.36 (2 C); 139.15 (1 C); 138.93 (2 C); 138.82 (2 C); 138.75 (2 C); 137.67 (2 C); 135.36 (2 C); 135.20 (2 C); 134.63 (1 C); 134.33 (2 C); 130.84 (4 C); 130.45 (8 C); 128.91 (2 C); 128.41 (1 C); 98.45 (1 C); 97.75 (1 C); 56.11 (1 C); 27.12 (4 C); 25.38 (8 C). MALDI-TOF MS (TPB): 1717 (*M*<sup>-</sup>), 1109 (Sc<sub>3</sub>N@*I*<sub>*b*</sub>-C<sub>80</sub><sup>-</sup>).

Synthesis of 14. The procedure was similar to that for 12. A toluene solution (25 ml) of 8a<sup>[49]</sup> (75.0 mg,  $8.0 \times 10^{-2}$  mmol),  $Sc_{3}N@l_{h}-C_{80}$ (3.0 mg, 2.7×  $10^{-3}$  mmol), and CS<sub>2</sub> (6.0 ml) in a *Pyrex* tube was degassed using freeze-pump-thaw cycles under reduced pressure, and irradiated by a 125 W mediumpressure mercury lamp for 2 h. Preparative HPLC separation of the reaction mixture with a 5PBB column ( $\phi$  10×250 mm) afforded **14** in 59% yield. Vis/NIR (CS<sub>2</sub>): 742. IR (KBr) 1020. <sup>1</sup>H-NMR (CDCl<sub>3</sub>/CS<sub>2</sub> 1:1): 6.78-6.75 (m, 8 H); 2.43-2.34 (m, 24 H); 2.24 (s, 6 H); 2.22 (s, 6 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>/CS<sub>2</sub> 1:1): 152.96 (2 C); 151.88 (2 C); 150.57 (2 C); 150.36 (2 C); 149.80 (2 C); 147.92 (2 C); 146.80 (2 C); 146.69 (2 C); 146.48 (2 C); 145.88 (1 C); 145.06 (1 C); 144.98 (2 C); 144.81 (2 C); 144.73 (2 C); 144.45 (2 C); 144.18 (1 C); 143.81 (2 C); 143.53 (2 C); 143.28-142.93 (4 C); 142.87 (2 C); 142.56 (2 C); 142.46 (2 C); 141.49 (2 C); 141.19 (2 C); 140.92 (4 C); 140.88 (2 C); 140.10 (2 C); 140.08 (2 C); 139.67 (2 C); 139.54 (2 C); 139.36 (2 C); 139.23 (1 C); 139.03 (1 C); 138.82 (2 C); 137.71 (2 C); 135.46 (1 C); 135.28 (4 C); 134.69 (2 C); 134.42 (2 C); 133.95 (2 C);132.54 (4 C); 130.14 (4 C); 129.96 (4 C); 123.88 (1 C); 122.10 (1 C); 56.82 (1 C); 25.22-24.67 (8 C); 21.17-20.91 (4 C). MALDI-TOF MS (TPB): 1804–1812 ( $M^+$ ), 1109 (Sc<sub>3</sub>N@ $I_h$ -C<sub>80</sub><sup>+</sup>).

#### Computational Method

All calculations were conducted using the Gaussian09<sup>[56]</sup> program. Optimized structures were obtained at the B3LYP<sup>[51–53]</sup> and the M06-2X<sup>[54]</sup> level of theory using basis sets of  $6-31G(d)^{[57]}$  [C, H, N, Si, S], LanL2DZ<sup>[58]</sup> [Sc, Ge].

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## **Author Contribution Statement**

*M. K.* and *T. A.* designed this project. *M. K.* planned the experimental work, and performed the computational calculations. *Y. A.* and *S. K.* conducted the experimental work. *M. Y.* and *Y. M.* carried out the analysis of the compounds. *M. K., M. F.*, and *T. A.* contributed to the writing of the manuscript.

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