DOI: 10.1002/chem.200902512

Regioselective Exohedral Functionalization of La@C_{82} and its 1,2,3,4,5-Pentamethylcyclopentadiene and Adamantylidene Adducts

Yutaka Maeda,[a] Satoru Sato,[b] Koji Inada,[a] Hidefumi Nikawa,[b] Michio Yamada,[b] Naomi Mizorogi,[b] Tadashi Hasegawa,*[a] Takahiro Tsuchiya,[b] Takeshi Akasaka,*[b] Tatsuhisa Kato,[c] Zdenek Slanina,[b] and Shigeru Nagase*[d]

Abstract: The first regioselective functionalization of La@C_{82} by two different groups has been performed. Bis-adducts of La@C_{82} with Cp* and adamantylidene were synthesized by using two different routes and characterized. Spectroscopic analysis and theoretical calculations reveal that the addition position is controlled by the charge density and p-orbital axis vector value of the fullerene cage.

Keywords: carbenes • cycloaddition • fullerenes • lanthanum • regioselectivity

Introduction

Endohedral metallofullerenes have attracted much attention because of their novel properties that result from intramolecular metal–fullerene cage interactions.[1] Structural analyses of monoadducts of endohedral metallofullerenes have revealed how the chemical reactivity and selectivity of empty fullerenes change upon endohedral metal doping and how the electronic properties of endohedral metallofullerenes change upon chemical functionalization. We have reported highly regioselective reactions of La@C_{82} and demonstrated that the local strain and charge density on the carbons control the reactivity toward nucleophilic[2] and electrophilic[3] reagents. Multiple functionalization of fullerenes has become an important topic because regioselectvity provides fundamental information about the chemical properties of fullerenes. Moreover, it is attractive for practical applications of fullerenes. Herein we present the regioselective formation of bis-adducts of La@C_{82} with different addenda. We chose 1,2,3,4,5-pentamethylcyclopentadiene (Cp*) and 2-adamantane-2,3-[3*H*]-diazirine (AdN_2) as reactants because cyclopentadiene (Cp) and AdN_2 afford the corresponding regioselective monoadducts of La@C_{82}.[2,4] The addition position of Cp has not been clarified yet because the retro reaction of La@C_{82} with Cp proceeds readily at room temperature.[4] Herein, structural analysis of the monoadduct of La@C_{82} with Cp* was conducted.

Results and Discussion

A solution of La@C_{82} (1.8×10^{-5} M) and Cp* (1.8×10^{-4} M) in toluene was placed in a quartz tube. After standing under an argon atmosphere for 5 h, La@C_{82}Cp* (80 % conversion yield; see Scheme 1) and La@C_{82}Cp*$_2$ were isolated by using HPLC (Figure 1). The ESR spectrum of La@C_{82}Cp* showed only one octet of signals, which confirms that one conformer is selectively formed as a monoadduct. The temperature-dependent stability of La@C_{82}Cp* was studied by using ESR analysis. In fact, 36 % of La@C_{82}Cp* decomposed to La@C_{82} and Cp* after sitting at 298 K for 12 h. On the other hand,

---

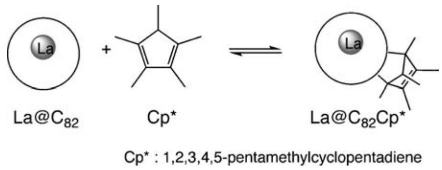
[a] Prof. Dr. Y. Maeda, K. Inada, Prof. Dr. T. Hasegawa
Department of Chemistry
Tokyo Gakugei University
Koganei, Tokyo 184-8501 (Japan)
Fax: (+81) 42-329-7496
E-mail: tadashi@u-gakugei.ac.jp

[b] S. Sato, H. Nikawa, Dr. M. Yamada, Dr. N. Mizorogi, Dr. T. Tsuchiya, Prof. Dr. T. Akasaka, Dr. Z. Slanina
Center for Tsukuba Advanced Research Alliance
University of Tsukuba
Tsukuba 305-8577 (Japan)
Fax: (+81) 29-853-6409
E-mail: akasaka@tara.tsukuba.ac.jp

[c] Prof. Dr. T. Kato
Department of Chemistry
Josai University
Sakado, Saitama 171-8501 (Japan)

[d] Prof. Dr. S. Nagase
Department of Theoretical and Computational Molecular Science
Institute for Molecular Science
Myodaiji, Okazaki 444-8585 (Japan)
Fax: (+81) 564-53-4660
E-mail: nagase@ims.ac.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902512.



Scheme 1.

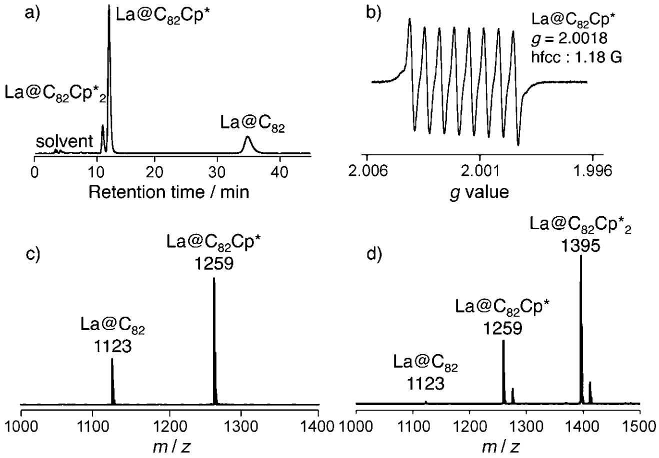


Figure 1. a) HPLC profile of reaction mixture of La@C_{82} and Cp*. b) ESR spectrum of La@C_{82}Cp*. ESI mass spectra of c) La@C_{82}Cp* and d) La@C_{82}Cp*$_2$.

after a week at 273 and 253 K only 19 % and 4 % of La@C_{82}Cp*, respectively, had decomposed to La@C_{82} and Cp*. These results suggest that the stability of La@C_{82}Cp* is considerably greater than that of La@C_{82}Cp (half-life at 298 K: 1.8 h) due to the substituent effect of methyl groups on the Cp ring.[4]

Redox potentials of La@C_{82}Cp* were measured by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). First reduction and oxidation potentials of La@C_{82}Cp* were slightly lower than those of La@C_{82} (see Table 1).[5] Repeated scanning during CV measurements showed that the reduction and oxidation states of La@C_{82}Cp* are stable.

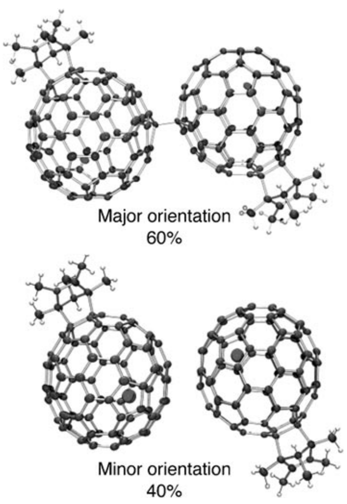


Figure 2. ORTEP drawings of La@C_{82}Cp* (major and minor orientation) showing thermal ellipsoids at the 50 % probability level. The CS_2 molecules are omitted for clarity.

Figure 2 shows the structure of La@C_{82}Cp* as determined by using X-ray crystallographic analysis.[6] It is particularly interesting that the addition position, C21–C23, is the same as that in the nucleophilic addition of La@C_{82}, and that the stereospecific monoadduct is produced selectively.[3] Theoretical study of La@C_{82} revealed that C21 and C23 have high p-orbital axis vector (POAV) angles and are the most positively charged carbon atoms.[2,3,7] On the other hand, the LUMO and SOMO of La@C_{82} have no large orbital coefficients on C21 and C23,[4] which suggests that the C21–C23 bond is selectively attacked by the electron-rich diene. To confirm the stereospecific and regioselective reactivity, the optimized structure and relative stability of two stereoisomers (**i** and **ii**) and one position isomer (**iii**; addition position C2–C3) were calculated (Figure 3).[4] C2 and C3 have large orbital coefficients in the SOMO of La@C_{82}.[8] The calculations revealed that La@C_{82}Cp* is 1.2, 6.2, and 4.9 kcal mol^{-1} more stable than isomers **i**, **ii**, and **iii**, respectively. These results suggest that La@C_{82}Cp* is the kinetically and thermodynamically preferred monoadduct.

Table 1. Redox potentials of La@C_{82} and its derivatives.

	E_1^{ox}	E_1^{red}	E_2^{red}	E_3^{red}
La@C_{82}Cp*[a]	0.02	−0.45	−1.71	−2.22
La@C_{82}-A[a,b]	0.07	−0.42	−1.37	−1.53
La@C_{82}Ad[a,c]	−0.01	−0.49	−1.44	−1.79
La@C_{82}CBr($COOC_2H_5$)$_2$[d,e]	0.38	−0.66	−1.31	−1.47
La@C_{82}(Mes_2Si_2)CH_2[e,f]	−0.07	−0.50	−1.71	−1.75

[a] Values obtained by CV. Electrolyte: 0.1 M (nBu)$_4$NPF$_6$; solvent: 1,2-dichlorobenzene; scan rate: 20 mV s.$^{-1}$ [b] Ref. [5]. [c] Ref. [2]. [d] Ref. [3]. [e] Values are relative to ferrocene/ferrocenium couple and obtained by DPV. [f] Ref. [5]. [c] Ref. [11].

X-ray analysis results show that La@C_{82}Cp* takes two orientations in the crystal structure, and 60 % of the monoad-

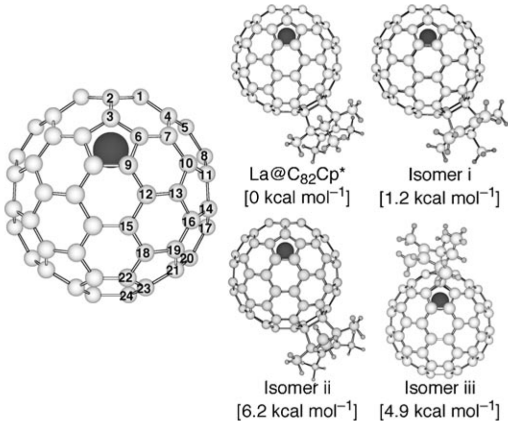


Figure 3. Optimized structures for La@C_{82}Cp*, stereoisomers **i** and **ii**, and position isomer **iii**, and their relative energies calculated at the B3LYP/6-31G* level.

duct forms a dimer in the solid state. The length of the C–C bond connecting two C_{82} cages in the La@C_{82}Cp* dimer (1.606 Å) is only about 0.1 Å longer than the typical C–C single bond length. Similar dimerization has been found in the crystal structure of La@C_{82}[CH(COOC_2H_5)$_2$]$_2$.[9] The single bond formation was explained by high POAV angles (11.0°) and spin density (0.028) of the bonded carbons.[9] It is interesting that very similar POAV angles (11.0°) and spin density (0.025) were calculated for La@C_{82}Cp*. In contrast, the closest carbon atoms (C···C distance: 2.666 Å) of two La@C_{82}Cp* molecules in the minor orientation have a small POAV value (9.7°) and spin density (0.022). Therefore, dimerization in the solid state might be controlled by the higher POAV angles and spin density.

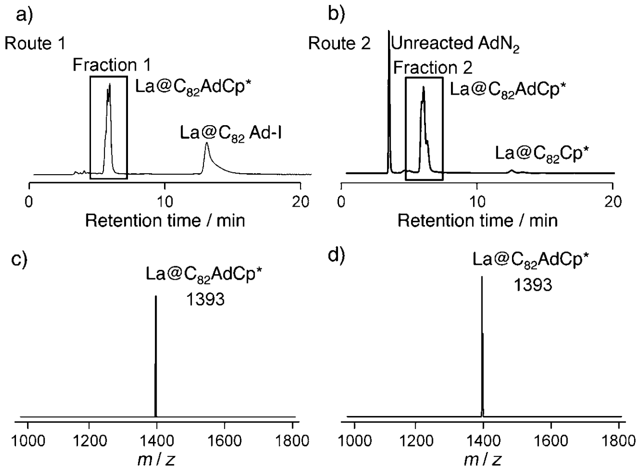
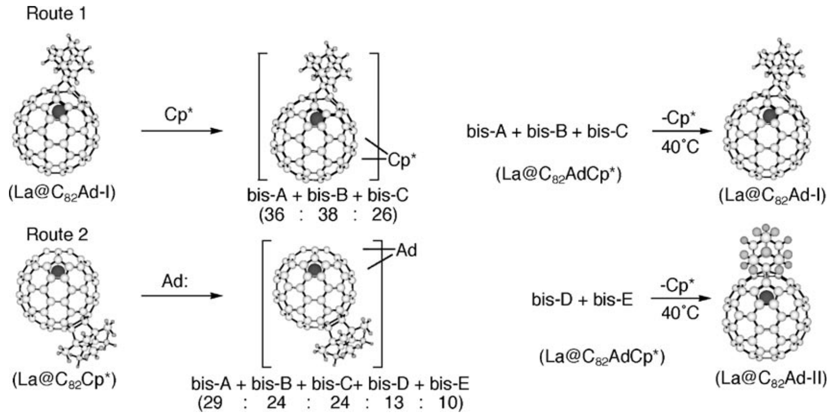


Figure 4. HPLC profile of mixtures of a) La@C_{82}Cp* with AdN_2 and b) La@C_{82}Ad with Cp*. ESI mass spectra of c) fraction 1 and d) fraction 2.



Scheme 2.

Functionalization of La@C_{82} derivatives was achieved by the addition of Cp* and adamantylidene (Ad) to La@C_{82}Ad and La@C_{82}Cp*, respectively (Scheme 2). La@C_{82}Ad is stable at 40 °C and La@C_{82}Cp* is stable under photochemical conditions. For this study, La@C_{82}Ad-I and La@C_{82}Ad-II[10] were prepared in conversion yields of 80 and 20 %, respectively, according to the reported procedure.[2] Treating La@C_{82}Ad-I (1.7×10^{-4} M) with Cp* (1.7×10^{-3} M) gave La@C_{82}AdCp* (route 1). Three isomers of La@C_{82}AdCp* (bis-A, bis-B, and bis-C) were isolated from fraction 1 (Figure 4). Photoreaction of La@$_{82}$Cp* (1.9×10^{-4} M) with AdN_2 (1.9×10^{-2} M) by using a high-pressure mercury arc lamp (cutoff <300 nm) gave La@C_{82}AdCp* (route 2). A mixture of two isomers of La@C_{82}AdCp* (bis-D and bis-E) was separated from fraction 2, accompanied by isolation of bis-A, bis-B, and bis-C. The abundance ratios of La@C_{82}AdCp* isomers for routes 1 and 2 were estimated by simulating the spectra of fractions 1 and 2 (Figure 5). At 40 °C and in the presence of maleic anhydride (used as a scavenger because of the elimination of Cp*), bis-A, bis-B, and bis-C gave La@C_{82}Ad-I and the mixture of bis-D and bis-E gave La@C_{82}Ad-II. (Figure 6). Formation of La@C_{82}Ad-I and La@C_{82}Ad-II (ca. 4:1 ratio) from La@C_{82}AdCp* in route 2 indicates that the addition position of Ad is unchanged compared with pristine La@C_{82} (C1–C2 and C2–C3). On the other hand, the formation of three regioisomers (bis-A, bis -B, and bis-C) in route 1 suggests that the addition position of Cp* is unchanged compared with pristine La@C_{82} (C21–C23). In fact, La@C_{82}Ad-I and La@C_{82}Ad-II have four and two sets of C21–C23 bonds, respectively, because La@C_{82}Ad-I has C_1 and La@C_{82}Ad-II has C_s symmetry. Moreover, La@C_{82}Cp* has C_1 symmetry. Therefore, it is a possibility that up to four and six position isomers of La@C_{82}AdCp* are produced in routes 1 and 2, respectively.

For La@C_{82}Ad-I, it was calculated that four sets of C21 and C23 atoms have high POAV angles and that these carbon atoms are the most positively charged. For La@C_{82}Cp*, it was calculated that four sets of C1 and C2 atoms and two sets of C2 and C3 atoms have high POAV angles and that these carbons are the most negatively charged. These results suggest that the local strain and charge density of cage carbons are responsible for high regioselectivity in the functionalization of La@C_{82} derivatives.

Conclusion

La@C_{82}Cp* has been isolated and characterized. Its retro reaction is controlled by changing the reaction temperature. An La@C_{82} adduct with two different functional groups, La@C_{82}AdCp*, was synthesized regioselectively by two different routes. X-ray crystal analysis of La@C_{82}Cp* and theoretical calculations of La@C_{82}, La@C_{82}Cp*, and La@C_{82}Ad

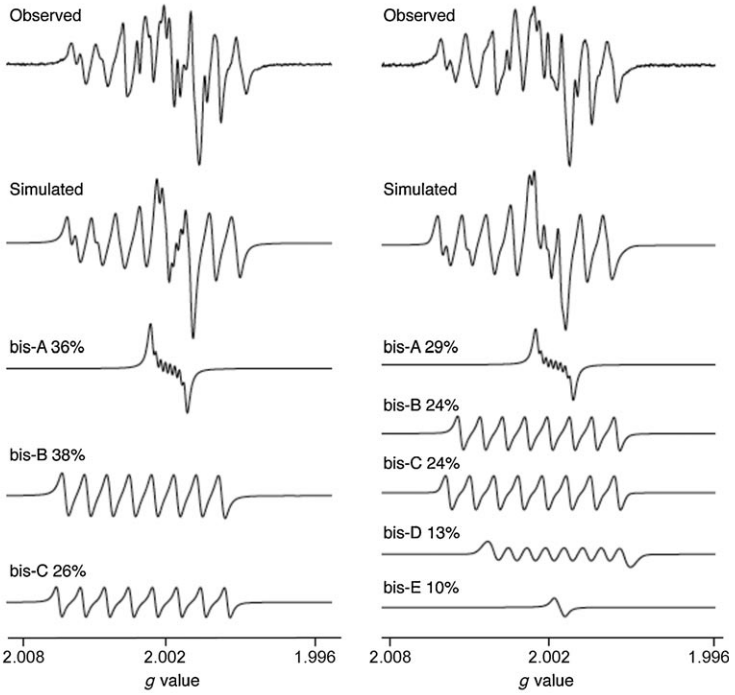


Figure 5. Experimental and simulated (calculated by using isolated La@C_{82}AdCp* parameters) ESR spectra of fractions 1 (left) and 2 (right).

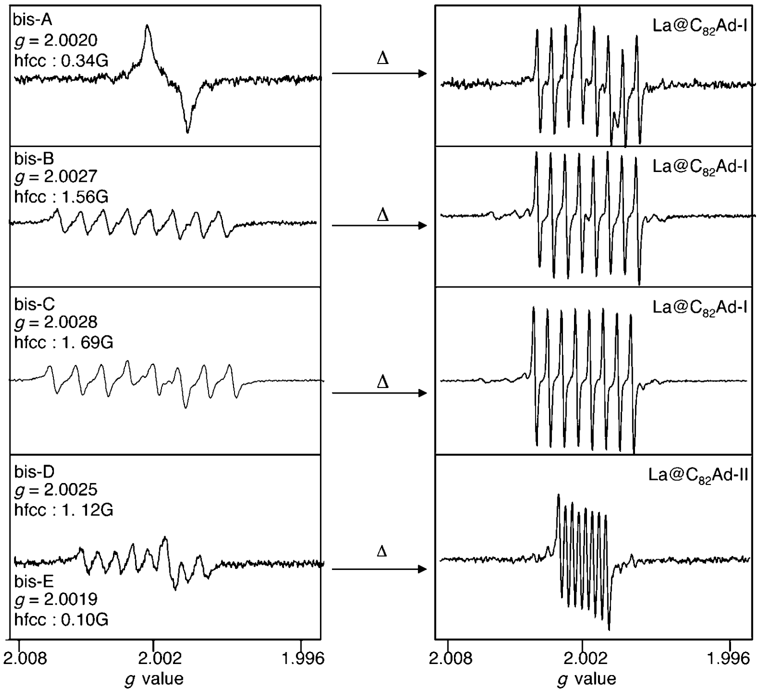


Figure 6. ESR spectra of La@C_{82}AdCp* (bis-A, bis-B, bis-C, and bis-D/bis-E mixture) and La@C_{82}Ad produced from La@C_{82}AdCp* by a retro reaction at 40°C in the presence of maleic anhydride.

reveal that the POAV angles and charge density on the fullerene cage play an important role in multiple functionalization of metallofullerenes.

Experimental Section

Electrochemical measurements: DPV, CV, and controlled-potential bulk electrolyses in 1,2-dichlorobenzene were performed by using a BAS CW-50 instrument. A conventional three-electrode cell consisting of a platinum working electrode, a platinum counter-electrode, and a saturated calomel reference electrode (SCE) was used for CV and DPV measurements. $(n\mathrm{Bu})_4\mathrm{NPF}_6$ was used as the supporting electrolyte. All potentials were recorded against SCE and corrected against ferrocene/ferrocenium. DPV and CV measurements were conducted at scan rates of 20 and 50 $\mathrm{mV\,s^{-1}}$, respectively.

XRD measurements: X-ray diffraction analysis was performed on La@C_{82}Cp*·CS_2, which was obtained by evaporation of CS_2 into a solution of La@C_{82}Cp* in toluene under argon at low temperature. For structural analysis, X-ray intensity data were collected by using a DSC imaging plate system (Rigaku) with Si-monochromated synchrotron radiation ($\lambda = 1.00000$ Å) at beamline BL-1B (Photon Factory, KEK, Japan).

Crystal data for La@C_{82}Cp·CS_2*: $C_{93}H_{16}LaS_2$; $M_r = 1336.09$; dimensions $0.07 \times 0.05 \times 0.05$ mm; triclinic; $P\bar{1}$ (no. 2); $a = 11.3614(16)$, $b = 14.306(4)$, $c = 14.991(2)$ Å; $\alpha = 91.515(12)$, $\beta = 105.443(5)$, $\gamma = 90.885(13)$°; $V = 2347.1(8)$ Å^3; $Z = 2$; $\rho_{\mathrm{calcd}} = 1.890\ \mathrm{g\,cm^{-3}}$; $T = 120$ K; 13044 refractions collected (10039 independent $R_{\mathrm{int}} = 0.0377$), $R_1 = 0.1165$, $wR_2 = 0.2786$ for all data, $R_1 = 0.0836$, $wR_2 = 0.2537$ for 6104 reflections ($I > 2.0\sigma(I)$) and 1026 parameters; GOF on $F^2 = 1.045$. The respective maximum and minimum residual electron densities are 1.231 and $-1.028\ \mathrm{e\,Å^{-3}}$. The La atom was observed to be disordered over four positions with occupancies and esd values of 0.4128(14), 0.276(2), 0.1834(14), and 0.128(2). The first and third positions were located in the major orientation C_{82} cage. The second and fourth positions were in the minor orientation C_{82} cage.

Synthesis of La@C_{82}Cp*: A solution of La@C_{82} (1.8×10^{-5} M) and Cp* (1.8×10^{-4} M) in toluene was placed in a quartz tube. After standing under argon for 5 h, La@C_{82}Cp* (80%) and La@C_{82}Cp*$_2$ were isolated by using a HPLC column (20×250 mm; Buckyprep Cosmosil; Nacalai Tesque). Retention times were 12.15 min for La@C_{82}Cp* and 11.18 min for La@C_{82}Cp*$_2$.

Synthesis of La@C_{82}AdCp* (route 1): A reaction between La@C_{82}Cp* (1.9×10^{-4} M) and $\mathrm{AdN_2}$ (1.9×10^{-2} M) in toluene was induced by irradiation with a high-pressure mercury arc lamp (cutoff <300 nm) and monitored by using HPLC. After irradiation, the products were isolated by using HPLC.

Synthesis of La@C_{82}AdCp* (route 2): A solution of La@C_{82}Ad-I (1.7×10^{-4} M) and Cp* (1.7×10^{-3} M) in toluene was placed in a Pyrex tube. After standing under argon for 5 h, the products were isolated by using HPLC.

Separation of the adducts (La@C_{82}AdCp*): The adducts (La@C_{82}AdCp*) were separated by using two-stage HPLC. In the first stage, a Buckyprep column was used to separate the mixture of bis-adducts from the reaction mixture. In the second stage, bis-A, bis-B, and bis-C were separated by recycling the crude mixture on a column (20×250 mm; Buckyprep M Cosmosil; Nacalai Tesque). Then bis-D and bis-E were separated together because of their similar retention times. Retention times were 6.98 min for bis-A, 7.18 min for bis-B, 7.68 min for bis-C, and 8.05 min for bis-D and bis-E.

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research on Innovation Areas (no. 20108001, "pi-Space"), a Grant-in-Aid for Scientific Research (A) (no. 20245006), a Grant-in-Aid for Young Scientists (B) (no. 19750027), the 21st Century COE Program, The Next Generation Super Computing Project (Nanoscience Project), Nanotechnology Support Project, and a Grant-in Aid for Scientific Research on Priority Area (nos. 20036008, 20038007) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

---

[1] For recent reviews, see a) M. Saunders, J. Cross in *Endofullerenes: A New Family of Carbon Clusters* (Eds.: T. Akasaka, S. Nagase), Kluewer, Dordrecht, **2002**, pp. 13–65; b) K. Kobayashi, S. Nagase, *Endofullerenes: A New Family of Carbon Clusters* (Eds.: T. Akasaka, S. Nagase), Kluewer, Dordrecht, **2002**, pp. 99–119; c) M. Diener, M. Alford, R. Bolskar, *Endofullerenes: A New Family of Carbon Clusters* (Eds.: T. Akasaka, S. Nagase), Kluewer, Dordrecht, **2002**, pp. 133–151.

[2] Y. Maeda, Y. Matsunaga, T. Wakahara, S. Takahashi, T. Tsuchiya, M. O. Ishitsuka, T. Hasegawa, T. Akasaka, M. T. H. Liu, K. Kokura, E. Horn, K. Yoza, T. Kato, S. Okubo, K. Kobayashi, S. Nagase, K. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 6858–6859.

[3] L. Feng, T. Nakahodo, T. Wakahara, T. Tsuchiya, Y. Maeda, T. Akasaka, T. Kato, E. Horn, K. Yoza, N. Mizorogi, S. Nagase, *J. Am. Chem. Soc.* **2005**, *127*, 17136–17137.

[4] Y. Maeda, J. Miyashita, T. Hasegawa, T. Wakahara, T. Tsuchiya, T. Nakahodo, T. Akasaka, M. Mizorogi, Kobayashi, S. Nagase, T. Kato, N. Ban, H. Nakajima, Y. Watanabe, *J. Am. Chem. Soc.* **2005**, *127*, 12190–12191.

[5] T. Suzuki, Y. Maruyama, T. Kato, K. Kikuchi, Y. Achiba, *J. Am. Chem. Soc.* **1993**, *115*, 11006–11007.

[6] All measurements were performed at beamline BL-1B of the Photon Factory, KEK, Japan. CCDC-721550 (La@C_{82}Cp*·CS_2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[7] a) R. C. Haddon, *Science* **1993**, *261*, 1545–1550; b) J. M. Hawkins, A. Meyer, M. A. Solow, *J. Am. Chem. Soc.* **1993**, *115*, 7499–7500; c) H. R. Karfunkel, A. Hirsch, *Angew. Chem.* **1992**, *104*, 1529–1531; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1468–1470.

[8] For B3LYP see: a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[9] L. Feng, T. Tsuchiya, T. Wakahara, T. Nakahodo, Q. Piao, Y. Maeda, T. Akasaka, T. Kato, K. Yoza, E. Horn, N. Mizorogi, S. Nagase, *J. Am. Chem. Soc.* **2006**, *128*, 5990–5991.

[10] Y. Matsunaga, Y. Maeda, T. Wakahara, T. Tsuchiya, M. O. Ishitsuka, T. Akasaka, N. Mizorogi, K. Kobayashi, K. Nagase, K. M. Kadish, *ITE Lett.* **2006**, *7*, 43–49.

[11] M. Yamada, L. Feng, T. Wakahara, T. Tsuchiya, Y. Maeda, Y. Lian, M. Kako, T. Akasaka, T. Kato, K. Kobayashi, S. Nagase, *J. Phys. Chem. B*, **2005**, *109*, 6049.

Received: September 11, 2009