

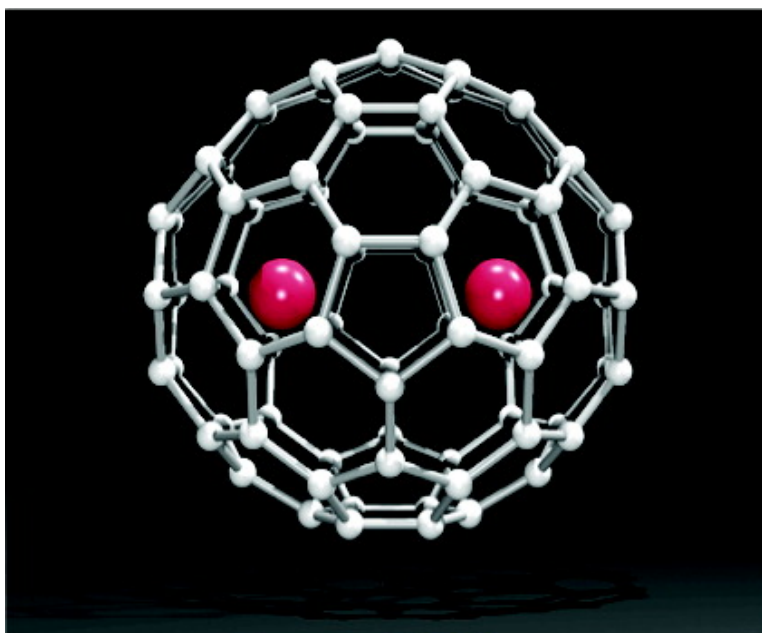
Communication

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Isolation, Characterization, and Theoretical Study of La₂@C₇₈

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Endohedral metallofullerenes have attracted attention not only for their unique structures and properties but also for their ability to stabilize novel cage isomers that have never been experimentally found in empty form.^{1–4} The most unstable C₈₀ cage isomers, *I_h*- and *D_{5h}*-C₈₀, can be generated by encapsulation of two La/Ti atoms or a metal cluster, Sc₃N.^{2–4} The only known violations of the isolated pentagon rule (IPR) are in endohedral metallofullerenes.^{5–7} As the first metallofullerenes that were macroscopically produced and isolated, La endohedrals are the typical representatives of these novel materials.¹ The lanthanum metallofullerenes isolated and structurally characterized thus far are La@C₈₂,^{8,9} La₂@C₈₀,² and La₂@C₇₂.¹⁰ Here we report the first isolation, ¹³C NMR structure characterization, and theoretical studies of a new metallofullerene, La₂@C₇₈. The results show that La₂@C₇₈ possesses a *D_{3h}*-C₇₈ (78:5) cage isomer.

La₂@C₇₈ was isolated using a recently developed method.¹¹ Briefly, the La metallofullerenes were produced by DC arc discharge method and extracted with 1,2,4-trichlorobenzene (TCB) under reflux. A controlled-potential bulk reduction of the extract in *o*-DCB solution in the presence of *n*-BuNClO₄ (3.0 × 10⁻² M) was carried out for selective reduction of the metallofullerenes into their anions, which left the empty fullerenes in the neutral state.^{8,9} After removal of the *o*-DCB and by use of selective extraction with a mixture of acetone/CS₂ (1:4 in volume), the metallofullerene anions were roughly separated from the abundant empty fullerenes. A moderate oxidant, CHCl₂COOH, was added to the acetone/CS₂ extract to convert the anions into neutral species that precipitated from the mixed solvent. The precipitates were then dissolved in toluene for HPLC separation. La₂@C₇₈ was well separated from the other metallofullerenes and readily isolated in isomer-free form by HPLC with a PYE column (Figure 1a). The purity of isolated La₂@C₇₈ is >99.9%, as confirmed by mass spectroscopic (Figure 1a, inset) and HPLC analyses. On the basis of HPLC analysis, the abundance of La₂@C₇₈ with regard to the major isomer of La@C₈₂ is ~3.8%.

The UV–vis–NIR absorption spectrum of La₂@C₇₈ presents several characteristic features at 647, 561, 533, and 386 nm, with an onset around 1000 nm (Figure 1b). The La₂@C₇₈/CS₂ solution is dark violet (Figure 1b, inset). The molar absorbance coefficients of La₂@C₇₈ in toluene solution at 647, 561, and 386 nm are 6500, 2800, and 5300 L mol⁻¹ cm⁻¹, respectively. On the basis of DPV measurement, the first reduction and oxidation potentials of La₂@C₇₈ (Table 1) are positively and negatively shifted, respectively, with respect to those of the empty *D₃*-C₇₈,¹² suggesting that

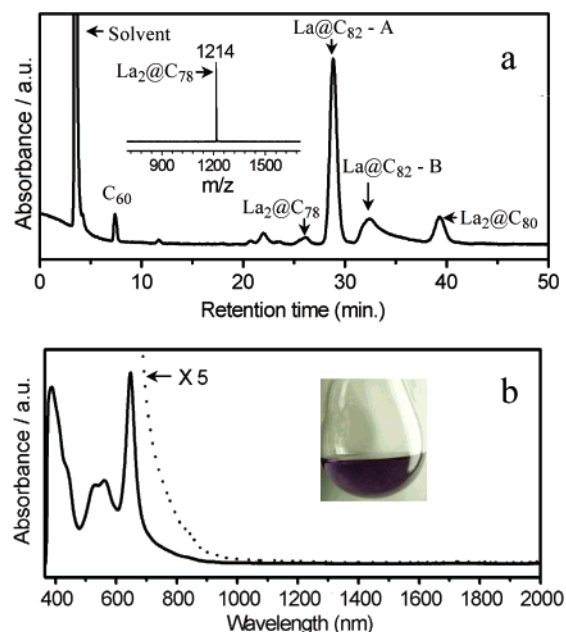


Figure 1. (a) HPLC chromatogram for isolation of La₂@C₇₈ (PYE column, φ 20 × 250 mm, Nacalai, toluene eluant, 10 mL/min); inset is the LD TOF mass spectrum of La₂@C₇₈. (b) UV–vis–NIR absorption spectrum of La₂@C₇₈ in CS₂; inset shows the color of La₂@C₇₈/CS₂ solution.

Table 1. Redox Potentials (V) of La₂@C₇₈^a and C₇₈ (*D₃*)^b

	ox E ₃	ox E ₂	ox E ₁	red E ₁	red E ₂	red E ₃
La ₂ @C ₇₈	1.11	0.62	0.26	-0.40	-1.84	-2.28
C ₇₈ (<i>D₃</i>)			0.65	-0.76	-1.06	-1.79

^a 0.1 M *n*-BuNPF₆, *o*-DCB solution, working electrode Pt wire, BAS-100 B/W, potentials vs ferrocene/ferrocenium couple. ^b Reference 12.

the capabilities of La₂@C₇₈ as an electron acceptor or donor are stronger than those of *D₃*-C₇₈. La₂@C₇₈ reacts photochemically, as well as thermally, with 1,1,2,2-tetrakis(2,4,6-trimethylphenyl)-1,2-disirane in toluene, affording mono- and bis-adducts, which is in sharp contrast to the empty *D₃*-C₇₈ that does not undergo the reaction.¹²

As seen in the ¹³C NMR spectrum of La₂@C₇₈ (Figure 2a), the lines at 152.20, 148.04, and 145.67 ppm are obviously at half intensity (numbers 1, 3, and 4) and those at 148.14, 145.42, and 140.17 ppm are at full intensity (numbers 2, 5, and 8). Compared with the others, the peak at 142.67 ppm is broad and its intensity is double the full intensity and 4-fold the half intensity, indicating it comes from two full-intensity lines (numbers 6 and 7). Consequently, eight lines in total are observed in the fullerene region in the ¹³C NMR spectrum of La₂@C₇₈. This ¹³C NMR pattern is

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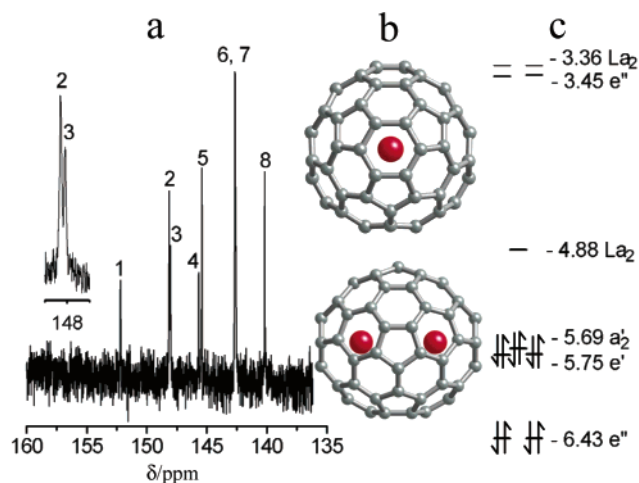


Figure 2. (a) ^{13}C NMR (125.78 MHz) spectrum of $\text{La}_2@C_{78}$ in CS_2 (D_2O in capillary as lock solvent, $\text{Cr}(\text{acac})_3$ as relaxant); inset shows the expanded lines, numbers 2 and 3. (b) Two views of the optimized structure of $\text{La}_2@C_{78}$. (c) The orbital levels in eV of $\text{La}_2@C_{78}$.

unambiguously attributed to a $D_{3h}\text{-C}_{78}$ cage, which theoretically presents five lines with full intensity and three lines with half intensity.¹³

C_{78} has two D_{3h} IPR cage isomers, $D_{3h}(78:4)$ and $D_{3h}(78:5)$.¹³ To figure out which isomer $\text{La}_2@C_{78}$ possesses, we performed theoretical studies on $\text{La}_2@C_{78}$.¹⁴ The results indicate that $\text{La}_2@C_{78}$ with the $D_{3h}\text{-C}_{78}(78:5)$ cage (Figure 2b) is more stable by 81 kcal mol^{-1} than that with the $D_{3h}\text{-C}_{78}(78:4)$ cage. Six electrons are transferred from the encapsulated La atoms to the $D_{3h}\text{-C}_{78}(78:5)$ cage; i.e., the electronic structure model of $\text{La}_2@C_{78}$ could be described as $(\text{La}^{3+})_2\text{C}_{78}^{6-}$. The calculated binding energy between the $D_{3h}\text{-C}_{78}(78:5)$ and two La atoms is 277 kcal mol^{-1} , indicating the $D_{3h}\text{-C}_{78}(78:5)$ has been greatly stabilized by encapsulation of two La atoms inside the cage.

In theory, C_{78} has five cage isomers satisfying IPR with symmetries $D_3(78:1)$, $C_{2v}(78:2)$, $C_{2v}(78:3)$, $D_{3h}(78:4)$, and $D_{3h}(78:5)$.¹³ The first three isomers have been isolated in empty form.^{15–17} The unstable C_{78} isomer, $D_{3h}(78:5)$, has been produced by encasing Sc_3N within the cage.^{18,19} $\text{Sc}_3\text{N}@C_{78}$ is the only C_{78} -based endohedral metallofullerene so far reported. Interestingly, $\text{La}_2@C_{78}$ is totally distinct from $\text{Sc}_3\text{N}@C_{78}$ in color, UV–vis–NIR absorption, and ^{13}C NMR pattern, even though they all possess $D_{3h}\text{-C}_{78}(78:5)$ with the same amount of intramolecular electron transfer. The discrepancies mentioned above strongly suggest that the geometric and electronic structures of $\text{La}_2@C_{78}$ are varied from those of $\text{Sc}_3\text{N}@C_{78}$. The HOMO–LUMO gap of the optimized structure of $\text{La}_2@C_{78}$ is 0.81 eV, which is much smaller than that of $\text{Sc}_3\text{N}@C_{78}$.¹⁹ The orbital levels of $\text{La}_2@C_{78}$ (Figure 2c) are clearly distinct from those of $\text{Sc}_3\text{N}@C_{78}$,¹⁹ which rationalizes the differences in optical absorption between the two metallofullerenes.

Accordingly, the difference in the structure of endohedrals in $\text{La}_2@C_{78}$ and $\text{Sc}_3\text{N}@C_{78}$ is responsible, at least in part, for all the discrepancies mentioned above between the two metallofullerenes.

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Supporting Information Available: Mass, DPV, and CV spectra, calculated data, and optimized structures of $\text{La}_2@C_{78}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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