

# Two-dimensional hopping motion of encapsulated La atoms in silylated $\text{La}_2@C_{80}$ †

Takatsugu Wakahara,<sup>a</sup> Michio Yamada,<sup>a</sup> Satomi Takahashi,<sup>a</sup> Tsukasa Nakahodo,<sup>‡a</sup> Takahiro Tsuchiya,<sup>a</sup> Yutaka Maeda,<sup>b</sup> Takeshi Akasaka,<sup>\*a</sup> Masahiro Kako,<sup>c</sup> Kenji Yoza,<sup>\*d</sup> Ernst Horn,<sup>e</sup> Naomi Mizorogi<sup>f</sup> and Shigeru Nagase<sup>\*f</sup>

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The  $^{139}\text{La}$  NMR study of the exohedrally functionalized derivatives of  $\text{La}_2@C_{80}$  metallofullerene,  $\text{La}_2@C_{80}(\text{Ar}_2\text{Si})_2\text{CH}_2$  (**3a**: Ar = Mes, Mes = mesityl, **3b**: Ar = Dep, Dep = 2,6-diethylphenyl), reveal that the two La atoms hop between two sites along the equator of the  $C_{80}$  cage.

Endohedral metallofullerenes<sup>1</sup> have long attracted special interest as promising spherical molecules for material and catalytic applications due to the unique structures and properties. In recent years, much interest has been directed toward the behavior of metal atoms encapsulated inside fullerene cages. Among many kinds of endohedral metallofullerenes,  $\text{La}_2@C_{80}$  is one of the most intriguing molecules because of the three-dimensional random motion of two La atoms inside the  $C_{80}$  cage.<sup>2–5</sup> Such an atomic or molecular rotation in a closed cage can be used as an on–off switch to store and retrieve information. Theoretical calculations show that the three-dimensional random motion of two La atoms in  $\text{La}_2@C_{80}$  can be restricted to the circular motion in a plane by attaching an electron-donating molecule, such as disilirane, on the outer surface of the  $C_{80}$  cage.<sup>6</sup> Very recently, we have reported the synthesis and characterization of the exohedrally silylated derivative of  $\text{Ce}_2@C_{80}$ ,  $\text{Ce}_2@C_{80}(\text{Mes}_2\text{Si})_2\text{CH}_2$  (**1**, Mes = mesityl), as an analogue of  $\text{La}_2@C_{80}$ . Two encapsulated Ce atoms are localized inside the silylated  $C_{80}$  cage, according to X-ray crystallographic and  $^{13}\text{C}$  NMR spectroscopic analyses.<sup>7</sup> However, the dynamic behavior of metal atoms inside the silylated  $C_{80}$  cage has not yet been clarified. We herein report the synthesis and characterization of  $\text{La}_2@C_{80}$  adducts of 1,1,2,2-tetrakisaryl-1,2-disilirane (**2a**: Ar = Mes, **2b**: Ar = Dep, Dep = 2,6-diethylphenyl), and the dynamic behavior of the encapsulated La

atoms inside the silylated fullerene cage by means of X-ray crystallographic analysis and  $^{139}\text{La}$  NMR study.

Although empty fullerenes such as  $C_{60}$  and  $C_{70}$  react only photochemically with disilirane,<sup>8</sup> dimetallofullerenes such as  $\text{La}_2@C_{80}$  can be exohedrally functionalized with disilirane in both thermal and photochemical ways owing to their low reduction potentials.<sup>9</sup>

A toluene solution of  $\text{La}_2@C_{80}$  and 1,1,2,2-tetrakis(2,6-diethylphenyl)-1,2-disilirane (**2b**) was heated at 80 °C for 4 h to afford the silylated adduct **3b**, which can be readily isolated by preparative HPLC (Scheme 1). The formation of **3b** was confirmed by mass spectroscopic measurement. Mass spectrometry of **3b** displays a parent peak at  $m/z$  1840 ( $\text{C}_{121}\text{H}_{54}\text{Si}_2\text{La}_2$ ) as well as a peak for  $\text{La}_2@C_{80}$  at  $m/z$  1238 due to the loss of the disilirane part from **3b**. The  $^1\text{H}$  NMR spectrum of **3b** shows a set of 19 signals, suggesting that **3b** has only one conformer on the NMR time scale. It was determined that **3b** has  $C_2$  symmetry by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral analyses. It is interesting that **3b** is thermally as stable as **1**. The adduct **3a** was also prepared and isolated in a similar way, but **3a** is thermally less stable than **3b** and **1**.§

The visible-near-infrared (vis-near-IR) absorption spectra of **3a** and **3b** show an absorption maximum at around 800 nm, which resemble that of **1**. The redox properties of **3a** and **3b** were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in 1,2-dichlorobenzene using  $(n\text{-Bu})_4\text{NPF}_6$  as a supporting electrolyte. The reduction potentials of **3a** and **3b** were cathodically shifted to 450 and 390 mV, and the oxidation potentials were also cathodically shifted to 620 and 590 mV, respectively, as compared to those of the pristine  $\text{La}_2@C_{80}$ . Interestingly, during the cathodic scan, the reduction wave corresponding to the parent  $\text{La}_2@C_{80}$  became more intense, while the reduction wave corresponding to the adduct became obviously weaker. After several scans, the HPLC profile of the resulting

<sup>a</sup>Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki, 305-8577, Japan.

E-mail: akasaka@tara.tsukuba.ac.jp; Fax: (+81) 298 53 6409;

Tel: (+81) 298 53 6409

<sup>b</sup>Department of Chemistry, Tokyo Gakugei University, Koganei, Tokyo, 184-8501, Japan

<sup>c</sup>Department of Applied Physics and Chemistry, University of Electro-Communications, Chofu, Tokyo, 182-8585, Japan

<sup>d</sup>Bruker AXS K. K., Yokohama, Kanagawa, 221-0022, Japan.

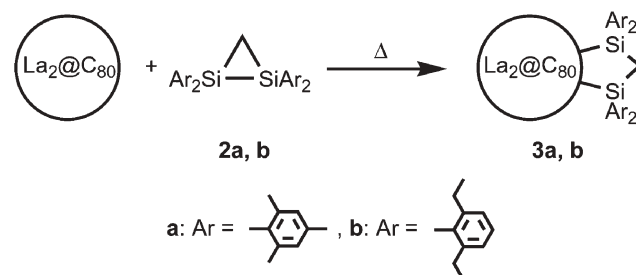
E-mail: kenji.yoza@bruker-axs.jp

<sup>e</sup>Department of Chemistry, Rikkyo University, Tokyo, 171-8501, Japan

<sup>f</sup>Department of Theoretical Molecular Science, Institute for Molecular Science, Okazaki, Aichi, 444-8585, Japan. E-mail: nagase@ims.ac.jp

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‡ Current address: Department of Applied Chemistry, Kinki University, Higashiosaka, Osaka 577-8502, Japan.



Scheme 1 Synthesis of the silylated derivatives of  $\text{La}_2@C_{80}$ .

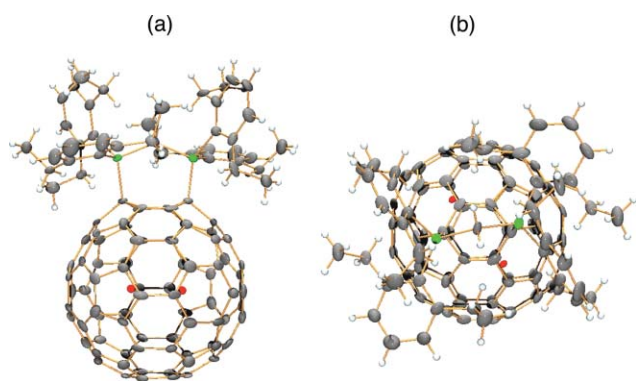
solution shows two peaks arising to the silylated  $\text{La}_2@C_{80}$  and pristine  $\text{La}_2@C_{80}$ , indicating that the quantitative retro-cycloaddition took place. Therefore, electrochemical oxidation would be useful for retro-cycloaddition<sup>10</sup> of the silylated metallofullerenes.

The molecular structure of **3b** was determined by X-ray crystallographic analysis,<sup>†</sup> and its ORTEP drawing is shown in Fig. 1. It is obvious from Fig. 1 that **3b** results from the 1,4-addition of **2a** to  $\text{La}_2@C_{80}$  and the two encapsulated La atoms are located at two positions directed toward the hexagonal ring at the equator, reflecting that these positions are energetically the most stable. Previously, the optimized structure of  $\text{La}_2@C_{80}(\text{H}_2\text{Si})_2\text{CH}_2$  was reported, in which each La faces toward the hexagonal ring of the  $C_{80}$  cage. Therefore, the theoretical calculations support the stable structure of **3b**.

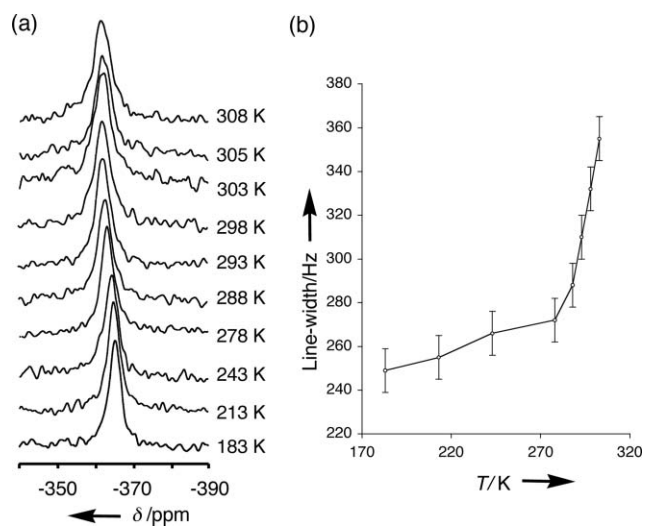
The variable-temperature  $^{139}\text{La}$  NMR spectra reveal the dynamic behavior of the La atoms inside the silylated  $C_{80}$  cage. For the pristine  $\text{La}_2@C_{80}$ , we observed a large broadening of the  $^{139}\text{La}$  NMR line-width with increasing temperature from 305 to 363 K due to the spin-rotation relaxation.<sup>3</sup> In contrast, no line-width broadening due to the spin-rotation relaxation was observed for the 6,6-adduct of pyrrolidinometallofullerene,  $\text{La}_2@C_{80}(\text{CH}_2)_2\text{NTrt}$ , because the two La atoms stand still inside the cage.<sup>11</sup> Fig. 2 shows the line-widths of the  $^{139}\text{La}$  NMR signal observed for **3b** as a function of temperatures. It is noticeable that a large broadening of the  $^{139}\text{La}$  NMR line-width was observed with increasing temperature from 183 to 308 K, indicating that two La atoms do not stand still but hop inside the silylated  $C_{80}$  cage in solution.

This is the first experimental evidence confirming that the encapsulated metal atoms hop dynamically in the metallofullerene derivatives. The paramagnetic  $^{13}\text{C}$  NMR shift analysis of **1** indicates that the motion of two Ce atoms is localized inside the silylated  $C_{80}$  cage. X-Ray crystallographic analysis of **1** shows that the two Ce atoms are localized at two positions directed toward the hexagonal ring at the equator. Therefore, the circulation of the two La atoms in **3b** is not three-dimensional, but two-dimensional hopping motion between two sites along the equatorial plane. Theoretical study also supports that the two La atoms in the silylated  $C_{80}$  cage are allowed to hop two-dimensionally along the equator.<sup>6</sup>

In conclusion, X-ray crystallographic analysis and  $^{139}\text{La}$  NMR study of the silylated  $\text{La}_2@C_{80}$  (**3a** and **3b**) reveal that the two La atoms hop two-dimensionally along the equator of the  $C_{80}$  cage. Such hopping motion restricted in a plane is expected to induce



**Fig. 1** (a) Side view and (b) top view of the ORTEP drawing of **3b** at 90 K. Thermal ellipsoids are shown at 50% probability level. The  $\text{CS}_2$  molecule and the minor La sites are omitted for clarity.



**Fig. 2** (a)  $^{139}\text{La}$  NMR spectra of **3b** at 183–303 K and (b) line-widths of the  $^{139}\text{La}$  NMR signal for **3b** as a function of temperatures.

unique electronic and magnetic fields in the direction perpendicular to the plane, which enrich the applications of endohedral metallofullerenes to molecular devices.

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## Notes and references

§ *Synthesis of 3a and 3b*: A toluene solution of 64 ml containing  $\text{La}_2@C_{80}$  (5.0 mg,  $4.0 \times 10^{-6}$  mmol) was heated at 80 °C for 2 h with 50 equiv. of **2a** under argon atmosphere to achieve the mono-adduct **3a**. Adduct **3a** can be readily isolated in 38% yield by the preparative HPLC using a Buckyprep column ( $\phi$  20 mm  $\times$  250 mm; Cosmosil, Nacal Tesque, Inc.). The adduct **3b** was synthesized and isolated in 41% yield in a similar manner. The color of **3a** and **3b** is dark brown in  $\text{CS}_2$  solution. Mass spectrometry was performed on a Bruker BIFLEX III with 9-nitroanthracene as matrix. The vis-near-IR spectra were measured between 400 and 1600 nm in toluene solution by using a SHIMADZU UV-3150 spectrophotometer. Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) were recorded on a BAS CV50W electrochemical analyzer. A platinum disk and a platinum wire were used as the working electrode and the counter electrode, respectively. The reference electrode was a saturated calomel reference electrode (SCE) filled with 0.1 M (*n*-Bu)<sub>4</sub>NPF<sub>6</sub> in 1,2-dichlorobenzene. All potentials are referenced to the ferrocene–ferrocenium couple (Fc/Fc<sup>+</sup>) as the standard. CV: scan rate, 20 mV s<sup>-1</sup>. DPV: pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV s<sup>-1</sup>. NMR spectra were obtained with Bruker AVANCE 300, AVANCE 500 with a CryoProbe system, and AVANCE 600. The  $^1\text{H}$  chemical shifts were calibrated with dichloromethane-*d*<sub>2</sub> as an internal reference ( $\delta$  5.23).  $^{13}\text{C}$  chemical shifts were calibrated with  $\text{CS}_2$  as an internal reference ( $\delta$  195.0).

Spectra data of  $\text{La}_2@C_{80}$ :  $^{13}\text{C}$  NMR (150 MHz,  $\text{CS}_2$  (acetone-*d*<sub>6</sub> in capillary as lock solvent), 298 K):  $\delta$  145.5 (60C), 138.5 (20C).

Spectra data of **3a**:  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2/\text{CS}_2$ , 213 K)  $\delta$  7.07 (s, 2H), 6.85 (s, 2H), 6.76 (s, 4H), 3.35 (s, 6H), 2.52 (s, 6H), 2.38 (s, 6H), 2.30 (s, 6H), 2.27 (s, 6H), 2.26 (s, 2H), 1.98 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2/\text{CS}_2$ , 283 K):  $\delta$  188.6 (2C), 166.6 (2C), 154.8 (2C), 153.7 (2C), 153.2 (2C), 152.3 (2C), 152.1 (2C), 151.3 (4C), 151.2 (2C), 150.9 (4C), 150.6 (2C), 148.1 (6C), 147.9 (2C), 146.2 (6C), 144.8 (2C), 143.8 (2C), 143.0 (4C), 142.2 (2C), 142.1 (2C), 141.8 (2C), 141.2 (2C), 139.8 (2C), 139.2 (2C), 138.3 (2C), 138.2 (4C), 137.8 (2C), 137.3 (2C), 137.2 (6C), 137.1 (2C), 136.7 (4C), 136.2

(2C), 134.3 (2C), 133.5 (2C), 133.2 (4C), 132.9 (2C), 132.0 (2C), 131.7 (2C), 130.9 (2C), 129.4 (2C), 68.1 (2C), 29.8 (2C), 28.9 (2C), 27.6 (2C), 26.0 (2C), 25.7 (2C), 23.9 (2C), 10.7 (1C);  $^{139}\text{La}$  NMR (70.6 MHz,  $\text{CD}_2\text{Cl}_2/\text{CS}_2$ , 295 K)  $\delta$  -400.0; Vis-NIR  $\lambda_{\text{max}}(\text{toluene})/\text{nm}$  808 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  3984); MALDI-TOF MS  $m/z$  1784 ( $\text{M}^-$ ) and 1238 ( $\text{M} - \text{Mes}_4\text{Si}_2\text{CH}_2$ ).

Spectra data of **3b**:  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2/\text{CS}_2$ , 288 K)  $\delta$  7.20 (t,  $J = 7$  Hz, 2H), 7.16 (d,  $J = 7$  Hz, 2H), 7.01 (t,  $J = 7$  Hz, 2H), 6.89 (d,  $J = 7$  Hz, 2H), 6.77 (d,  $J = 7$  Hz, 4H), 3.56 (dq,  $J = 7, 14$  Hz, 2H), 3.41 (dq,  $J = 7, 14$  Hz, 2H), 2.63 (dq,  $J = 7, 14$  Hz, 2H), 2.53 (dq,  $J = 7, 14$  Hz, 2H), 2.51 (dq,  $J = 7, 14$  Hz, 2H), 2.29 (dq,  $J = 7, 14$  Hz, 4H), 2.17 (dq,  $J = 7, 14$  Hz, 2H), 1.75 (s, 2H), 1.53 (t,  $J = 7$  Hz, 6H), 0.46 (t,  $J = 7$  Hz, 6H), 0.35 (t,  $J = 7$  Hz, 6H), 0.32 (t,  $J = 7$  Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2/\text{CS}_2$ , 288 K):  $\delta$  188.1 (2C), 166.5 (2C), 154.9 (2C), 153.7 (2C), 153.2 (2C), 152.2 (2C), 152.0 (2C), 151.3 (2C), 151.1 (2C), 150.9 (2C), 150.8 (2C), 150.5 (2C), 150.4 (2C), 148.2 (2C), 148.1 (2C), 147.9 (2C), 147.3 (2C), 146.2 (2C), 145.6 (2C), 144.8 (2C), 143.9 (2C), 143.0 (2C), 142.3 (2C), 142.2 (2C), 141.8 (2C), 141.2 (2C), 139.8 (2C), 139.1 (2C), 138.5 (2C), 138.3 (2C), 138.2 (2C), 137.9 (2C), 137.4 (2C), 137.3 (4C), 137.2 (2C), 136.8 (4C), 136.2 (2C), 134.3 (2C), 133.3 (2C), 132.8 (2C), 132.6 (4C), 132.1 (4C), 130.7 (2C), 130.2 (2C), 129.2 (2C), 129.1 (2C), 126.6 (2C), 68.2 (2C), 35.2 (2C), 34.4 (2C), 32.5 (2C), 31.9 (2C), 17.4 (2C), 17.3 (2C), 17.1 (2C), 17.0 (2C), 13.9 (1C);  $^{29}\text{Si}$  NMR (99 MHz,  $\text{CD}_2\text{Cl}_2/\text{CS}_2$ , 288 K)  $\delta$  8.43;  $^{139}\text{La}$  NMR (66.5 MHz,  $\text{CD}_2\text{Cl}_2/\text{CS}_2$ , 298 K)  $\delta$  -362.1. Vis-NIR  $\lambda_{\text{max}}(\text{toluene})/\text{nm}$  800; MALDI-TOF MS  $m/z$  1840 ( $\text{M}^-$ ), 1238 ( $\text{M} - \text{Dep}_4\text{Si}_2\text{CH}_2$ ).

¶ Black crystals of **3b** were obtained by evaporating slowly a solution of **3b** in  $\text{CS}_2$  and hexane. Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX equipped with a CCD area detector using Mo-K $\alpha$  radiation in the scan range  $1.44 < \theta < 27.80^\circ$ . Crystal data for **3b**· $\text{CS}_2$ :  $\text{C}_{122}\text{H}_{54}\text{La}_2\text{S}_2\text{Si}_2$ ,  $M_r = 1917.77$ , monoclinic, space group  $P2_1/n$ ,  $a = 18.234(2)$ ,  $b = 19.326(3)$ ,  $c = 20.834(3)$  Å,  $\beta = 90.445(2)^\circ$ ,  $V = 7341.5(16)$  Å $^3$ ,  $Z = 4$ ,  $D_c = 1.735 \text{ Mg m}^{-3}$ ,  $\mu = 1.303 \text{ mm}^{-1}$ ,  $T = 90 \text{ K}$ , crystal size  $0.07 \times 0.06 \times 0.03 \text{ mm}$ . 75762 reflections, 16035 unique reflections; 12892 with  $I > 2\sigma(I)$ ;  $R_1 = 0.1165$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.3006$  (all data), GOF (on  $F^2$ ) = 1.176. The maximum residual electron density is equal to  $0.922 \text{ e \AA}^{-3}$ . CCDC 631668. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703473c

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