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CHEMICAL MODIFICATION OF ENDOHEDRAL METALLOFULLERENE La@C_{82} WITH 3-CHLORO-3-PHENYLDIAZIRINE

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The photochemical reaction of an endohedral metallofullerene La@C_{82} with 3-chloro-3-phenyldiazirine (3) affords the monoadduct as a phenylchlorocarbene (:CClPh) derivative. Spectroscopic analyses of UV-vis-near infrared and electron spin resonance and the theoretical calculations reveal that this monoadduct is a pair of stereoisomers with carbene substituents, and the carbene addition occurs regioselectively to the carbons having a high charge density and a high local strain of the C_{82} cage.

Keywords Carbene; diazirine; endohedral metallofullerene; functionalization

INTRODUCTION

Endohedral metallofullerenes have attracted considerable interest as promising spherical molecules for material and biomedical applications, because of their unique properties that are unexpected from empty fullerenes.¹ It is known that M@C_{82} ($\text{M} = \text{La}, \text{Y}, \text{Ce}, \text{Pr}$) is one of the most abundantly produced endohedral metallofullerenes, and it has a paramagnetic character. Among these, La@C_{82} has been recognized as a prototype of endohedral metallofullerenes since its first extraction in 1991 by Chai et al.² Theoretical and experimental studies of La@C_{82} reveal that an electron transfer occurs from the encapsulated metal to the carbon cage, and then the formal electronic structure of La@C_{82} is described

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

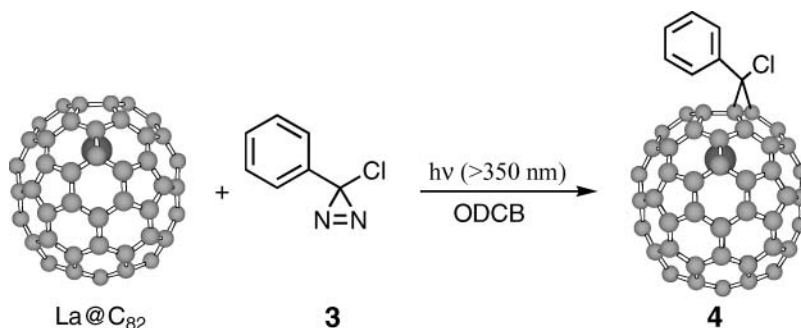
We thank T. Wakahara for interesting discussions. This work was supported in part by a Grant-in-Aid and the 21st Century COE Program, Nanotechnology Support Project, The Next Generation Super Computing Project (Nanoscience Project), and Scientific Research on Priority Area from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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as $\text{La}^{3+}\text{C}_{82}^{3-}$. A chemical derivatization of endohedral metallofullerenes provides new physical and chemical properties to the corresponding metallofullerenes.

The addition reaction of La@C_{82} (C_{2v} symmetry) can yield many regioisomers because it has 24 nonequivalent carbon atoms and 19 nonequivalent 6–6 bonds in La@C_{82} . Actually, the reaction of La@C_{82} with disilirane³ and diphenyldiazomethane⁴ affords a mixture of several isomers of the monoadducts. Meanwhile, we have recently reported the first example of the regioselective reaction of La@C_{82} with 1-adamantane-2,3-[3H]-diazirine (AdN_2 , **1**).⁵ In this reaction, an electrophilic adamantylidene (Ad:) attacks selectively the nucleophilic site on the C_{82}^{3-} cage to afford two isomers of the monoadduct, $\text{La@C}_{82}\text{Ad}$ (**2**), in which the structure of the major isomer of **2** was unambiguously determined by X-ray single crystal analysis. Very recently the regioselective adamantylidene addition of another La@C_{82} isomer (C_s symmetry), which has 44 nonequivalent carbon atoms, also succeeded to afford two major monoadducts.⁶ Furthermore, we synthesized the derivatives of several other endohedral metallofullerenes with **1** and succeeded in the structure determinations of monoadducts, such as $\text{Sc}_3\text{C}_2@\text{C}_{80}\text{Ad}$,⁷ $\text{Sc}_2\text{C}_2@\text{C}_{82}\text{Ad}$,⁸ $\text{Ce}_2@\text{C}_{80}\text{Ad}$,⁹ and $\text{La}_2@\text{C}_{80}\text{Ad}$.⁹

Meanwhile, the photochemistry of diazirines has been well investigated,¹⁰ and among them, aryldiazirines have been utilized not only as a carbene precursor in organic synthesis but also as a photoaffinity labeling reagent in the field of biochemistry, such as phenyltrifluoromethyldiazirine.¹¹ 3-Chloro-3-phenyldiazirine (ClPhCN_2 , **3**), which can be synthesized from the corresponding amidine,¹² is known to exclusively afford the phenylchlorocarbene ($:\text{CClPh}$) by photolysis, and also by thermolysis. The reaction of C_{60} with **3** in refluxing toluene was reported to give the methanofullerene adduct, $\text{C}_{60}(\text{CClPh})$.¹³ In this article, we report for the first time the reaction of endohedral metallofullerene La@C_{82} with diazirine **3** (Scheme 1).



Scheme 1

RESULTS AND DISCUSSION

An *o*-dichlorobenzene (ODCB) solution of La@C_{82} (1.4 mg, $3.0 \times 10^{-4} \text{ M}$) and a 50-equivalent molar amount of **3** in a Pyrex glass tube was photoirradiated at room temperature with a high-pressure mercury-arc lamp (cutoff $< 350 \text{ nm}$). The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of the reaction mixture exhibits a molecular ion peak of the monoadduct as well as weak peaks of multiadducts. Purification by three-step preparative HPLCs afforded the monoadduct as a major product of the reaction (Figure 1). It shows a molecular ion peak at m/z 1247 for $\text{La@C}_{82}(\text{CClPh})$

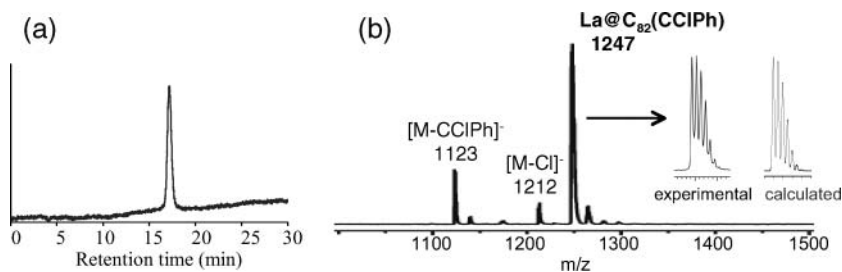


Figure 1 (a) HPLC profile of the purified **4** [column: Buckyprep ϕ 4.6 mm \times 250 mm; eluent: toluene; flow rate: 1.0 mL/min; UV monitored by 330 nm]; (b) MALDI-TOF mass spectrum of **4** [neg mode; matrix: 1,1,4,4-tetraphenyl-1,3-butadiene].

(**4**) in MALDI-TOF mass spectrum, of which the isotopic distribution is consistent with the calculated one, and also a peak at m/z 1212 due to the loss of the chlorine atom ($[M-Cl]$) and at m/z 1123 due to the loss of the addend ($[M-CClPh]$). Furthermore, HPLCs of the purified monoadduct with five different kinds of columns all showed one peak, indicating that the adduct **4** was successfully isolated.

The electron spin resonance (EPR) spectrum of **4** unexpectedly does not show a single isolated spectrum. We carried out the simulation analysis of its EPR spectrum and found that it contains two components with a 1:1 ratio that have very close g -values and hyperfine coupling constants (hfcc) [component A ($g = 2.0013$, hfcc = 1.15 G) and component B ($g = 2.0014$, hfcc = 1.16 G)] (Figure 2). In the case of La@C₈₂Ad (**2**), the hfcc values of two isomers are largely different (major isomer: 0.89 G, minor isomer: 0.41 G). Then we carried out further purification of **4** by a recycling HPLC, but it did not show any separation. This indicates that the two components should be a pair of monoadduct isomers with very similar structures each other.

To consider the reactivity of an endohedral metallofullerene, the local strain on cage carbons plays an important role. The pyramidalization angles from the π -orbital axis vector analysis POAV ($\theta_{\sigma\pi} - 90^\circ$) angles provide a useful index of the local strain.¹⁴ The Mulliken charge densities and POAV angles calculated for La@C₈₂ are shown in Figure 3.⁵

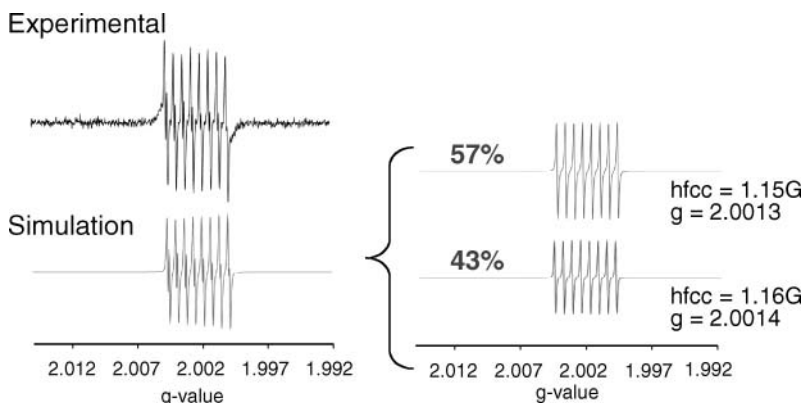


Figure 2 EPR spectrum of **4** in CS₂ [microwave frequency: 9.743 GHz; microwave power: 0.633 mW; mod. Frequency: 100 kHz; mod. amplitude: 0.25 G; temperature: r.t.] and EPR spectrum simulation.

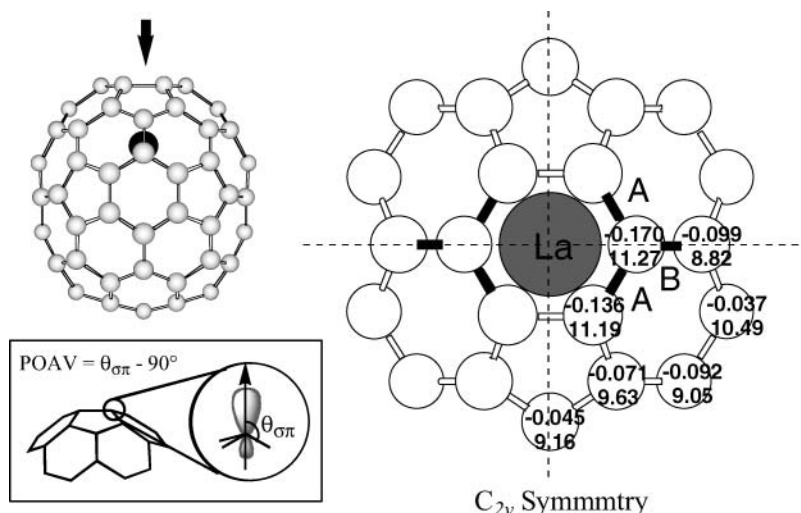


Figure 3 Selective charge densities (upper) and POAV ($\theta_{\sigma\pi} - 90^\circ$) angles (lower) in La@C_{82} .

In the case of **2**, the adamantylidene (Ad:) electrophilically attacks the carbon (site A) that has the highest charge density and the largest POAV angle of C_{82} cage to afford the major adduct. In addition, the minor adduct that the carbene attacks the site B is obtained. Phenylchlorocarbene ($:\text{CClPh}$) is supposed to mainly attack the site A on C_{82} cage in the same way as the adamantylidene does. Bonding of phenylchlorocarbene to the site A, however, may afford two diastereomers having a different direction of chlorine and phenyl substituents, because the adduct on site A has C_1 symmetry. The addition of phenylchlorocarbene upon site B affords a single adduct, since the adduct on site B has C_s symmetry and the C–C bond of site B is on the symmetry plane. From these theoretical thoughts, **4** is very likely to be a pair of the diastereomers with the addend attaching on site A.

The UV-vis-near-infrared absorption spectra of **4** and La@C_{82} are shown in Figure 4. The spectrum of **4** is similar to that of pristine in shape, although the wavelength (1021 nm)

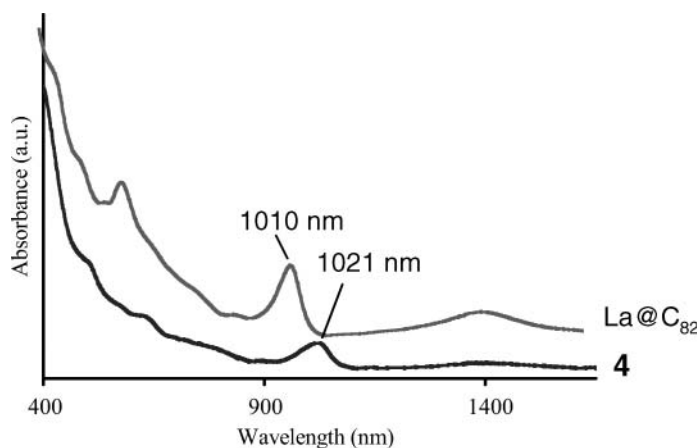


Figure 4 UV-vis-NIR spectra of La@C_{82} and **4** in CS_2 .

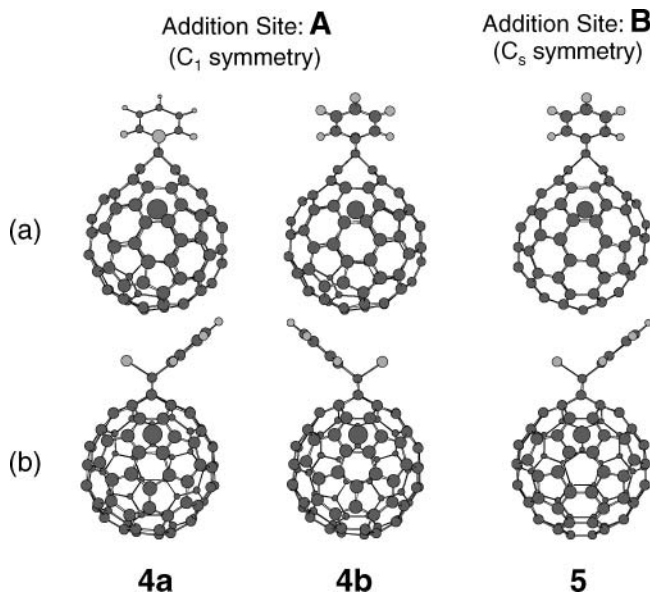


Figure 5 (a) Front and (b) side views of the optimized structures for the monoadducts La@C₈₂(CCIPh) (**4a**, **4b**, **5**) calculated at the B3LYP/6-31G*.

of **4** is a little red-shifted compared to that of pristine (1010 nm). It is known that the shape of absorption spectra is affected by the electronic and structural character of the fullerene cage, so this result suggests that the adduct **4** retains the essential character of La@C₈₂. Meanwhile, in the case of **2**, the major adduct (C₁ symmetry) absorbs at 1010 nm in UV-vis-NIR absorption spectrum that is the same wavelength as pristine, but the minor adduct (C_s symmetry) absorbs at 978 nm, which is largely blue-shifted by 32 nm.⁵ These results strongly suggest that **4** is the adduct with C₁ symmetry.

In order to obtain more information about the structure of **4**, we calculated the relative energies for three isomers, **4a**, **4b** and **5**, as shown in Figure 5. The relative energies of **4a**, **4b**, and **5** are 0, 0.12, and −3.02 kcal/mol. Results showed no big differences in the energies of all the three isomers. In fact, the stabilities of two diastereomers, **4a** and **4b**, are almost equal, which is in good agreement with the results that EPR spectra of **4** show two similar components with the ratio of 1:1, and these two are unable to separate on HPLC.

In this study we found that the 3-chloro-3-phenyldiazirine (**3**) is usable for the derivatization of endohedral metallofullerenes as well as the usage of adamantanediazirine (**1**). Using modified phenylchlorodiazirines by introducing various substituents to the benzene ring, it will be possible to synthesize a variety of functionalized endohedral metallofullerenes.

CONCLUSION

The phenylchlorocarbene derivative of endohedral metallofullerene, La@C₈₂(CCIPh) (**4**), was synthesized for the first time by the reaction of La@C₈₂ with 3-chloro-3-phenyldiazirine (**3**), and characterized by absorption and EPR spectroscopic analyses.

It is found that the phenylchlorocarbene reacts with the electron-rich and highly strained carbons of C₈₂ cage to afford the adduct **4** in a regioselective manner.

EXPERIMENTAL

o-Dichlorobenzene (ODCB) was distilled over P₂O₅ under vacuum prior to use. The mass spectroscopic measurements were carried out using a Bruker MALDI Biflex III. The Vis-near-IR absorption spectra were measured on a Shimadzu UV-3150 spectrometer in CS₂. The EPR spectra in CS₂ were recorded on a Bruker EMX-T. HPLC isolation was performed on a LC-918 (Japan Analytical Industry Co., Ltd.).

Preparation and Purification of La@C₈₂

Soot containing endohedral metallofullerenes was produced by the arc vaporization method using a composite anode rod containing graphite and a metal oxide. The composite rod was subjected to an arc discharge as the anode in a helium atmosphere at 50 Torr. The soot was collected and suspended in 1,2,4-trichlorobenzene (TCB). After refluxing for 16 h, the TCB solution was filtered and then subjected to HPLC in order to separate La@C₈₂; a PBB column (ϕ 20 mm × 250 mm; Nacalai Tesque Inc.) and chlorobenzene as the mobile phase were used in the first step, and a Buckyprep column (ϕ 20 mm × 250 mm; Nacalai Tesque, Inc.) and toluene were used in the second step.

Reaction of La@C₈₂ with 3-Chloro-3-phenyldiazirine (**3**)

3 was prepared according to the method in the literature,¹² and purified by a short-column SiO₂ chromatography prior to use for the reactions. An *o*-dichlorobenzene (ODCB) solution of La@C₈₂ (1.4 mg, 3.0 × 10⁻⁴ M) and a 50-equivalent amount (10 mg, 1.5 × 10⁻² M) of **3** were placed in a ϕ 20 mm Pyrex glass tube, degassed by freeze-thaw cycles under the reduced pressure, and then irradiated using a high-pressure mercury-arc lamp (cutoff < 350 nm) at room temperature for 70 sec. The reaction mixture was subjected to three-step preparative HPLCs to isolate the monoadduct La@C₈₂(CClPh) (**4**) as a major product (conversion yield: 30%); a Buckyprep column (ϕ 20 mm × 250 mm; Nacalai Tesque, Inc.) in the first step, a Buckyprep M column (ϕ 20 mm × 250 mm; Nacalai Tesque, Inc.) in the second step, and a Buckyprep column for recycling HPLC in the third step were used (eluent, toluene; flow rate, 9.9 mL/min). In addition to the minor product, of which the amount was about one-fifth of **4**, was isolated, but its structure could not be characterized. HPLCs of the purified **4** were analyzed with five different columns (Buckyprep, r.t. 17.1 min; Buckyprep M, 13.8 min; 5PYE, 11.8 min; Buckyclutcher, 4.4 min; 5PBB, 31 min; ϕ 4.6 mm × 250 mm; eluent, toluene; flow rate, 1.0 mL/min) and showed one peak in all cases.

La@C₈₂(CClPh) (**4**)

MALDI-TOF MS (*m/z*, negative ion mode) 1247 [M]⁻, 1212 [M-Cl]⁻, 1123 [M-CClPh]⁻. UV-vis-NIR absorption (in CS₂) λ_{max} 637, 1021 nm. EPR (simulation values) component A: *g* = 2.0013, *hfcc* = 1.15 G, component B: *g* = 2.0014, *hfcc* = 1.16 G.

Theoretical Calculations

Geometries of La@C₈₂(CClPh) isomers were optimized using the Gaussian 03 program¹⁵ with hybrid density functional theory at the B3LYP¹⁶ level. The relativistic effective core potential and the corresponding basis set¹⁷ were used for La, and electrons in the outermost core orbitals were explicitly treated as valence electrons. For C and H, the splitvalence 3-21G basis set^{18a} was used for geometry optimization and the larger 6-31G* basis set^{18b} for energy calculations. For La, the (5s5p3d)/[4s4p3d] contraction scheme^{17a} was employed in the geometry optimizations (B3LYP/3-21G_{1a}), whereas for energy calculations either the B3LYP/6-31G*_{1a} treatment was applied or its modification with the SDD basis set^{17b} on La (B3LYP/6-31G*_{sdd}), both in the B3LYP/3-21G_{1a} optimized geometries.

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