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J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/ja3073929 • Publication Date (Web): 04 Sep 2012 Downloaded from http://pubs.acs.org on September 7, 2012

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Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Synthesis of a Silylene-Bridged Endohedral Metallofullerene $Lu_3N@I_h-C_{80}$

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Abstract:

Functionalization of endohedral metallofullerenes has been shown to differ depending on photochemical or thermal pathways. We report that Lu₃N@ I_h -C₈₀ reacts with thermally generated bis(2,6-diethylphenyl)silylene with high selectivity and forms a mono-silylated derivative **1b**. Unexpectedly, **1b** undergoes photochemical conversion to afford an isomer **1a** under ambient light. These adducts were characterized using NMR, visible-near-IR spectroscopy, and MALDI-TOF mass spectrometry. Single crystal X-ray structure determination of **1a** reveals a rare example of an open 1,2-adduct at the [5,6]-ring junction of the I_h -C₈₀ cage. The electrochemical study reveals that the redox potentials of **1a** and **1b** are shifted cathodically compared to those of pristine Lu₃N@ I_h -C₈₀, and that mono-silylation is effective to fine-tune the electronic properties of endohedral metallofullerenes as well as empty fullerenes. Density functional theory calculations were also performed, which provide a theoretical basis for the structures and the behavior of the encapsulated Lu₃N cluster.

Introduction

Many research groups have investigated the chemical reactivity of endohedral metallofullerenes (EMFs), the properties of which have been proven to differ greatly from those of empty fullerenes.¹ The electronic structures of EMFs are of great interest because the encaged metal atoms and the carbon cages are regarded to have cationic and anionic characters, respectively, as a result of electron transfer. After many years of study, exohedral chemical functionalization^{1b-e} is widely recognized as an effective method for modifying the physical and chemical properties of EMFs, which can serve as functional materials in molecular electronics, nanomaterials sciences,² and biochemistry.³

To design new valuable organofullerenes for these applications, it is necessary to understand how exohedral chemical functionalization affects the electronic properties of fullerenes. Introduction of heteroatoms such as electropositive silicon directly onto fullerene surfaces has induced remarkable changes in the electronic characteristics of fullerenes.⁴ We have described the derivatization of EMFs by the addition of reactive silicon compounds, such as disiliranes⁵ and siliranes.⁶ In fact, electrochemical analysis and theoretical calculation revealed that silylated fullerene derivatives have more negative charge on the cage than the parent fullerenes have. Moreover, we have demonstrated that the number of silicon atoms on the fullerene surface plays an important role in the electronic properties and the movement of the encapsulated metal atoms. For example, the three-dimensional movement of metal atoms in $M_2@I_h$ -C₈₀ is restricted to the two-dimensional movement because silvlation alters the electrostatic potentials and thereby the dynamic behavior of the cationic metals.^{5a-c} Such regulation of the dynamic behavior of the encaged species will be useful for the application of EMFs as functional materials in molecular electronics. Nevertheless, silvlation of EMFs has been hitherto limited to bis-silvlation⁵ and carbosilylation⁶ using disiliranes and siliranes. Therefore, it is valuable to develop convenient and versatile synthetic methods for silvlation to provide various silvlated EMFs. As a candidate for mono-silvlating reagents for EMFs, silvlenes, divalent silicon species, are promising compounds because the addition of silvlenes to unsaturated C-C bonds occurs readily.⁷ Carbenes, the carbon analogues of silvlenes, are well known as common reagents for exohedral functionalization of EMFs^{1,8} and hollow fullerenes.⁹ In fact, photochemically generated silylenes react with C_{60} and C_{70} to afford the corresponding silylene adducts.¹⁰

This report describes the mono-silylation of $Lu_3N@I_h-C_{80}$,¹¹ which is widely known as a trimetallic nitride templated (TNT) endohedral metallofullerene. To achieve effective silylation, we used a new silylene precursor, 9,9-bis(2,6-diethylphenyl)-9-silabicyclo[6.1.0]nonane **2**, which can generate silylene efficiently under both thermal and photochemical conditions (Scheme 1). Additionally described is the detailed characterization of two obtained products corresponding to $Lu_3N@I_h-C_{80}(SiDep_2)$. Of particular interest is the isolation of a silylene-bridged silafulleroid structure, which represents a rare example of an open type of 1,2-adduct at the [5,6]-ring junction of the I_h-C_{80} cage. To the best of our knowledge, the only other example is a recent report of azide addition to $Sc_3N@I_h-C_{80}$ to form a [5,6] azafulleroid.^{8g}

Results and Discussion

Synthesis of Lu₃N@ I_h -C₈₀(SiDep₂) 1a and 1b. The reaction of Lu₃N@ I_h -C₈₀ with the silvlene precursor 2 (see Supporting Information) was conducted as follows (Scheme 1). A solution of Lu₃N@ I_h -C₈₀ (2.0 mg, 1.3 × 10⁻⁶ mol) and 2 (13.7 mg, 3.4 × 10⁻⁵ mol) in 1,2-dichlorobenzene (ODCB, 20 mL) was placed in a Pyrex tube and degassed using

freeze-pump-thaw cycles under reduced pressure. It was then heated for 23 min at 180 °C under an argon atmosphere in the dark. After cooling the solution, a small portion of the solution was analyzed by HPLC using a Buckyprep column. The HPLC chromatogram revealed a new fraction (peak F_1) corresponding to a product with high intensity (Figure 1). In addition, another fraction (F_2) appeared at a slightly earlier retention time which gradually increased when the reaction mixture was exposed to ambient light at room temperature, as shown in Figure 2.

Subsequently, the reaction mixture was separated by preparative HPLC using a Buckyprep and a 5NPE column. Two compounds, **1a** and **1b**, were obtained from the HPLC fractions F_2 and F_1 (Figure S1, see Supporting Information). Additional analysis of **1a** and **1b** using MALDI-TOF mass spectrometry showed weak peaks at m/z 1793, which correspond to the molecular ion peak for the isomeric silylene adducts, Lu₃N@ I_h -C₈₀(SiDep₂) (see Supporting Information, Figure S2). In addition, strong fragment peaks were observed at m/z 1499 for **1a** and **1b**, which are assignable to the parent cage, Lu₃N@ I_h -C₈₀. Therefore, it is reasonable to assume that the silylene Dep₂Si, generated by the thermal extrusion from **2**, reacted with Lu₃N@ I_h -C₈₀ to afford **1b**, which isomerized slowly to **1a** under room light. It is noteworthy that multi-adducts such as Lu₃N@ I_h -C₈₀(SiDep₂)₂ were not observed. Consequently, silylation using **2** produces selective derivatization of Lu₃N@ I_h -C₈₀. It is further confirmed that exposure of a degassed ODCB solution of **1b** to ambient light afforded **1a** and pristine Lu₃N@ I_h -C₈₀ within 24 h (Figure 3a). Under the same conditions, **1a** in ODCB decomposed to give Lu₃N@ I_h -C₈₀ (Figure 4a). Although **1a** and **1b** are photolabile, both isomers are stable in the dark at room temperature (Figures 3b, 4b).

Although 2 efficiently generates the silylene Dep_2Si by irradiation using a medium pressure mercury lamp, UV irradiation of an ODCB solution of 2 and $Lu_3N@I_h-C_{80}$ gave neither 1a nor 1b, while starting materials were consumed. The cophotolysis of $Lu_3N@I_h-C_{80}$ and 2 is expected to be disadvantageous for the synthesis of 1a and 1b because these adducts degrade to eliminate the silylene addend by photoirradiation, as described above.

For comparison, we examined the reaction of $Sc_3N@I_h-C_{80}$,^{1e} which is the most abundant and well-explored TNT EMF, with Dep₂Si. However, the addition reactions of $Sc_3N@I_h-C_{80}$ and Dep₂Si proceeded much less efficiently to afford poor yields of adducts under the thermal or the photochemical conditions that are identical with those for Lu₃N@I_h-C₈₀. The isolation and structural analyses were frustrated because of low quantities of the adducts, which were confirmed only by MALDI-TOF mass spectrometry. Recently, Echegoyen et al. reported the reactions of electrochemically generated $M_3N@I_h-C_{80}$ dianions (M = Sc, Lu) with electrophiles and ascribed the superior reactivity of Lu₃N@I_h-C₈₀ dianion according to the localization of its HOMO on the cage.^{13c} Although the origin of the different reactivities of $M_3N@I_h-C_{80}$ toward

Dep₂Si has not been clarified at present, the HOMOs of $M_3N@I_h-C_{80}$ may play an important role on the reactions with silylenes, weak electrophiles. We are currently investigating the reactivities of $M_3N@I_h-C_{80}$ with several organosilicon compounds.

Structural Determination of 1a and 1b. For the structural characterization of 1a and 1b, NMR analysis and X-ray crystallography were performed. There are four possible isomeric structures for the derivatized I_h -C₈₀ cage resulting from 1,2-addition of a silvlene bridge as shown in Figure 5. The ¹H NMR spectra of **1a** and **1b** are shown in Figure S3 (see Supporting Information). The addition of Dep₂Si at the [5,6]-ring junction will make the two Dep substituents nonequivalent, whereas addition at the [6,6]-ring junction will produce equivalent Dep moieties. Therefore, we specifically examined the ¹H NMR signals of the *para* aryl protons of the Dep rings. The spectrum of **1a** displays a pair of triplets at 7.47 and 7.42 ppm, which are assigned as nonequivalent para aryl protons, and suggests that the Dep₂Si group is bridged over the [5,6]-ring junction (Figure S3a). In contrast, the spectrum of **1b** exhibits one triplet signal at 7.50 ppm, which reflects the equivalency of the two Dep groups (Figure S3b). These observations suggest that 1a and 1b are Dep₂Si adducts at the [5,6]-ring and [6,6]-ring junctions, respectively. ¹³C NMR measurements can help to establish whether these compounds are silacyclopropane derivatives or open cage silafulleroids. The ¹³C NMR spectrum of **1a** showed 44 signals from the sp² carbon atoms of the I_{h} -C₈₀ cage, as well as four quaternary sp² carbons of the Dep groups between 70 ppm and 155 ppm (Figure S4, see Supporting Information). In addition, four tertiary sp^2 carbons and two sets of ethyl carbons of the nonequivalent Dep groups were observed, which is consistent with ¹H NMR results described above. These spectral data suggest that **1a** has C_s symmetry, resulting from 1,2-addition of Dep₂Si at the [5,6]-ring junction of the I_h -C₈₀ cage. Consequently, the structure of **1a** is determined to be the silvlene-bridged silafulleroid type, which represents the rare example of an [5,6]-open I_h -C₈₀ EMF derivative. However, the ¹³C NMR spectrum of **1b** showed two nonequivalent singlet signals at 85.14 and 77.17 ppm, which are ascribed to the sp³ carbons of the silacyclopropane ring (Figure S5 in Supporting Information). Previously, we reported the synthesis of the fullerene-silylene adducts $C_{60}SiDip_2^{10a}$ and $C_{70}SiDip_2^{10b}$ (Dip = 2,6-diisopropylphenyl) with silacyclopropane structures. The sp³ carbon signals of the silacyclopropane rings were observed at 71.12 ppm for C₆₀SiDip₂ and 78.51 and 67.77 ppm for C₇₀SiDip₂, respectively. In the ¹³C NMR spectrum of 1b, 45 sp² carbon signals are assigned to 42 carbons of the I_h -C₈₀ cage and three quaternary aromatic carbons of the Dep groups. As for the tertiary sp² ring carbons of the Dep groups, one signal for the *para*-position and two signals for the *meta*-positions are observed, respectively. An additional four sp³ carbon signals are also found for the two sets of ethyl groups in the upfield region. The lowered spectral symmetry of the Dep groups is rationalized

based on restriction of the free rotation of the two equivalent Dep rings in **1b** as a result of steric constraints. These observations are consistent with the structure of **1b** with C_s symmetry. Therefore, it is concluded that **1b** should be a "closed" silamethano fullerene rather than a silafulleroid (Figure S3b).

Visible-near-infrared (Vis-NIR) spectroscopy is a useful method for characterization of the electronic structures of hollow fullerenes and EMFs. Moreover, exohedrally functionalized fullerenes show characteristic Vis-NIR spectra that are more dependent on the regiochemistry of functionalization than on the type of functional group.^{6,8,11,15,16} For example, the spectra of 1,4-Sc₃N@ I_h -C₈₀(Mes₂Si)₂CH₂^{5b} and 1,4-Sc₃N@ I_h -C₈₀(CH₂C₆H₅)₂¹² are quite similar, with absorption maxima around 900 nm, although they have different substituents. The Vis-NIR absorption spectra of **1a** and **1b** are shown with that of Lu₃N@ I_h -C₈₀ in Figure 6. The spectrum of **1b** shows a distinctive absorption maxima around 700 nm, which resembles those of the reported [6,6]-methano bridged Lu₃N@ I_h -C₈₀ derivatives.¹³ This spectral similarity supports the assignment of **1b** as the [6,6]-adduct, as determined by ¹H and ¹³C NMR analyses. Meanwhile, **1a** shows a broad and gently sloping absorption around 700 nm with no characteristic absorption maximum. This finding also confirmed that Vis-NIR spectra of derivatized isomers of EMFs are specific to the regiochemistry of derivatization. It is worthwhile noting that the spectrum of **1a** shows no resemblance to that of 1,4-Lu₃N@ I_h -C₈₀(CH₂C₆H₅)₂, which was reported to have a noticeable absorption maximum around 800 nm.¹²

Fortunately, a thin red crystal suitable for X-ray diffraction was obtained from a solution of **1a** in a mixture of CS₂/ODCB at 0 °C with the addition of hexane to lower the solubility of the adduct. The structure of **1a** was determined by X-ray structural analysis. A drawing of the adduct is shown in Figure S6 (see Supporting Information), with selected bond lengths in Table S1. The crystal structure of **1a** shows some disorder both in the positions of the Lu₃N cluster and the cage carbon atoms. There are two cage orientations of the C₈₀ cage that have a pseudo- D_{5d} symmetry of the derivatized I_h -C₈₀. These cages are related by a crystallographic mirror plane and occupy a common site. Such disorder is frequently observed when addition occurs at [5,6] ring junctions.^{15b}

Only one of these orientations and the primary Lu_3N unit, which consists of N1, Lu1, Lu3, and Lu3' (symmetry code' = 1/2-x, 1/2-y, z), are shown in Figure S7. Lu1 is situated on the crystallographic mirror plane with a fractional occupancy of 0.96. Lu3 and Lu3' have fractional occupancies of 0.85. Lu3' is generated by reflection of Lu3 through a crystallographic mirror plane.

The X-ray structure showed unambiguously that the addition of silylene to the I_h -C₈₀ cage

had occurred at the [5,6]-ring junction. In addition, the C1–C2 distance at the site of silylene functionalization elongated to 2.25(5) Å, which confirms that **1a** possesses an open structure. The open structure with aza-bridged 4-isopropoxyphenynitrene at the [5,6] position of $Sc_3N@I_h-C_{80}$ yielded a C1–C2 distance of 2.161(2) Å, in general agreement with the shorter covalent radius of N relative to Si.^{8g} Open structures at [6,6]-ring junctions on the I_h -C₈₀ cage have been reported for La₂@ I_h -C₈₀(Ad) and Y₃N@ I_h -C₈₀C(CO₂CH₂Ph)₂, for which the functionalized C–C distances are 2.164(3) Å and 2.30(3) Å, respectively.^{8e,14a} The distance of the C1–C2 separation at the [5,6]-ring junctions. The Si–C bond lengths (Si1–C1, 1.87(3) Å; Si1–C2, 1.88(3) Å) between the addend and the I_h -C₈₀ cage are close to the normal Si–C single bond lengths in organosilanes.

The encapsulated Lu₃N cluster shows disorder of the Lu atoms, whereas the N atom has one site, which lies on a crystallographic mirror plane. The primary Lu₃N unit is planar with the sum of Lu–N–Lu bond angles being 360.0° (Lu1–N1–Lu3, 120.3(7)°; Lu1–N1–Lu3', 120.3(7)°; Lu3–N1–Lu3', 119.4(7)°). The Lu–N bond lengths (Lu1–N1, 2.03(1) Å; Lu3–N1, 2.096(7) Å; Lu3'–N1, 2.096(7) Å) are comparable to those reported for pristine Lu₃N@*I*_h-C₈₀, which range from 1.980(6)–2.0819(8) Å (Table S1).¹¹ The Lu1 atom is pointing to the silylated site, and is almost collinear with the N1 and Si1 atoms, as indicated by the N1–Lu1–Si1 bond angle (180.0(4)°).

The positional relation between the cage and Lu atoms was also investigated. As shown in Figure 7, Lu3 and Lu3' reside close to a hexagon and a pentagon highlighted respectively in yellow-green and purple in the interior of the cage. The distances from Lu3 to the nearest carbon atoms of the cage range from 2.37(3) Å to 2.47(3) Å, whereas those from Lu3' fall within a range from 2.23(3) Å to 2.56(3) Å. In addition, the distances between Lu1 and C1 and C2, the [5,6]-ring carbons functionalized by silylene, are 2.54(3) and 2.53(3) Å, respectively. These nonbonded Lu–C distances are slightly elongated compared to those of pristine Lu₃N@*I*_h-C₈₀ (2.112(7)–2.220(7) Å),¹¹ as a result of the addition of the silylene. The orientation of the Lu₃N cluster, in which one Lu atom is pointing to the functionalized site, is similar to those of the methanofulleroid derivatives of M₃N@*I*_h-C₈₀ (M = Sc, Y).¹⁴

Electrochemical Properties of 1a and 1b. The redox potentials of 1a and 1b were measured using cyclic voltammetry (CV) and differential pulse voltammetry (DPV), and are listed in Table 1 along with those of related compounds. The voltammograms of 1a and 1b are presented in Figure S8 (see Supporting Information). These silvlated EMFs afforded irreversible oxidation and reduction processes. The first oxidation of the silvlated derivatives led to removal of the addend from the carbon cage to give $Lu_3N@I_h-C_{80}$, as observed for other silvlated EMFs

such as $Sc_3N@I_b-C_{80}(Mes_2Si)_2CH_2$.^{5b} The first oxidation peak potentials of **1a** and **1b** were shifted cathodically by 340 and 180 mV, respectively, compared to those of Lu₃N@ I_h -C₈₀. The first reduction peak potentials were also cathodically shifted by 40 mV for 1a and 130 mV for 1b, respectively. In addition, these cathodic shifts of the redox potentials of 1a and 1b, compared to those of pristine $Lu_3N@I_h-C_{80}$, are smaller than those observed for the bis-silvlated EMFs, $Sc_3N@I_h-C_{80}(Mes_2Si)_2CH_2$,^{5b} and $La_2@I_h-C_{80}(Dep_2Si)_2CH_2$.^{5c} Similar weak effects on the reported for potentials have been the carbosilylated redox EMFs. $La_2@I_h-C_{80}Dep_2Si(CH_2)CH(t-BuPh)$.⁶ In contrast, the redox potentials of the carbene and the Bingel–Hirsch derivatives of EMFs are shifted less cathodically than 1a and 1b, as expected for electronically neutral carbon functional groups.^{2d,13} For example, the cathodic shifts of the first oxidation potentials of carbon-bridged methano $Lu_3N@I_h-C_{80}$ derivatives are observed between 20-70 mV as reported by Echegoyen et al.^{13b,c} These results demonstrate that introduction of silicon atoms onto the Lu₃N@ I_h -C₈₀ cages represents an effective way to raise the LUMO levels of EMF derivatives. By comparing the redox data for 1a and 1b, it is noteworthy that the redox potentials of the silvlated EMFs depend on both the electronic properties of the exohedral functionality and the π -conjugation of the cage structures.

Theoretical Calculations. To obtain insight into the structures of the silvlated products, theoretical calculations were conducted for 1a and 1b. The geometries of the compounds were optimized at the M06-2X¹⁸/6-31G(d)¹⁹[C, H, N, Si], LanL2DZ²⁰[Lu] levels as shown in Figure 8. The optimized structure of **1a** shows good agreement with the result of X-ray crystal analysis. The important calculated bond lengths are shown in Table S1 for comparison with those obtained from X-ray analysis. The silylene functionalized C-C distance is calculated as 2.261 Å, and the Si–C bond length between the addend and the I_h -C₈₀ cage is almost within regular values. These results also confirm that the structure of **1a** is an open silafulleroid, which strongly supports the spectroscopic data. As shown in the X-ray structure of **1a**, the Lu1 atom is pointing at the silvlated site with an almost collinear orientation of Si1, Lu1, and N1 atoms. Therefore, we have also calculated four optimized structures I-IV, for isomers of 1a with varied orientations of the encapsulated Lu₃N cluster (Figure S9 in Supporting Information). The relative energies of I-IV compared to that of 1a are in the narrow range of 4 kcal/mol (Table S2). Thus, the Lu_3N cluster can be assumed to rotate inside the cage around an axis passing along the Lu-N bond that is pointing to the open C-C bond. In contrast, the isomer V, in which the Lu₃N cluster is positioned on the equatorial plane viewed from the silvlated site as the pole, was calculated as 18.4 kcal/mol less stable than 1a. The calculated structure of 1b is shown in Figure 8b. Based on the relative energies, these results show that **1b** is 19.2 kcal/mol less stable than 1a. In the optimized structure of 1b, the Lu_3N cluster is located almost coplanar with the

silacyclopropane ring, and one of the Lu atoms is directed to the opposite side of the silylated C–C bond. However, no energy minimum is obtained for **1b** if the orientation of the Lu_3N cluster is reversed so that one of the Lu atoms is oriented to point at the silylated site. In this case, the silylated C–C bond is broken during the structural optimization process.

Conclusion

We have described the first example of a reaction of $Lu_3N@I_h-C_{80}$ with a thermally generated silylene. A silylene adduct of $Lu_3N@I_h-C_{80}$, **1b**, is obtained as the sole product during the thermal reaction in the dark. It is particularly interesting that **1b** is transformed slowly into an isomeric product 1a under ambient light. Characterization using NMR, Vis-NIR, and MS elucidated the structures of **1a** and **1b**, which were assigned respectively to [5,6]-silafulleroid and [6,6]-silacyclopropane. The structure of **1a** has been established unequivocally using single-crystal X-ray analysis. In comparison with the Prato and the Bingel-Hirsch adducts of $M_3N@I_h-C_{80}$ (M = Sc, Y), for which [5,6]-closed and [6,6]-open derivatives have been reported, respectively, the silvlene addition is remarkable because it leads to [5,6]-open and [6,6]-closed structures. The theoretically optimized structure of 1a verified the structural features inferred from X-ray analysis. From the calculated relative energies, 1a is postulated to be more stable than 1b, which might offer some clue about the photochemical transformation of 1b into 1a. The results of electrochemical examination indicate that, because of the electron-donating silyl groups, 1a and 1b are more electronegative than pristine $Lu_3N@I_h-C_{80}$. In addition to the electronic effect, exohedral functionalization affects the movement of the encapsulated cluster. Thus, the development of silvlation procedures broadens the scope of functionalization of EMFs for future applications.

Experimental Section

General. All chemicals were of reagent grade, purchased from Wako Pure Chemical Inds. Ltd. Lu₃N@ I_h -C₈₀ was purchased from Luna Innovations Inc. 1,2-Dichlorobenzene (ODCB) was distilled from P₂O₅ under vacuum before use. Reagents were used as purchased unless otherwise specified. High-performance liquid chromatography (HPLC) was performed on a LC-908 apparatus (Japan Analytical Industry Co. Ltd.) monitored using a UV detector at 330 nm. Buckyprep (i. d. 20 mm × 250 mm) and 5NPE (i. d. 20 mm × 250 mm) columns (Nacalai Tesque Inc.) were used for preparative HPLC separation. Toluene was used as the eluent for HPLC. The ¹H, ¹³C, and ²⁹Si NMR measurements were conducted on spectrometers (AVANCE 500, 600; Bruker Analytik GmbH) with a CryoProbe system (Bruker Biospin K.K.) in 1,1,2,2-tetrachloroethane- d_2 . The outer standard reference was TMS for ²⁹Si NMR. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass experiments

were recorded (Biflex III; Bruker) 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 spectrophotometer (UV-3150; Shimadzu Corp.). Cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) were recorded on an electrochemical analyzer (BAS CV50W; 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⁺) as the standard. 0.1 M (n-Bu)₄NPF₆ in ODCB was used as the supporting electrolyte solution. The CVs were recorded using a scan rate of 100 mV/s. The DPVs 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.

Thermal Reaction of $Lu_3N@I_h-C_{80}$ with 2. An ODCB solution (20 mL) of $Lu_3N@I_h-C_{80}$ (2.0 mg, 1.3×10^{-6} mol) and 2 (13.7 mg, 3.4×10^{-5} mol) was degassed using freeze-pump-thaw cycles under reduced pressure in a Pyrex tube. The solution was heated at 180 °C for 23 min under an argon atmosphere in the dark. When the reaction was finished, **1b** was detected as the sole product. Subsequently, slow photochemical transformation of **1b** into **1a** was observed under ambient light. The reaction mixture was separated by preparative HPLC with Buckyprep and 5NPE columns to isolate **1a** and **1b**, respectively, in 20% and 33% yields.

Data for 1a: red solid; ¹H NMR (500 MHz, C₂D₂Cl₄, 293 K) δ 7.47 (t, J = 8 Hz, 1H), 7.42 (t, J = 8 Hz, 1H), 7.30 (d, J = 7.5 Hz, 2H), 7.21 (d, J = 8 Hz, 2H), 3.88–3.81 (m, 2H), 3.67–3.55 (m, 4H), 3.29–3.21 (m, 2H), 1.46 (t, J = 7.5 Hz, 6H), 1.43 (t, J = 7.5 Hz, 6H); ¹³C NMR (125 MHz, C₂D₂Cl₄, 293 K) δ 151.24 (2C; *o*-Ar), 151.10 (2C; *o*-Ar), 150.86 (2C), 148.28 (2C), 148.04 (1C), 147.76 (2C), 146.70 (2C), 145.82 (2C), 145.51 (1C), 145.23 (2C), 145.12 (2C), 144.92 (2C), 143.58 (1C), 143.43 (4C), 143.30 (2C), 143.00 (2C), 142.82 (2C), 142.63 (2C), 142.36 (2C), 142.24 (2C), 142.16 (2C), 141.69 (2C), 141.64 (2C), 141.55 (2C), 140.92 (2C), 140.63 (2C), 140.51 (2C), 140.26 (2C), 139.93 (2C), 139.63 (1C), 139.50 (1C), 139.25 (2C), 139.06 (2C), 138.31 (1C), 138.02 (2C), 136.85 (2C), 136.32 (2C), 136.06 (2C), 135.74 (2C), 133.11 (1C), 132.15 (1C), 121.79 (1C; *p*-Ar), 131.57 (1C; *p*-Ar), 126.80 (2C; *m*-Ar), 126.75 (2C; *m*-Ar), 125.01 (1C), 124.85 (1C), 123.80 (2C), 122.72 (2C), 110.82 (2C), 72.80 (2C; C₈₀Si), 31.42 (2C; CH₂), 30.73 (2C; CH₂), 16.16 (2C; CH₃), 15.76 (2C; CH₃); ²⁹Si NMR (119.4 MHz, C₂D₂Cl₄, 298 K) δ –57.24; MALDI-TOF MS (TPB) *m/z* 1793 ([M]⁺), 1499 ([M – C₂₀H₂₆Si]⁺).

Data for 1b: red solid; ¹H NMR (500 MHz, $C_2D_2Cl_4$, 293 K) δ 7.50 (t, 2H, *J* = 7.5 Hz), 7.31 (br, 2H), 7.25 (br, 2H), 3.48 (br, 4H), 3.40 (br, 2H), 3.31 (br, 2H), 1.43 (br, 6H), 1.30 (br, 6H); ¹³C NMR (125 MHz, $C_2D_2Cl_4$, 293 K) δ 152.22 (2C), 151.18 (2C; *o*-Ar), 151.00 (2C; *o*-Ar),

150.05 (2C), 148.34 (2C), 146.76 (2C), 146.40 (2C), 146.05 (1C), 145.52 (2C), 145.40 (2C), 145.10 (2C), 144.74 (2C), 144.47 (2C), 143.97 (2C), 143.92 (2C), 143.66 (2C), 143.02 (2C), 142.99 (4C), 142.83 (2C), 142.72 (1C), 142.10 (2C), 141.90 (2C), 141.78 (2C), 141.31 (1C), 141.02 (2C), 140.86 (2C), 140.51 (2C), 140.44 (2C), 140.12 (2C), 139.60 (2C), 138.86 (2C), 138.29 (1C), 137.64 (2C), 135.43 (1C), 135.35 (2C), 135.23 (2C), 134.77 (2C), 134.05 (3C), 132.01 (2C; *p*-Ar), 127.87 (2C), 126.84 (2C; *m*-Ar), 126.70 (2C; *m*-Ar), 126.54 (2C), 125.81 (2C), 124.91 (2C), 122.33 (2C), 85.14 (1C; C_{80} Si), 77.17 (1C; C_{80} Si), 31.34 (2C; CH_2), 31.13 (2C; CH_2), 15.86 (2C; CH_3), 15.44 (2C; CH_3); ²⁹Si NMR (119.4 MHz, C₂D₂Cl₄, 298 K) δ -53.12; vis-NIR (CS₂) λ_{max} 698 nm; MALDI-TOF MS (TPB) *m*/*z* 1793 ([M]⁺), 1499 ([M – C₂₀H₂₆Si]⁺).

X-ray Crystallography of 1a. Crystals of 1a were obtained using liquid–liquid bilayer diffusion method of an $CS_2/ODCB = 1/1$ solution of 1a using hexane as a poor solvent at 0 °C. Single-crystal X-ray diffraction data of 1a were collected on a Bruker AXS machine equipped with an Apex II CCD detector and a liquid-nitrogen low-temperature apparatus providing a constant temperature at 90 K.

Crystal data for 1a, Lu₃N@ I_h -C₈₀-SiDep₂•CS₂: C₁₀₁H₂₆Lu₃NS₂Si, Mr = 1870.35, red platelet, 0.18 × 0.16 × 0.04 mm, orthorhombic, *Pccn* (No.56), a = 10.9576(10) Å, b = 17.2860(15) Å, c = 28.760(2) Å, V = 5447.5(8) Å³, Z = 4, $\lambda = 0.71073$ Å, μ (Mo K α) = 5.564 mm⁻¹, $\theta_{max} = 28.69^{\circ}$, $D_{calc} = 2.281$ g/cm³, T = 90 K, 34063 measured reflections, 6916 independent reflections, 473 refined parameters, $R_1 = 0.1221$, $wR_2 = 0.2339$ for all data, GOF = 1.278 for all data; $R_1 = 0.1043$ for 6916 independent reflections [$I > 2.0\sigma(I)$] with 473 parameter and 776 restraints.

Computational Method. Theoretical calculations were conducted for **1a** and **1b**. The geometries of the compounds were optimized at the $M06-2X^{18}/6-31G(d)^{19}[C, H, N, Si]$, LanL2DZ²⁰[Lu] level using the Gaussian 09²¹ program.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data for **1a** in CIF format, spectroscopic data for **1a** and **1b**, synthesis of **2**, complete list of authors for refs 2c, 2d, 2e, 3b, 4b, 5a, 5b, 5c, 8a, 8b, 8c, 8f, 12, 14b, 15b, 21. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

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ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas (No. 20108001, "pi-Space"), a Grant-in-Aid for Scientific Research (A) (No. 20245006) and (B) (No. 24350019), The Next Generation Super Computing Project (Nanoscience Project), Nanotechnology Support Project, Grants-in-Aid for Scientific Research on Priority Area (Nos. 20036008 and 20038007), Specially Promoted Research (No. 22000009) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and The Strategic Japanese–Spanish Cooperative Program funded by JST and MICINN.

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Scheme 1.



Figure 1. HPLC profiles of the crude reaction mixture. Conditions: Buckyprep column (ϕ 4.6 × 250 mm); eluent, toluene; flow rate, 1.0 mL/min; wavelength, 330 nm; temperature, room temperature.



Figure 2. (a) HPLC profiles of the reaction mixture exposed to ambient light. Conditions: Buckyprep column (ϕ 4.6 × 250 mm); eluent, toluene; flow rate, 1.0 mL/min; wavelength, 330 nm; temperature, room temperature. (b) HPLC profile of the reaction mixture exposed to ambient light for 12 h. Conditions: 5NPE column (ϕ 4.6 × 250 mm); eluent, toluene; flow rate, 1.0 mL/min; wavelength, 330 nm; temperature, room temperature.





Figure 3. HPLC monitoring of a solution of 1b in ODCB under degassed conditions at room temperature (a) in the presence of ambient light and (b) in the absence of ambient light. Conditions: 5NPE column (ϕ 4.6 × 250 mm); eluent, toluene; flow rate, 1.0 mL/min; wavelength, 330 nm; temperature, room temperature.



Figure 4. HPLC monitoring of a solution of **1a** in ODCB under degassed conditions at room temperature (a) in the presence of ambient light and (b) in the absence of ambient light. Conditions: 5NPE column (ϕ 4.6 × 250 mm); eluent, toluene; flow rate, 1.0 mL/min; wavelength, 330 nm; temperature, room temperature.



Figure 5. Addition patterns of $Lu_3N@I_h-C_{80}(SiDep_2)$.



Figure 6. Vis-NIR absorption spectra of 1a, 1b, and $Lu_3N@I_h-C_{80}$.

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Figure 7. Relation between cage and Lu atoms in **1a**. Lu, red; N, blue, Si, green; C closest to Lu3, yellow-green; C closest to Lu3', purple.

compound	E_{1}^{ox}	$E^{\rm red}_{1}$	$E^{\rm red}_{2}$	$E^{\rm red}_{3}$
$Lu_3N@I_h-C_{80}$	+0.61	-1.39 ^b	-1.83 ^b	-2.16 ^b
1a	$+0.27^{b}$	-1.43^{b}	-1.72^{b}	-1.94^{b}
1b	$+0.43^{b}$	-1.52^{b}	-1.73^{b}	-1.99^{b}
$Sc_3N@I_h-C_{80}^{c}$	+0.62	-1.22		
$Sc_3N@I_h-C_{80}(Mes_2Si)_2CH_2^{c}$	$+0.08^{b}$	-1.45		
$La_2@I_h-C_{80}^{d}$	+0.56	-0.31	-1.71	-2.13
$\mathrm{La}_2@I_h\text{-}\mathrm{C}_{80}(\mathrm{Dep}_2\mathrm{Si})_2\mathrm{CH}_2^e$	-0.04 ^b	-0.70		
$La_2@I_h-C_{80}(Dep_2Si)CH_2CH(t-BuPh)-2A^f$	$+0.11^{b}$	-0.50		
$La_2@I_h-C_{80}(Dep_2Si)CH_2CH(t-BuPh)-2B^f$	$+0.13^{b}$	-0.53		

Table 1. Redox Potentials $(V)^a$ of **1a**, **1b**, Lu₃N@ I_h -C₈₀, and Silylated EMFs

^{*a*} Values obtained by DPV are in volts relative to ferrocene/ferrocenium couple. ^{*b*} Irreversible. ^{*c*} Data from ref 5b. ^{*d*} Data from ref 17. ^{*e*} Data from ref 5c. ^{*f*} Data from ref 6.



Figure 8. Optimized structures of (a) 1a and (b) 1b.





