

La@C₇₂ Having a Non-IPR Carbon Cage

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Fullerenes have an even number of three-coordinate carbon atoms (n) and consist of 12 pentagonal and $(n/2 - 10)$ hexagonal carbon rings (e.g., C₆₀ has 12 pentagons and 20 hexagons). It has been established as the isolated-pentagon rule (IPR) that all pentagons are isolated in the most stable fullerene.¹ Since the first proposal by Kroto in 1987,^{2,3} the IPR has proved particularly valuable in unraveling cage structures of higher fullerenes and metallofullerenes.^{4–10} Recently, Sc₂@C₆₆ and Sc₃N@C₆₈ have been reported as the examples of endohedral metallofullerenes having a non-IPR cage.^{11–13} Since no IPR-satisfying cage structure is available for C₆₆ and C₆₈, it remains still an open question whether metallofullerenes that have a non-IPR cage are isolable or not.

For C₇₂, there is only one IPR-satisfying structure with D_{6d} symmetry. Theoretical investigation of C₇₂ and Ca@C₇₂ suggests that non-IPR cage structures are more stable than the IPR-satisfying one.^{14–16} Recently, Shinohara et al. reported the NMR study on La₂@C₇₂, which indicates that La₂@C₇₂ has a non-IPR cage.^{17,18} However, there is no conclusive evidence for the structural characterization. Meanwhile, we succeeded in the extraction, isolation, and characterization of a missing metallofullerene La@C₇₄ as a derivative, La@C₇₄(C₆H₃Cl₂).¹⁹ This derivative method opened a way for the experimental structural investigation of unconventional metallofullerenes. We herein report the first structural determination of a monometallofullerene derivative, La@C₇₂(C₆H₃Cl₂), that has a non-IPR cage by spectroscopic and X-ray crystallographic analysis. In addition, the unique electronic properties and high reactivity of La@C₇₂ are discussed on the basis of the theoretical study.

Soot containing lanthanum metallofullerenes was produced by the arc discharge method,²⁰ and three adducts (A, B, and C) were extracted in 1,2,4-trichlorobenzene and isolated from the raw soot by the method previously reported.¹⁹ The MALDI-TOF mass spectra of the adducts show a molecular ion peak at m/z 1155–1148 which is attributed to the adduct of La@C₇₂ (m/z 1003) with the dichlorophenyl (C₆H₃Cl₂) group (m/z 145). This suggests that the adducts are formed during the extraction by the reaction of La@C₇₂ and 1,2,4-trichlorobenzene, as found for the La@C₇₄ case.¹⁹ The EPR measurement shows that the adducts (A, B, and C) are EPR inactive, indicative of a closed-shell electronic structure.

In order to determine the structures of the adducts (A, B, and C), La@C₇₂(C₆H₃Cl₂), we performed ¹H NMR, ¹³C NMR, and 2D NMR (HMOC and HMBC) measurements. The NMR spectra

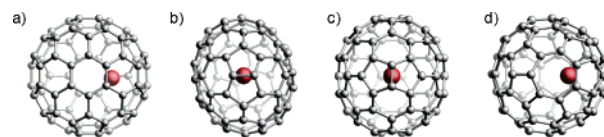


Figure 1. The optimized structures of La@C₇₂: (a) IPR-satisfying cage structure of La@C₇₂ with D_{6d} symmetry; (b) non-IPR cage structure containing a pair of fused pentagons with C_2 symmetry; (c) non-IPR cage structure containing a pair of fused pentagons with C_{2v} symmetry; (d) non-IPR cage structure containing one heptagon with C_s symmetry.

exhibit that the isomers A, B, and C have 2,4-dichlorophenyl, 2,5-dichlorophenyl, and 3,4-dichlorophenyl groups, respectively. Similar ¹³C NMR signals for the carbon cage and UV–visible–near-infrared absorption were observed for A, B, and C, indicating that these three isomers have the same cage structure and addition site. The ¹³C NMR spectra of A, B, and C show a total of 78 lines (72 lines from the C₇₂ cage and 6 lines from the dichlorophenyl group), indicating that these isomers have C_1 symmetry. The signal at 58–56 ppm is assuredly assigned to the sp³ carbons on C₇₂ by ¹H-¹³C long-range coupling NMR measurements. The ¹³⁹La NMR spectra of A, B, and C exhibit a single broad signal with a line width of 2100 Hz at 300 K. The ¹³⁹La NMR chemical shifts at –605(A), –603(B), and –618(C) ppm are close to that observed for La₂@C₇₂ (–576 ppm)¹⁷ and are significantly lower than those observed for La@C₇₄(C₆H₃Cl₂)(A) (–511 ppm),¹⁹ La₂@C₈₀ (–403 ppm),²¹ and [La@C₈₂(C_{2v})][–]*n*-Bu₄N⁺ (–470 ppm).⁹ These suggest a correlation between the ¹³⁹La NMR chemical shift and the carbon cage size.

As Figure 1 shows, we carried out density functional calculations on the four isomers of La@C₇₂.²² Structure **a** (C_s) satisfies the IPR, while **b** (C_2) and **c** (C_{2v}) contain the fused pentagons, and **d** (C_s) has one heptagon surrounded by five fused pentagons. The cage structures of **b**, **c**, and **d** do not obey the IPR well-known in fullerene science. These structures were reported for Ca@C₇₂ to suggest that **b**, **c**, and **d** are more stable than **a**.^{14,15} For La@C₇₂, it was calculated at the B3LYP/6-31G(d)//B3LYP/3-21G level that **b**, **c**, and **d** are 37.4, 37.1, and 20.3 kcal/mol more stable than **a**, respectively.²² This suggests that La@C₇₄(C₆H₃Cl₂) is a dichlorophenyl derivative of La@C₇₂ that has a non-IPR cage.

We have succeeded in the X-ray crystallographic analysis²³ of La@C₇₂(C₆H₃Cl₂)(A). As is obvious from Figure 2, La@C₇₂(C₆H₃Cl₂)(A) is formed from the addition of a 2,4-dichlorophenyl group to the most stable La@C₇₂(**b**). The dichlorophenyl group is attached to the C(1) atom in the fused pentagons. La@C₇₂(C₆H₃Cl₂)(A) is chiral, and the ratio of these enantiomers is 1:1 in the crystalline state. In addition, the enantiomers have the conformational isomer owing to a dichlorophenyl group in the 9:1 ratio in the crystalline

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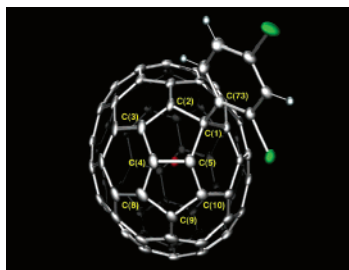


Figure 2. Crystal structure of La@C₇₂(C₆H₃Cl₂)(A) at 153 K. The CS₂ molecule is omitted for clarity.

Table 1. Redox Potentials (V),^a Ionization Potentials (eV), and Electron Affinities (eV) of La@C₇₂(b), La@C₇₂(C₆H₃Cl₂)(A–C), and La@C₈₂(C_{2v})

compound	oxE ₁	redE ₁	redE ₂	IP/Ea
La@C ₇₂ (b)				5.91/2.94
La@C ₇₂ (C ₆ H ₃ Cl ₂)(A)	0.44	−1.00	−1.37	6.57/2.66
La@C ₇₂ (C ₆ H ₃ Cl ₂)(B)	0.42	−1.00	−1.36	
La@C ₇₂ (C ₆ H ₃ Cl ₂)(C)	0.46	−0.95	−1.29	
La@C ₈₂ (C _{2v}) ^b	0.07	−0.42	−1.37	6.19/3.38

^a Versus Fc/Fc⁺. In 1,2-dichlorobenzene with 0.1 M (*n*-Bu)₄NPF₆ at a Pt working electrode. CV: scan rate, 20 mV·s^{−1}. ^b Reference 25.

state. The encapsulated La atom is located near the fused pentagons. The position of the La atom in La@C₇₂(C₆H₃Cl₂)(A) is slightly different from that in La@C₇₂(b). Density functional calculations show that three valence electrons on La are transferred to C₇₂(C₆H₃Cl₂), the resultant electronic structure being described as La³⁺[C₇₂(C₆H₃Cl₂)]^{3−}. Therefore, the La³⁺ cation is located near the minimum of the electrostatic potentials inside [C₇₂(C₆H₃Cl₂)]^{3−}. The observed La–C(4) and La–C(5) distances of 2.615 and 2.605 Å are somewhat shorter than the calculated values of 2.714 and 2.680 Å, respectively. The observed C(4)–C(5) distance of 1.424(4) Å is in good agreement with the calculated value of 1.429 Å. The addition position (C(1)) of the dichlorophenyl group has both the high SOMO spin-density and the high π -orbital axis vector (POAV) pyramidalization angle²⁴ on La@C₇₂(b) (see Table S5 in Supporting Information). These results suggest that the high reactivity of La@C₇₂(b) toward a radical species is ascribed to the radical character and local strain of the C(1) atom.

In view of the fact that La@C₇₂ is not extracted in common organic solvents and La@C₇₂(C₆H₃Cl₂) is produced during the extraction process, there is considerable interest in the electronic property and reactivity of La@C₇₂(b). First, we calculated the ionization potential (IP) and electronic affinity (Ea) of La@C₇₂(b) at the B3LYP/6-31+G(d)/B3LYP/6-31G(d) level.²² As Table 1 shows, La@C₇₂(b) has a smaller IP than La@C₈₂(C_{2v}). The calculated IP value of La@C₇₂(b) is the smallest among the reported lanthanum metallofullerenes.¹⁹ Because of this small IP, La@C₇₂(b) may interact strongly with amorphous carbon in soot and become thereby insoluble in common organic solvents. The adduct, La@C₇₂(C₆H₃Cl₂)(A), has a higher IP than La@C₇₂(b), this being also supported by their redox potentials (Table 1). These results suggest that the addition of a dichlorophenyl group to La@C₇₂(C₂) leads to stable endohedral metallofullerene derivatives, which can be extracted in common organic solvents. The redox potentials of La@C₇₂(C₆H₃Cl₂)(A, B, and C) and La@C₈₂(C_{2v}) are summarized in Table 1.

In conclusion, it is determined that La@C₇₂(b) has a non-IPR carbon cage. The small IP of La@C₇₂(b) accounts for its electronic

property and high reactivity. The addition of a dichlorophenyl radical on La@C₇₂(b) leads to La@C₇₂(C₆H₃Cl₂) with a closed-shell structure. The successful isolation of the La@C₇₂(C₆H₃Cl₂) derivative suggests that many other insoluble and unknown endohedral metallofullerenes still remain in raw soot, which will open up the new material science of metallofullerenes.

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Supporting Information Available: Experimental details and spectroscopic and theoretical data for La@C₇₂(C₆H₃Cl₂) and La@C₇₂; X-ray crystallographic details including CIF file; complete refs 9, 10, and 19. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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