Photoreactions of Endohedral Metallofullerene with Siliranes: Electronic Properties of Carbosilylated Lu$_3$N@$_h$-C$_{80}$†

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† Dedicated to Professor Marian Mikołajczyk on the occasion of his 80th birthday.

Abstract: Photochemical carbosilylation of Lu$_3$N@$_h$-C$_{80}$ was performed using siliranes (silacyclopropanes) to afford the corresponding [5,6]- and [6,6]-adducts. Electrochemical studies indicated that the redox potentials of the carbosilylated derivatives were shifted cathodically in comparison with those of the [5,6]-pyrrolidino adducts. The electronic effect of the silirane addends on Lu$_3$N@$_h$-C$_{80}$ was verified on the basis of density functional theory calculations.

Keywords: endohedral metallofullerene; Lu$_3$N@$_h$-C$_{80}$; carbosilylation; silirane; redox property

1. Introduction

Endohedral metallofullerenes (EMFs) [1–12] have attracted much interest because of their fascinating structural and electronic properties. On the basis of the encapsulated metals, the properties and reactivities of EMFs are significantly different from those of empty fullerenes. For the last few decades, trimetallic nitride template endohedral metallofullerenes (TNT EMFs), M$_3$N@$_l$-C$_{80}$ (M = Sc, Lu, Y, and Gd), have been extensively studied as representatives of cluster fullerenes, for which potential applications have been explored in the fields of molecular electronics, nanomaterials, and biochemistry [1–14]. For example, Lu$_3$N@$_l$-C$_{80}$ is an attractive compound from a practical viewpoint. The reduction potential of Lu$_3$N@$_l$-C$_{80}$ is lower than those of the other trimetallic nitride template (TNT) EMFs, M$_3$N@$_l$-C$_{80}$ (M = Sc, Y, etc.), C$_{60}$, and C$_{70}$. This property of Lu$_3$N@$_l$-C$_{80}$ is expected to be advantageous with respect to its use as an acceptor in organic photovoltaic (OPV) devices. Previously, OPV devices using some Lu$_3$N@$_l$-C$_{80}$ derivatives with lower reduction potentials were reported to show higher power conversion efficiency than that of C$_{60}$-based analogous devices [15–17].

Meanwhile, the exohedral functionalization of EMFs has been studied extensively as an effective method for modifying the properties of EMFs for many applications [1–12]. As a part of our
study of the chemical derivatization of EMFs, we reported the addition reactions of Lu3N@Ih-C80 with disilirane, silylene, and digermirane to afford the corresponding silylated and germylated adducts [18–20]. The redox potentials of these derivatives were shifted cathodically relative to that of pristine Lu3N@Ih-C80, as expected from the electron-donating effect of silyl and germyl groups. These results prompted us to apply alternative silylation methods to Lu3N@Ih-C80, which will enable fine-tuning of its electronic properties. More recently, we reported the photochemical addition of Sc3N@Ih-C80 and silirane (silacyclopropane) 1 to afford three isomeric carbosilylated derivatives of Sc3N@Ih-C80 [21]. Spectroscopic measurements indicated that the addition of 1 occurred at the [5,6] (a pentagon and a hexagon), and the [6,6] (two hexagons) ring junctions. In addition, the oxidation potentials of the carbosilylated adducts were shifted moderately compared to that of pristine Sc3N@Ih-C80. Herein, we report the carbosilylation of Lu3N@Ih-C80 via photoreactions using siliranes 1 [21] and 2 [22] to afford the corresponding [5,6]- and [6,6]-adducts. The electronic effect of silylirane addition on Lu3N@Ih-C80 is discussed in comparison with that of the 1,3-dipolar addition of azomethine ylides [23,24].

2. Results and Discussion

2.1. Preparation and Structural Analysis of the Carbosilylated Derivatives of Lu3N@Ih-C80

A toluene solution of Lu3N@Ih-C80 and 1 was photo-irradiated using two 500 W halogen lamps (cutoff < 400 nm) (Scheme 1). After photolysis for 60 h, preparative high performance liquid chromatography (HPLC) of the reaction mixture was performed to separate three compounds 3a, 3b, and 3c (Figures S1 and S2, in the Supporting Information). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry of 3a, 3b, and 3c exhibited molecular ion peaks at m/z 2009 (M⁺), as expected for 1:1 adducts of Lu3N@Ih-C80 and 1 (Figure S3). The spectra also show base peaks at m/z 1499 for the fragment ion Lu3N@Ih-C80−. Similarly, photoreaction of Lu3N@Ih-C80 and 2 provided three isomeric adducts 4a, 4b, and 4c. The yields of 3a, 3b, 4a, and 4b were calculated to be 30%, 7%, 26% and 16%, respectively, whereas those of 3c and 4c were not determined because they contained inseparable impurities.

Assuming 1,2-addition of 1 and 2 to Lu3N@Ih-C80, four structures A–D are possible for the addition sites (Figure 1). To obtain an insight into their addition patterns, visible-near-infrared (vis-NIR) spectroscopy was conducted for the adducts (Figure 2). Previous studies indicate that the vis-NIR spectra of the [5,6]- and [6,6]-pyrrolidino derivatives of Lu3N@Ih-C80 exhibit absorption maxima at approximately 870 and 820 nm, respectively [24,25]. The vis-NIR spectra of 3a, 3b, 4a, and 4b show absorption maxima around 880 nm, which are similar to those of the [5,6]-pyrrolidino derivatives [24,25] (Figure 2). Meanwhile, the vis-NIR spectra of 3c and 4c show broad absorption maxima at 811 and 803 nm, which resemble those of the [6,6]-pyrrolidino derivatives [24,25]. Therefore,
3a, 3b, 4a, and 4b are assignable to the [5,6]-adducts A and B. On the other hand, 3c and 4c are probably the [6,6]-adducts C and/or D (See also Figure 3).

![Figure 1](image1.png)

**Figure 1.** Possible addition patterns of 1,2-adducts derived from Lu3N@Ih-C80 and siliranes.

![Figure 2](image2.png)

**Figure 2.** Vis–NIR absorption spectra of 3a–c and 4a–c in CS2.

![Figure 3](image3.png)

**Figure 3.** Partial structures of the Lu3N@Ih-C80 derivatives.

In the 1H-NMR spectrum of 3a, signals for four methyl groups and three tert-butyl groups, as well as aromatic protons were observed (Figure S5). The ring protons of the silacyclopentane addend of 3a constitute an ABX spin system at 3.66, 2.85, and 1.84 ppm as double doublets. Meanwhile, the 13C-NMR spectrum of 3a exhibited 86 quaternary and six tertiary sp2 carbon signals, as well as two sp3 carbon signals of the Ih-C80 cage (Figure S7). The carbon signals of the methylene and methine of the silacyclopentane ring, the three tert-butyl and four methyl groups were also shown in the spectrum. These spectral data are consistent with the structure of 3a as the [5,6]-adduct with C1 symmetry. The 1H-NMR spectrum of 3b is very similar to that of 3a (Figure S6). On the basis of the vis-NIR and 1H-NMR spectra, 3a and 3b were determined to be a pair of diastereomers A and B, although the absolute configurations of 4-tert-butylphenyl (denoted as tBp) groups remain unknown.

The 13C-NMR spectrum of 4a, the main product obtained from 2, is similar to that of 3a, showing 86 sp2 carbon atom signals (Figure S10). The carbon signals of the silirane addend and two sp3 carbon signals of the Ih-C80 cage were also observed. The 1H-NMR spectra of 4a and 4b also indicate the structures of the silirane addends as for the case of 3a and 3b (Figures S8 and S9). As shown in the vis-NIR spectra, it is suggested that 4a and 4b are a pair of diastereomers of the [5,6]-adducts. On the
other hand, spectroscopic studies of 3c and 4c have hitherto been unsuccessful because of their low yields and impurities.

2.2. Electrochemical Studies

The electrochemical properties of 3a, 3b, 4a, and 4b were measured using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The redox potentials of the related compounds are summarized in Table 1. As shown in Figures S11 and S12, the oxidation of 3a, 3b, 4a, and 4b resulted in the removal of the silirane addends during the electrochemical analyses, affording pristine Lu3N@Ih-C80. The first oxidation (E°1) potentials of 3a, 3b, 4a, and 4b are lower than that of Lu3N@Ih-C80 within the range of 360–400 mV. These remarkable cathodic shifts of the oxidation potentials are commonly observed for silylated fullerenes because of the electron-donating properties of the silyl groups [18–21]. Meanwhile, the values of the first reduction (E°1) potentials of 3a, 3b, 4a, and 4b are close to that of Lu3N@Ih-C80. These redox data are compared to those of 5 [23] and 6 [24] as the [5,6]-pyrrolidino adducts of Lu3N@Ih-C80. The first reduction potentials of 5 and 6 are −1.13 and −1.14 V, respectively. According to the reported voltammograms, the E°1 potentials of 5 and 6 are both about +0.34 V, respectively, although the exact E°1 values are not given in the literature [23,24]. As a result, the redox potentials of 3a, 3b, 4a, and 4b shift cathodically compared to those of 5 and 6. These effects of silyl functional groups are also observed for carbosilylated derivatives of Sc3N@Ih-C80 [21].

| compound | E°1 | E°1 | E°1 |
|-----------|-----|-----|-----|
| Lu3N@Ih-C80 | +0.23 | −1.38 | −1.73 |
| 3a | +0.23 | −1.35 | −1.71 |
| 3b | +0.25 | −1.37 | −1.75 |
| 4a | +0.22 | −1.41 | −1.77 |
| 4b | +0.21 | −1.13 | −1.64 |
| 5 | | | |
| 6 | | | |

Table 1. Redox potentials (V) a of 3a, 3b, 4a, 4b, and related compounds.

The E°1 potentials of 3a, 3b, 4a, and 4b are interesting from the viewpoints of Lu3N@Ih-C80-based OPV acceptors, for which optimization of the lowest unoccupied molecular orbital (LUMO) levels is an important factor in improving the open circuit voltages of the corresponding solar cells [15,16]. The E°1 potentials of the [5,6]-pyrrolidino adducts 5 [23] and 6 [24] are shifted positively relative to that of Lu3N@Ih-C80. In contrast, 3a, 3b, 4a, and 4b maintain the low reduction potential of pristine Lu3N@Ih-C80. Although the functions of 3a, 3b, 4a, and 4b as OPV acceptors are unknown, carbosilylation would be an effective method to adjust the electronic properties of fullerenes for electronic functional materials.

2.3. Theoretical Calculations

To obtain an insight into the structural and electronic properties of 3a, 3b, 4a, and 4b, isomers of [5,6]-carbosilylated Lu3N@Ih-C80 were calculated by the density functional theory using the B3LYP method [26–28]. The partial structures of the calculated molecules are shown in Figure 4 with the relative energies. The optimized structures of these molecules are also shown in Figures S13–S16. These structures were calculated with a few different orientations of the Lu3N cluster. As for the configurations of the silirane addend, 3A-I, 3A-II, 3A-III, 4A-I, 4A-II, and 4A-III are calculated molecules for the diastereomer A in Figure 1, while 3B-I, 3B-II, 3B-III, 4B-I, 4B-II, and 4B-III correspond to B. These structures are grouped into four configurations: (3A-I, 3A-II, 3A-III); (3B-I, 3B-II, 3B-III); (4A-I, 4A-II, 4A-III); and (4B-I, 4B-II, 4B-III). Each of the structural groups has three orientations of the...
Lu₃N cluster, as shown in Figure 4. As expected, the relative energies of the adducts vary depending on the orientations of the Lu₃N cluster and the configurations of the silirane addends. Among these isomers, 3A-I, 4A-I, 3B-I, and 4B-I, in which the Y-shaped Lu₃N clusters straddle the addition sites, have relatively lower energies. These calculations indicate that the orientations of the Lu₃N clusters in 3a, 3b, 4a, and 4b should be somewhat restricted. As a result, we regard 3A-I, 3B-I, 4A-I, and 4B-I as the most preferable optimized structures for 3a, 3b, 4a, and 4b, although the absolute configurations of the tBp groups remain unclear.

In addition, the redox properties of carbosilylated Lu₃N@I₇₇-C₈₀ are consistent with the calculated energies of the highest occupied molecular orbital (HOMO) and LUMO levels of the optimized structures. As shown in Table 2, the HOMOs of 3A-I, 3B-I, 4A-I, and 4B-I are higher within the range of 0.45–0.53 eV compared with that of pristine Lu₃N@I₇₇-C₈₀. In contrast, the LUMO energies of 3A-I, 3B-I, 4A-I, and 4B-I are almost the same as that of pristine Lu₃N@I₇₇-C₈₀. These results are fully consistent
with the experimental redox properties of 3a, 3b, 4a, and 4b. Therefore, the carbosilylated structures were verified given the electron-donating properties of the silyl groups.

| compound       | HOMO  | LUMO  |
|----------------|-------|-------|
| Lu$_3$N@I$_h$-C$_{80}$ | -5.47 | -2.90 |
| 3A-I          | -4.98 | -2.90 |
| 3B-I          | -4.99 | -2.91 |
| 4A-I          | -5.01 | -2.92 |
| 4B-I          | -5.02 | -2.95 |

3. Materials and Methods

3.1. General

All chemicals were reagent grade, purchased from Wako Pure Chemical Industries Ltd (Osaka, Japan). Lu$_3$N@I$_h$-C$_{80}$ was purchased from Luna Innovations Inc. (Danville, CA, USA). 1,2-dichlorobenzene (ODCB) was distilled from P$_2$O$_5$ under vacuum before use. Toluene was distilled from benzophenone sodium ketyl under dry N$_2$ prior to use. Reagents were used as purchased unless otherwise specified. HPLC was performed on an LC-908 apparatus (Japan Analytical Industry Co. Ltd., Tokyo, Japan) monitored using a UV3702 detector. Analytical HPLC was performed on a PU-1586 pump with a UV-1575 detector (JASCO Corp., Tokyo, Japan). Buckyprep (i.d. 20 mm × 250 mm, 4.6 mm × 250 mm), Buckyprep-M (i.d. 10 mm × 250 mm, 4.6 mm × 250 mm), and 5PBB (i.d. 10 mm × 250 mm, 4.6 mm × 250 mm) columns (Nacalai Tesque Inc., Kyoto, Japan) were used for HPLC separation. Toluene was used as the eluent for HPLC. The $^1$H and $^{13}$C-NMR measurements were conducted on a JEOL ECA-500 spectrometer (JEOL Ltd., Tokyo, Japan). MALDI-TOF mass experiments were performed (Autoflex III Smartbeam, Bruker Daltonics, Billerica, MA, USA) 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., Kyoto, Japan). Cyclic voltammograms and differential pulse voltammograms were recorded on an electrochemical analyzer (BAS CV50W, BAS Inc., Tokyo, Japan). 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. ($n$-Bu)$_4$NPF$_6$ (0.1 M) in ODCB was used as the supporting electrolyte solution.

3.2. Photoreaction of Lu$_3$N@I$_h$-C$_{80}$ with 1

A Pyrex tube (7 mm i.d.) containing Lu$_3$N@I$_h$-C$_{80}$ (0.7 mg, 4.7 × 10$^{-4}$ mmol), 1 (11.5 mg, 2.3 × 10$^{-3}$ mmol), and toluene (3.0 mL) was prepared and degassed using freeze-pump-thaw cycles under reduced pressure. Subsequently, the solution was irradiated for 60 h with a 500 W halogen lamp using an aqueous sodium nitrite filter solution (cutoff < 400 nm) under an argon atmosphere. The resulting reaction mixtures were separated using preparative HPLC with Buckyprep-M, Buckyprep, and 5PBB columns to isolate 3a, 3b, and 3c.

3a: $^1$H-NMR (CD$_2$Cl$_2$) δ 7.49–7.32 (m, 4H), 7.28 (s, 1H), 7.04 (s, 1H), 7.02 (s, 1H), 6.95 (s, 1H), 3.66 (dd, 1H, J = 2.5 Hz, 15.0 Hz), 3.00 (s, 3H), 2.85 (dd, 1H, J = 13.5 Hz, 15.0 Hz), 2.73 (s, 3H), 2.43 (s, 3H), 2.11 (s, 3H), 1.84 (dd, 1H, J = 2.5 Hz, 13.5 Hz), 1.40 (s, 9H), 1.31 (s, 9H), 1.23 (s, 9H); $^{13}$C-NMR (CDCl$_3$;CS$_2$ = 1:1) δ 156.88 (1C), 156.79 (1C), 155.84 (1C), 155.47 (1C), 153.73 (1C), 153.24 (1C), 153.11 (1C), 152.31 (1C), 151.08 (1C), 150.93 (1C), 148.85 (1C), 148.65 (1C), 148.34 (1C), 147.88 (1C), 147.56 (1C), 147.22 (1C), 146.66 (1C), 146.38 (1C), 144.88 (1C), 144.64 (1C), 144.34 (1C), 144.29 (1C), 144.20 (1C), 144.01 (1C), 143.57 (1C), 142.97 (1C), 142.58 (1C), 142.35 (1C), 142.32 (1C), 142.26 (1C), 142.13 (2C), 142.01 (1C).
A Pyrex tube (20 mm i.d.) containing Lu$_3$N@I$_4$-C$_{80}$ (1.1 mg, 7.3 × 10$^{-4}$ mmol), 2 (49.4 mg, 1.1 × 10$^{-1}$ mmol), and toluene (20 mL) was prepared and degassed using freeze-pump-thaw cycles under reduced pressure. These solutions were irradiated for 20 h under the same conditions. The reaction mixture was separated using preparative HPLC with Buckyprep-M and Buckyprep columns to isolate 4a, 4b, and 4c.

4a: $^1$H-NMR (CDCl$_3$:CS$_2$ = 1:1) $\delta$ 7.50 (t, 1H, $J = 7.5$ Hz), 7.47–7.42 (m, 2H), 7.40 (d, 1H, $J = 7.5$ Hz), 7.38–7.34 (m, 2H), 7.23 (t, 1H, $J = 7.5$ Hz), 7.12 (d, 1H, $J = 7.5$ Hz), 7.05 (d, 1H, $J = 7.5$ Hz), 6.99 (d, 1H, $J = 7.5$ Hz), 3.69 (dd, 1H, $J = 2.5$ Hz, 15.5 Hz), 3.51 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 3.44 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 3.14 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 3.03 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 2.89 (dd, 1H, $J = 13.5$ Hz, 15.0 Hz), 2.84 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 2.76 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 2.53 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 2.52 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 1.84 (dd, 1H, $J = 2.5$ Hz, 13.5 Hz), 1.66 (t, 3H, $J = 7.5$ Hz), 1.43 (s, 9H), 1.22 (t, 3H, $J = 7.5$ Hz), 0.64 (t, 3H, $J = 7.5$ Hz), 0.31 (t, 3H, $J = 7.5$ Hz); $^{13}$C-NMR (CDCl$_3$) $\delta$ 157.35 (1C), 156.99 (1C), 156.81 (1C), 155.88 (1C), 155.56 (1C), 155.53 (1C), 154.44 (1C), 154.39 (1C), 153.31 (1C), 153.14 (1C), 151.45 (1C), 151.29 (1C), 150.51 (1C), 149.14 (1C), 148.84 (1C), 148.67 (1C), 148.17 (1C), 147.93 (1C), 147.48 (1C), 147.35 (1C), 147.14 (1C), 146.66 (1C), 146.38 (1C), 144.81 (1C), 144.76 (1C), 144.63 (1C), 144.42 (1C), 144.32 (1C), 144.23 (1C), 143.90 (1C), 142.90 (1C), 142.64 (1C), 142.31 (1C), 142.19 (1C), 142.12 (1C), 141.99 (1C), 141.82 (1C), 141.42 (1C), 140.94 (1C), 140.85 (1C), 140.64 (1C), 140.34 (1C), 139.57 (1C), 139.43 (1C), 139.34 (1C), 138.79 (1C), 138.73 (1C), 138.49 (1C), 138.02 (1C), 137.63 (1C), 137.06 (1C), 137.00 (1C), 136.72 (1C), 136.41 (1C), 136.27 (1C), 136.15 (1C), 136.02 (1C), 135.31 (1C), 135.23 (1C), 135.17 (1C), 135.09 (1C), 135.05 (1C), 134.84 (1C), 134.59 (1C), 134.13 (1C), 131.56 (1C), 130.99 (1C), 130.64 (1C), 130.26 (1C), 129.84 (1C), 129.45 (1C), 129.14 (1C), 128.90 (1C), 128.34 (1C), 127.81 (1C), 127.29 (1C), 127.17 (1C), 126.03 (1C), 125.34 (1C), 124.90 (2C), 118.00 (1C), 110.10 (1C), 109.34 (1C), 103.64 (1C), 63.34 (1C), 58.45 (1C), 55.24 (1C), 34.68 (1C), 34.15 (1C), 33.56 (1C), 31.55 (1C), 30.27 (1C), 29.53 (1C), 21.62 (1C), 15.19 (1C), 15.09 (1C), 15.01 (1C), 14.83 (1C); vis-NIR (CS$_2$) $\lambda_{max}$ 879 nm; MALDI-TOF MS m/z 1952 (M$^+$), 1499 (Lu$_3$N@I$_4$-C$_{80}^-$).

4b: $^1$H-NMR (CDCl$_3$:CS$_2$ = 1:1) $\delta$ 7.32 (d, 2H, $J = 8.0$ Hz), 7.34 (d, 2H, $J = 4.5$ Hz), 7.31 (d, 2H, $J = 8.0$ Hz), 7.10 (t, 1H, $J = 7.5$ Hz), 7.02 (t, 1H, $J = 4.5$ Hz), 6.92 (d, 1H, $J = 7.5$ Hz), 6.86 (d, 1H, $J = 7.5$ Hz), 3.79 (dd, 1H, $J = 2.5$ Hz, 15.5 Hz), 3.74 (q, 2H, $J = 7.5$ Hz), 3.29 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 3.02 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 2.99 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 2.84 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 2.72 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 2.69 (dq, 1H, $J = 7.5$ Hz, 15.0 Hz), 2.64 (dd, 1H, $J = 13.5$ Hz, 15.5 Hz), 1.84 (t, 3H, $J = 7.5$ Hz),
1.75 (dd, 1H, J = 2.5 Hz, 13.5 Hz), 1.26 (s, 9H), 1.21 (t, 3H, J = 7.5 Hz), 0.56 (t, 3H, J = 7.5 Hz); vis-NIR (CS$_2$) $\lambda_{\text{max}}$ 882 nm; MALDI-TOF MS $m/z$ 1952 ($M^-$), 1499 (Lu$_3$N@I$_h$-C$_{80}^{-}$). 

4c: vis-NIR (CS$_2$) $\lambda_{\text{max}}$ 803 nm; MALDI-TOF MS $m/z$ 1952 ($M^-$), 1499 (Lu$_3$N@I$_h$-C$_{80}^{-}$).

3.4. Computational Method

All calculations were conducted using the Gaussian09 [29] program. The optimized geometries were calculated at the B3LYP [26–28] level of theory using basis sets of 6-31G(d) [30] for C, H, N, Si atoms, and SDD [31] for Lu atoms.

4. Conclusions

In summary, the photochemical addition of siliranes 1 and 2 to Lu$_3$N@I$_h$-C$_{80}$ afforded the corresponding [5,6]- and [6,6]-adducts. The [5,6]-adducts 3a, 3b, 4a, and 4b were characterized on the basis of spectroscopic and electrochemical studies and theoretical calculations. The electron-donating effect of carbosilylation on Lu$_3$N@I$_h$-C$_{80}$ was confirmed by the redox properties of 3a, 3b, 4a, and 4b, which showed remarkably low first oxidation potentials. The carbosilylation also resulted in cathodic shifts of the first reduction potentials compared to those of the [5,6]-pyrrolidino adducts. Such functional groups with various electronic effects will contribute to the utilization of EMFs for future applications. Further studies of novel functionalizing methods based on organosilanes are now underway.

Supplementary Materials: Supplementary materials are available online.

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