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Communication

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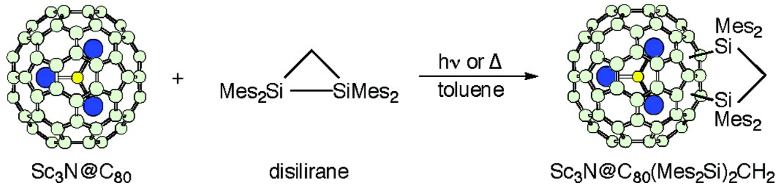

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COMMUNICATIONS

Chemical Reactivity of $Sc_3N@C_{80}$ and $La_2@C_{80}$

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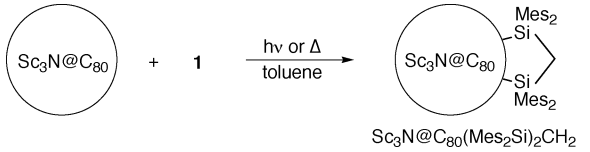
Endohedral metallofullerenes have attracted special interest because of the unique properties that are unexpected for empty fullerenes.[1−3] One of the most distinct features of endohedral metallofullerenes is that they can be viewed as consisting of a positively charged metal core and a negatively charged carbon cage. For example, the La atom in $La@C_{82}$ donates three valence electrons to the carbon cage, providing an open-shell electronic structure formally described as $La^{3+}C_{82}^{3-}$.[4,5] Consequently, the interesting properties of endohedral metallofullerenes depend on the structure and electronic state of the carbon cage.

It is well-known that the main isomers of $M@C_{82}$ (M = Y, La, Ce, and Pr) show very similar UV−vis−NIR absorption spectra[6−9] and redox potentials[10] because of the same cage structure (C_{2v}) and electronic state (C_{82}^{3-}). In a series of our studies on the chemical functionalization of metallofullerenes, we have also found that the main isomers of $M@C_{82}$ (M = Y, La, Ce, and Pr) show similar reactivities toward 1,1,2,2-tetrakis(2,4,6-trimethylphenyl)-1,2-disilirane (**1**).[11−15] Recently, Dorn et al.[16] have developed a new synthetic method to afford a novel endohedral metallofullerene, $Sc_3N@C_{80}$, in a high yield. This has the same carbon cage (I_h) and electronic state (C_{80}^{6-}) as $La_2@C_{80}$.[17−20] Therefore, it may be expected that $Sc_3N@C_{80}$ resembles $La_2@C_{80}$ in reactivity. We herein report that the reactivity of $Sc_3N@C_{80}$ toward **1** is different from that of $La_2@C_{80}$.[21]

Scheme 1



A toluene solution of $Sc_3N@C_{80}$ and an excess amount of **1** was photoirradiated with a halogen lamp (cut off < 400 nm) for 2 h. Formation of the corresponding adduct was confirmed by means of a matrix-assisted laser desorption ionization (MALDI) TOF mass analysis by using 9-nitroantrathene as matrix and HPLC analysis of the reaction mixture. A MALDI-TOF mass spectrum verified the formation of the 1:1 adduct, $Sc_3N@C_{80}(Mes_2Si)_2CH_2$. HPLC profile showed that a new peak appears as the peak of $Sc_3N@C_{80}$ disappears. The thermal reaction was also investigated. A solution of $Sc_3N@C_{80}$ and an excess amount of **1** in toluene was heated at 80 °C for 2 h. A molecular ion peak of the monoadduct could not be detected by MALDI-TOF mass measurement of the reaction mixture. HPLC profile of the reaction mixture was unchanged. These results reveal that $Sc_3N@C_{80}$ reacts only photochemically with **1** and is in contrast with the fact that $La_2@C_{80}$ reacts both photochemically and thermally with **1** to afford the monoadduct. This difference in reactivity is noticeable as the first example due to encapsulated species.

Table 1. Redox Potentials (V) and HOMO/LUMO Levels (eV) of $Sc_3N@C_{80}$ and $La_2@C_{80}$

compound	${}^{ox}E_1$	${}^{red}E_1$	${}^{red}E_2$	${}^{red}E_3$	HOMO	LUMO
$Sc_3N@C_{80}$ [a]	+0.62	−1.22	−1.59	−1.90	−5.48	−3.14
$Sc_3N@C_{80}$ [b]	+0.62	−1.24	−1.62			
$La_2@C_{80}$ [c]	+0.56	−0.31	−1.72	−2.13	−5.40	−4.21

[a] Half-cell potentials unless otherwise stated. Values are relative to ferrocene/ferrocenium couple. In 1,2-dichlorobenzene with 0.1 M $(n\text{-}Bu)_4NPF_6$ at a Pt working electrode. Scan rate = 20 mV s^{-1}. [b] Ref 22. [c] Ref 18.

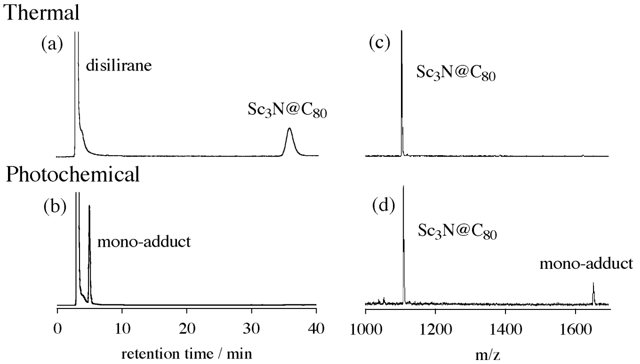


Figure 1. Photochemical and thermal reactions of $Sc_3N@C_{80}$ with **1** were monitored by HPLC and mass spectroscopic analyses: (a and b) HPLC profiles and (c and d) MALDI-TOF mass spectra.

The redox potentials of $Sc_3N@C_{80}$ were measured by cyclic voltammetry (CV) and differential pulse voltammetry (DPV)[22] since they provide important information on the chemical reactivity of endohedral metallofullerenes as well as fullerenes.[10−15] The measured redox potentials of $Sc_3N@C_{80}$ are listed in Table 1 together with those of $La_2@C_{80}$. The CV spectrum of $Sc_3N@C_{80}$ exhibits one reversible oxidation and three reversible reductions. The oxidation potential of $Sc_3N@C_{80}$ is similar to that of $La_2@C_{80}$. However, the first reduction potential (−1.22 V) of $Sc_3N@C_{80}$ is much more negative than that of $La_2@C_{80}$ (−0.31 V vs Fc/Fc^+). This suggests that $Sc_3N@C_{80}$ is much less reactive toward nucleophiles such as **1** than is $La_2@C_{80}$, in accord with the fact that $Sc_3N@C_{80}$ does not react thermally with **1**.

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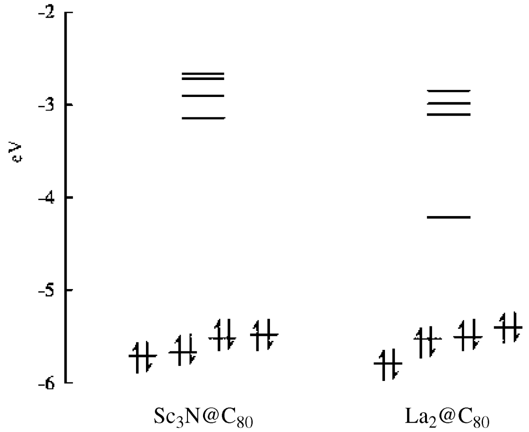

Figure 2. The MO diagrams of $Sc_3N@C_{80}$ and $La_2@C_{80}$.

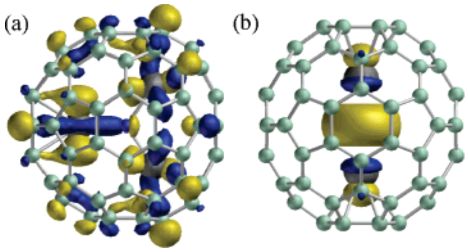

Figure 3. The LUMOs of (a) $Sc_3N@C_{80}$ and (b) $La_2@C_{80}$.

We have also carried out theoretical calculation.[23] The MO diagrams calculated for $Sc_3N@C_{80}$ and $La_2@C_{80}$ are shown in Figure 2. $Sc_3N@C_{80}$ and $La_2@C_{80}$ have almost the same HOMO levels. However, $Sc_3N@C_{80}$ has a much higher LUMO level than $La_2@C_{80}$. These are consistent with the trends of the redox potentials, supporting the poor thermal reactivity of $Sc_3N@C_{80}$ toward **1**. As Figure 3 shows, the LUMO of $Sc_3N@C_{80}$ is delocalized not only on the Sc_3N cation but also on the C_{80} cage. In contrast, the LUMO of $La_2@C_{80}$ is localized onto the two La^{3+} cations and is more suitable as an electron accommodation.[30]

In conclusion, we have found that $Sc_3N@C_{80}$ has a much lower thermal reactivity toward disilirane than $La_2@C_{80}$, though these two metallofullerenes have the same electronic structure described as C_{80}^{6-}. The reactivity difference is ascribed to the difference in the energy level and spatial distribution of LUMO between $Sc_3N@C_{80}$ and $La_2@C_{80}$. It is interesting that the difference is caused by encapsulated species.

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Supporting Information Available: Experimental details, CV and DPV spectra of $Sc_3N@C_{80}$ and molecular orbitals of $Sc_3N@C_{80}$ and $La_2@C_{80}$. The complete list of authors for ref 27. This material is available free of charge via the Internet at http://pubs.acs.org.

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