

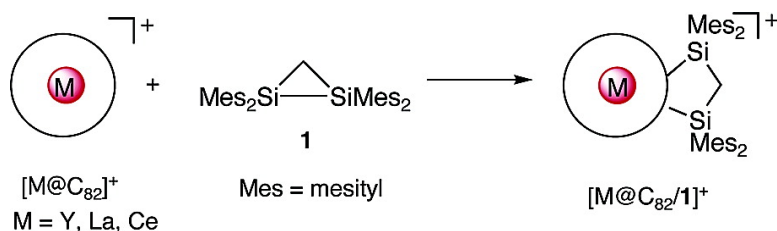
Article

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## Chemical Reactivities of the Cation and Anion of $M@C_{82}$ ( $M = Y, La, \text{ and } Ce$ )

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**Abstract:** The chemical reduction and oxidation of  $M@C_{82}$  ( $M = Y, La, \text{ and } Ce$ ) afford the corresponding anion and cation, respectively, which show unique and interesting chemical reactivities. It is found that the successful reversible gain or loss of electrons by ionization is useful for controlling the stability and reactivity of  $M@C_{82}$  toward both nucleophiles and electrophiles.

### Introduction

Endohedral metallofullerenes encapsulating one or more metal atoms inside a hollow carbon cage have attracted special interest because of their spherical structures with unique properties.<sup>1–3</sup> Theoretical and experimental studies reveal that an electron transfer occurs from the encapsulated metal(s) to the carbon cage. For example, the formal electronic structure of  $La@C_{82}$  is described as  $La^{3+}C_{82}^{3-}$ .<sup>4,5</sup> Characteristic redox properties of  $La@C_{82}$  are significantly different from those of the empty fullerene  $C_{82}$ ,<sup>6</sup> that is, the first oxidation and first reduction potentials of  $La@C_{82}$  are lower than those of  $C_{82}$ . In other words,  $La@C_{82}$  is a strong electron donor as well as a strong electron acceptor compared to the empty fullerene.<sup>7</sup>

We have reported the first exohedral functionalization of endohedral metallofullerenes with a disilirane, which can be used as a mechanistic probe to clarify electronic and chemical

properties of fullerenes.<sup>8</sup> Empty fullerenes, such as  $C_{60}$  and  $C_{70}$ , react with the disilirane only in a photochemical way.<sup>9,10</sup> In contrast, endohedral metallofullerenes react with the disilirane not only photochemically but also thermally. The strong electron-accepting character of endohedral metallofullerenes can rationalize the facile thermal addition to the disilirane. Recently, we have verified the structures of paramagnetic metallofullerenes,  $M@C_{82}$  ( $M = Y,$ <sup>11</sup>  $La,$ <sup>12,13</sup>  $Ce,$ <sup>14</sup> and  $Pr$ <sup>15</sup>), by analyzing the <sup>13</sup>C NMR spectra of their diamagnetic anions

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generated electrochemically. In addition to electrochemical ionization, chemical ionization of  $M@C_{82}$  is quite important for its application because it can be easily and widely used by organic chemists. In this context, it remains as an important subject to establish the chemical formation of the anion and cation of endohedral metallofullerenes and to verify their chemical reactivities. We report here the chemical ionization of  $M@C_{82}$  ( $M = Y, La, \text{ and } Ce^{1616}$ ) and the reactivity of the cation and anion.

## Experimental Section

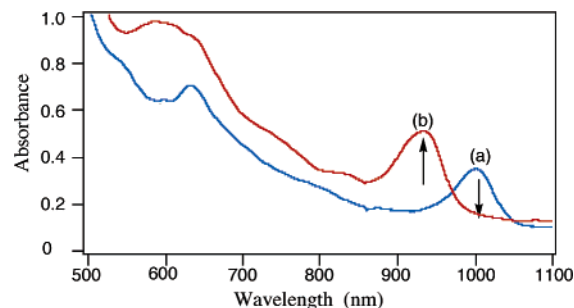
Soot containing endohedral metallofullerenes was produced by the standard arc vaporization method with a composite anode rod containing graphite and a metal oxide.<sup>17</sup> The composite rod was subjected to an arc discharge under a helium atmosphere of 50 Torr. The raw soot was collected and suspended in 1,2,4-trichlorobenzene (TCB). The mixture was refluxed for 16 h. The TCB solution was collected and injected into HPLC in order to separate endohedral metallofullerenes; a PBB column ( $\phi 20 \text{ mm} \times 250 \text{ mm}$ ; Cosmoses, Nacalai Tesque Inc.) and chlorobenzene as a mobile phase were used in the first step, and a Buckyprep column ( $\phi 20 \text{ mm} \times 250 \text{ mm} \times 2$ ; Cosmoses, Nacalai Tesque Inc.) and toluene were used in the second step.

Chemical reduction and oxidation were performed in 1,2-dichlorobenzene (ODCB) under an argon atmosphere. A typical ionization procedure is as follows; an ODCB solution of  $La@C_{82}-A$  ( $2.9 \times 10^{-4} \text{ M}$ ) was treated with small excess sodium thiomethoxide (Aldrich, used as received) at room temperature for reduction, and the ODCB solution was treated with tris(4-bromophenyl)aminium hexachloroantimonate (Aldrich, used as received) for the oxidation. The reaction process was traced with vis–near–IR spectra.

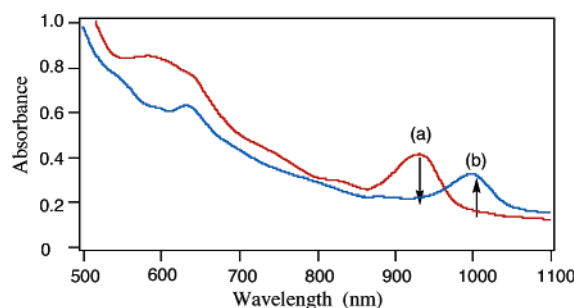
The tungsten–halogen lamp, a Ushio JCV100V-500W, was used as the light source, and irradiation was performed through a sodium nitrate filter solution (cutoff  $< 400 \text{ nm}$ ). 1,1,2,2-Tetrakis(2,4,6-trimethylphenyl)-1,2-disilirane was prepared according to the literature method.<sup>18</sup> Mass spectroscopic measurements were carried out on a JEOL JMS SX 102 mass spectrometer and a Bruker MALDI Biflex III. The vis–near–IR absorption spectra were measured on a Shimadzu UV-3150 spectrometer in ODCB.

Geometries were optimized using the Gaussian 98 program<sup>19</sup> at the B3LYP level<sup>20</sup> (effective core potential and (5s5p3d)/[4s4p3d] for Y and  $La^{21}$  and the all-electron 3-21G for  $C^{22}$ ). In the HOMO/LUMO calculations, the larger 6-31+G(d) basis set<sup>23</sup> was used for C.

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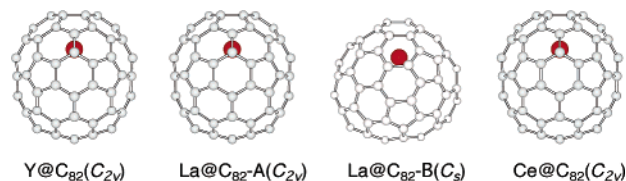


**Figure 1.** Changes of vis–near–IR spectra in the chemical reduction of  $La@C_{82}-A$ . (a)  $La@C_{82}-A$ . (b)  $[La@C_{82}-A]^{-}Na^{+}$ .



**Figure 2.** Changes of vis–near–IR spectra in chemical oxidation of  $[La@C_{82}-A]^{-}Na^{+}$ . (a)  $[La@C_{82}-A]^{-}Na^{+}$ . (b)  $La@C_{82}-A$ .

### Chart 1

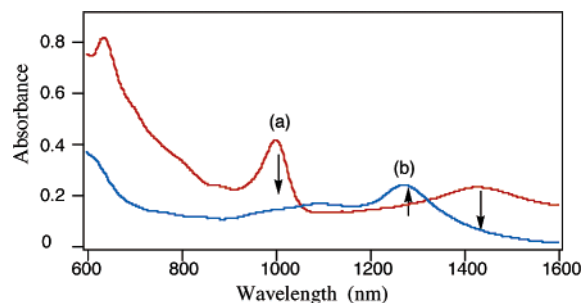


## Results and Discussion

The  $La@C_{82}-A$  (Chart 1) shows broad absorption bands from the near-IR region to 2300 nm due to its open-shell electronic structure, described formally as  $La^{3+}C_{82}^{3-}$ .<sup>12</sup> Upon addition of sodium thiomethoxide to  $La@C_{82}-A$  ( $2.9 \times 10^{-4} \text{ M}$ ) in ODCB, a significant change in the near-IR spectra was observed. The peak at 1000 nm in the vis–near–IR spectrum of  $La@C_{82}-A$  decreases with an increase of the amount of  $MeS^{-}Na^{+}$  added, and a new peak appears at 934 nm (Figure 1). The new peak is due to the formation of a  $[La@C_{82}-A]^{-}$  anion.<sup>12</sup> The presence of a clear isosbestic point in the spectra shows that  $La@C_{82}-A$  is reduced quantitatively to its anion. The absorption coefficient of  $[La@C_{82}-A]^{-}Na^{+}$  at 934 nm was evaluated to be  $5.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  by comparison with that of  $La@C_{82}-A$ .<sup>24</sup> The absorption maximum of the chemically generated anion  $[La@C_{82}-A]^{-}Na^{+}$  is the same as that of the electrochemically generated anion  $[La@C_{82}-A]^{-}Bu_4N^{+}$ .<sup>12</sup> This shows that the effect of the counterion is negligible.

Chemical oxidation of  $[La@C_{82}-A]^{-}Na^{+}$  ( $1.4 \times 10^{-4} \text{ M}$ ) was performed using tris(*p*-bromophenyl)aminium hexachloroantimonate [ $(p\text{-BrC}_6\text{H}_4)_3\text{N}^{+}\text{SbCl}_6^{-}$ ] in ODCB. Figure 2 shows the changes in the vis–near–IR spectra during the oxidation of  $[La@C_{82}-A]^{-}Na^{+}$  to  $La@C_{82}-A$ . The presence of a clear

- (24) The absorption coefficient of  $La@C_{82}-A$  is  $2.9 \times 10^3/1010 \text{ nm}$ . Akiyama et al. also reported the absorption coefficient of  $La@C_{82}-A$ : Akiyama, K.; Sueki, K.; Kodama, T.; Kikuchi, K.; Ikemoto, I.; Katada, M.; Nakahara, H. *J. Phys. Chem. A* **2000**, *104*, 7224.



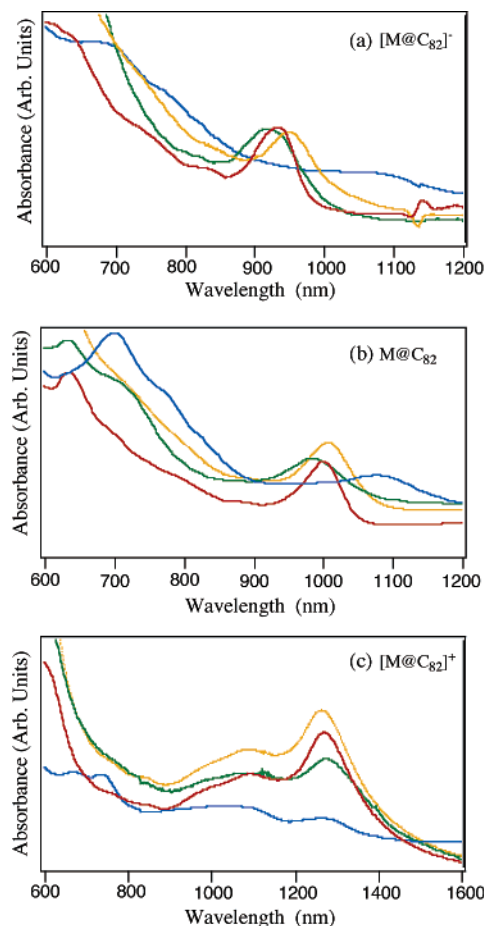
**Figure 3.** Changes of vis-near-IR spectra in chemical oxidation of  $La@C_{82}-A$ . (a)  $La@C_{82}-A$ . (b)  $[La@C_{82}-A]^+SbCl_6^-$ .

isosbestic point in the spectra shows that  $[La@C_{82}-A]^-Na^+$  is oxidized quantitatively to neutral  $La@C_{82}-A$ . Addition of more than 1 equiv of oxidant to  $La@C_{82}-A$  led to additional changes in the absorption spectrum because of the formation of the  $[La@C_{82}-A]^+$  cation. When  $La@C_{82}-A$  ( $1.4 \times 10^{-4}$  M) was chemically treated with  $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$  to afford  $[La@C_{82}-A]^+SbCl_6^-$  in ODCB, the same changes were observed (Figure 3).

The absorption coefficient of  $[La@C_{82}-A]^+$  at 1272 nm was evaluated to be  $2.8 \times 10^3$   $M^{-1} cm^{-1}$  by comparison with that of  $La@C_{82}-A$ . A small difference was observed between the absorption maximum of  $[La@C_{82}-A]^+SbCl_6^-$  generated chemically and that of  $[La@C_{82}-A]^+ClO_4^-$  (1280 nm) generated electrochemically.<sup>12</sup> This feature may be caused by a difference of the counteranion species.

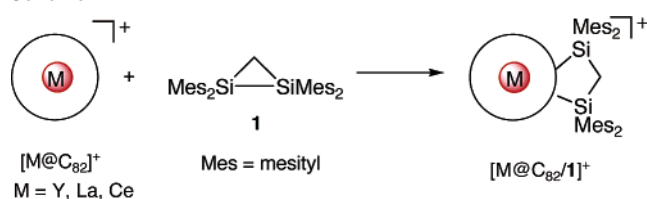
Chemical oxidation and reduction of  $Y@C_{82}$ ,<sup>11</sup>  $La@C_{82}-B$ ,<sup>17b</sup> and  $Ce@C_{82}$ <sup>14</sup> were also performed in order to clarify the influence of metals encapsulated in the fullerene and also to better understand the structure of the fullerene cage (Chart 1). Figure 4 shows vis-near-IR spectra of  $M@C_{82}$  ( $M = Y, La,$  and  $Ce$ ),  $[M@C_{82}-A]^-Na^+$ , and  $[M@C_{82}-A]^+SbCl_6^-$ . The sodium salts,  $[Y@C_{82}]^-Na^+$ ,  $[La@C_{82}-A]^-Na^+$ , and  $[Ce@C_{82}]^-Na^+$ , have very similar absorption. The hexachloroantimonate salts,  $[Y@C_{82}]^+SbCl_6^-$ ,  $[La@C_{82}-A]^+SbCl_6^-$ , and  $[Ce@C_{82}]^+SbCl_6^-$ , also have very similar absorption. The vis-near-IR spectra of  $La@C_{82}-B$  and its ions differ significantly from those of the corresponding  $Y@C_{82}$ ,  $La@C_{82}-A$ , and  $Ce@C_{82}$  due to the different carbon cage, as shown in Chart 1.

Elucidation of the chemical reactivity of the  $M@C_{82}$  ions is a challenge for developing new chemistry of endohedral metallofullerenes. The chemical properties of the endohedral metallofullerenes can be changed by reduction and oxidation. In this context, we carried out the reaction of endohedral metallofullerene ions with a disilirane.<sup>8</sup> The reaction of  $[La@C_{82}-A]^+SbCl_6^-$  with an excess amount of 1,1,2,2-tetrakis-(2,4,6-trimethylphenyl)-1,2-disilirane (**1**) in ODCB at room temperature in the dark resulted in the formation of the corresponding 1:1 adduct, which was confirmed on the basis of the FAB mass spectrum of the reaction mixture in a *m*-nitrobenzyl alcohol matrix. No ESR signal was observed for the reaction mixture. This reveals that the adduct is diamagnetic, suggesting a cationic form of its carbon cage (Scheme 1). We also carried out the reactions of  $[Y@C_{82}]^+SbCl_6^-$ ,  $[La@C_{82}-B]^+SbCl_6^-$ , and  $[Ce@C_{82}]^+SbCl_6^-$  with **1** under the same conditions and confirmed the formation of the corresponding 1:1 adduct. These results indicate that oxidation is an effective method for increasing the reactivity of endohedral metallofullerenes.



**Figure 4.** Vis-near-IR spectra of (a)  $[M@C_{82}]^-Na^+$ , (b)  $M@C_{82}$ , and (c)  $[M@C_{82}]^+SbCl_6^-$ .  $Y@C_{82}$  (green),  $La@C_{82}-A$  (red),  $La@C_{82}-B$  (blue), and  $Ce@C_{82}$  (orange).

#### Scheme 1



We also investigated the reactivity of  $[M@C_{82}]^-Na^+$  toward disilirane **1**. However, no adduct was formed, either thermally (80 °C) or photochemically (<400 nm). This behavior of  $[M@C_{82}]^-$  is quite different from that of  $M@C_{82}$  because the latter reacts with the disilirane thermally and photochemically. We have reported earlier that empty fullerenes, such as  $C_{60}$ ,  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$ ,  $C_{82}$ , or  $C_{84}$ , do not react with disilirane **1** thermally.<sup>25,26</sup> Studies using a laser flash photolysis technique showed that  $C_{60}$  acts as an electron acceptor while disilirane **1** acts as an electron donor.<sup>27,28</sup> Redox properties are very

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**Table 1.** Reactivities, Oxidation ( $^{ox}E$ ) and Reduction ( $^{red}E$ ) Potentials (volts), and HOMO/LUMO Levels (in electronvolts)

compound	Reactivity <sup>a</sup>		$^{ox}E1^b$	$^{red}E1^b$	HOMO/LUMO
	$h\nu$	heat			
Y@C <sub>82</sub>	yes	yes (80 °C)	+0.10 <sup>c</sup>	-0.37 <sup>c</sup>	
La@C <sub>82</sub> -A	yes <sup>d</sup>	yes (80 °C) <sup>d</sup>	+0.07 <sup>d</sup>	-0.42 <sup>d</sup>	-5.15/-4.39
La@C <sub>82</sub> -B	yes <sup>e</sup>	yes (80 °C) <sup>e</sup>	-0.07 <sup>e</sup>	-0.47 <sup>e</sup>	
Ce@C <sub>82</sub>	yes <sup>f</sup>	yes (80 °C) <sup>f</sup>	+0.08 <sup>f</sup>	-0.41 <sup>f</sup>	
[Y@C <sub>82</sub> ] <sup>-c</sup>	no	no (80 °C)	-0.37 <sup>c</sup>	-1.34 <sup>c</sup>	
[La@C <sub>82</sub> -A] <sup>-</sup>	no	no (80 °C)	-0.42 <sup>d</sup>	-1.37 <sup>d</sup>	
[La@C <sub>82</sub> -B] <sup>-g</sup>	no		-0.47 <sup>e</sup>	-1.40 <sup>e</sup>	
[Ce@C <sub>82</sub> ] <sup>+</sup>	no		-0.41 <sup>f</sup>	-1.41 <sup>f</sup>	
[Y@C <sub>82</sub> ] <sup>+</sup>		yes (r.t.)	+1.07 <sup>c</sup>	+0.10 <sup>c</sup>	
[La@C <sub>82</sub> -A] <sup>+</sup>		yes (r.t.)	+1.07 <sup>d</sup>	+0.07 <sup>d</sup>	-8.73/-7.13
[La@C <sub>82</sub> -B] <sup>+</sup>		yes (r.t.)	+1.08 <sup>e</sup>	+0.07 <sup>e</sup>	
[Ce@C <sub>82</sub> ] <sup>+</sup>		yes (r.t.)	+1.08 <sup>f</sup>	+0.08 <sup>f</sup>	
C <sub>60</sub>	yes <sup>d</sup>	no (80 °C) <sup>d</sup>	+1.21 <sup>d,g</sup>	-1.12 <sup>d</sup>	-6.43/-3.63
C <sub>82</sub>	yes <sup>d</sup>	no (80 °C) <sup>d</sup>	+0.72 <sup>d,g</sup>	-0.69 <sup>d</sup>	-5.77/-4.12

<sup>a</sup> “Yes” implies the formation of a 1:1 adduct of M@C<sub>82</sub> and **1**; “No” implies that a 1:1 adduct was not formed, and no change in the starting fullerene was observed. <sup>b</sup> Half-wave potentials unless otherwise stated. Values are relative to the ferrocene-ferrocenium couple. <sup>c</sup> Kikuchi, K.; Nakao, Y.; Suzuki, S.; Achiba, Y.; Suzuki, T.; Maruyama, Y. *J. Am. Chem. Soc.* **1994**, *116*, 9367. <sup>d</sup> From ref 8a. <sup>e</sup> From ref 15. <sup>f</sup> From ref 14. <sup>g</sup> Irreversible. Values were obtained by differential pulse voltammetry (DPV).

important in determining the reactivity of fullerenes and endohedral metallofullerenes. Table 1 summarizes the chemical reactivity and HOMO/LUMO levels of M@C<sub>82</sub>, [M@C<sub>82</sub>]<sup>+</sup>, [M@C<sub>82</sub>]<sup>-</sup>, C<sub>60</sub>, and C<sub>82</sub>. There is an interesting correlation

between the reactivity toward disilirane **1** and the redox potentials, as well as their HOMO/LUMO levels. Electronically positive fullerenes, such as [M@C<sub>82</sub>]<sup>+</sup>, react readily with the nucleophilic **1**. Electronically negative fullerenes, such as [M@C<sub>82</sub>]<sup>-</sup>, do not react with **1**. This difference may result from the electrophilicity of fullerenes. In other words, the reactivity of M@C<sub>82</sub> toward disilirane **1** increases by oxidation and decreases by reduction. It is noticeable that the reactivity of M@C<sub>82</sub> can be tuned by ionization.

## Conclusions

A chemical derivatization of endohedral metallofullerenes leads to new physical and chemical properties that the corresponding empty fullerenes do not have. The reversible ionization of endohedral metallofullerenes is a new stepping-stone in controlling the stability and reactivity of fullerenes and develops interesting applications in material science.

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