J. Am. Chem. Soc. **1994,** *116,* 9367-9368 9367

Characterization of the Isolated Y@C_{82}

Koichi Kikuchi,* Yasuhiko Nakao, Sinzo Suzuki, and
Yohji Achiba

Department of Chemistry
Tokyo Metropolitan University
Hachioji, Tokyo 192-03, Japan

Toshiyasu Suzuki* and Yusei Maruyama

Institute for Molecular Science
Myodaiji, Okazaki 444, Japan

Received July 6, 1994

Although the first production of lanthanide-containing fullerenes was achieved just after the isolation of C_{60}, low yields, air-sensitivity, and difficulty of purification have prevented researchers from exploring the chemistry of these attractive molecules.[1,2] Physical measurements, such as mass spectrometry,[3,4] EPR,[4] extended X-ray absorption fine structure (EXAFS),[5] and X-ray photoelectron spectroscopy (XPS),[4b] were done with the extracts containing the mixture of metallofullerenes and empty fullerenes. Recently, milligram quantities of La@C_{82} have been isolated by two groups, allowing the researchers to measure the electronic absorption spectrum of the pure material.[6,7] The cyclic voltammogram of the pure La@C_{82} indicated that this compound is a good electron donor as well as a stronger electron acceptor than empty fullerenes.[8] It was concluded that La@C_{82} is a semiconductor in the solid state by ultraviolet photoelectron spectroscopy (UPS) and XPS.[9] It is interesting to see how its electronic properties change with different lanthanide atoms whose ionization potentials steadily increase in the order La < Ce to Lu < Y < Sc. We report here the first isolation and characterization of Y@C_{82} in comparison with La@C_{82}.

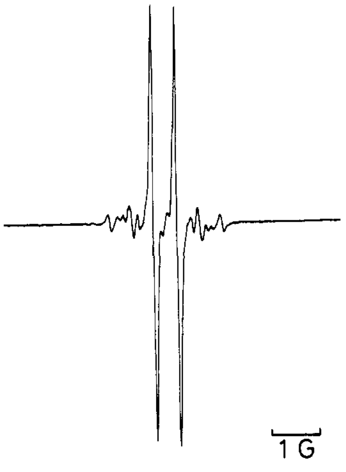

Figure 1. EPR spectrum of the isolated Y@C_{82} in toluene.

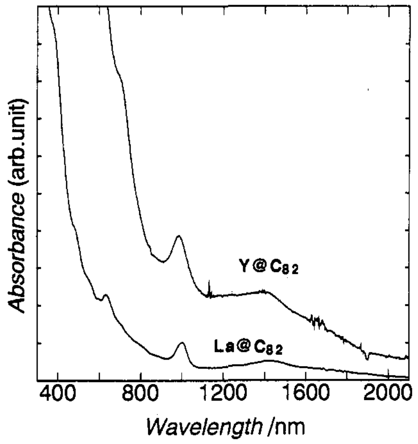

Figure 2. Comparative UV-vis-near-IR absorption spectra of Y@C_{82}-A (top) and La@C_{82}-A (bottom) in toluene.

The production and purification of Y@C_{82} were essentially the same as reported for La@C_{82}.[6a] The soot containing Y@C_{82} was prepared by an arc heating of the Y_2O_3 and graphite composite rods with the Y/C ratio 1:100. The polystyrene (JAIGEL Co., CS_2 eluant) and Buckyclucher I columns (Regis Co., toluene eluant) gave HPLC profiles similar to those of La@C_{82}.[10] The time-of-flight (TOF) mass spectrum indicates that higher fullerenes, such as C_{84}, C_{86}, and C_{88}, were completely removed. The EPR spectrum in Figure 1 shows only one doublet (g = 2.0006; hyperfine coupling constant, 0.49 G) due to the major Y@C_{82} isomer (Y@C_{82}-A) with weak ^{13}C hyperfine lines. The minor doublet (g = 2.0001; hyperfine coupling constant, 0.32 G) due to the minor Y@C_{82} isomer (Y@C_{82}-B) has not been detected after HPLC separation because of decomposition.[4c,e] The UV-vis-near-IR absorption spectrum of Y@C_{82}-A in Figure 2 is strikingly similar to that of the major La@C_{82} isomer (La@C_{82}-A).[11] Two characteristic peaks (990 and 1405 nm) are slightly shifted to the short wavelengths relative to those of La@C_{82}-A (1000 and 1420 nm).[6a]

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of Y@C_{82}-A were conducted, and the voltammograms were recorded on a BAS-100B/W with a three-electrode configuration. As seen in Figure 3a, one reversible oxidation and four reversible reductions were observed by CV. The second oxidation remained irreversible at faster scan rates up to 1000

---

(1) For a recent review on metallofullerenes, see: Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S. *Nature* **1993**, *366*, 123.

(2) Chai, Y.; Guo, T.; Jin, C.; Haufler, R. E.; Chibante, L. P. F.; Fure, J.; Wang, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 7564.

(3) (a) Alvarez, M. M.; Gillan, E. G.; Holczer, K.; Kaner, R. B.; Min, K. S.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 10561. (b) Ross, M. M.; Nelson, H. H.; Callahan, J. H.; McElvany, S. W. *J. Phys. Chem.* **1992**, *96*, 5231. (c) Gillan, E. G.; Yeretzian, C.; Min, K. S.; Alvarez, M. M.; Whetten, R. L.; Kaner, R. B. *J. Phys. Chem.* **1992**, *96*, 6869. (d) Moro, L.; Ruoff, R. S.; Becker, C. H.; Lorents, D. C.; Malhotra, R. *J. Phys. Chem.* **1993**, *97*, 6801.

(4) (a) Johnson, R. D.; de Vries, M. S.; Salem, J.; Bethune, D. S.; Yannoni, C. S. *Nature* **1992**, *355*, 239. (b) Weaver, J. H.; Chai, Y.; Kroll, G. H.; Jin, C.; Ohno, T. R.; Haufler, R. E.; Guo, T.; Alford, J. M.; Conceicao, J.; Chibante, L. P. F.; Jain, A.; Palmer, G.; Smalley, R. E. *Chem. Phys. Lett.* **1992**, *190*, 460. (c) Hoinkis, M.; Yannoni, C. S.; Bethune, D. S.; Salem, J. R.; Johnson, R. D.; Crowder, M. S.; de Vries, M. S. *Chem. Phys. Lett.* **1992**, *198*, 461. (d) Shinohara, H.; Sato, H.; Saito, Y.; Ohkohchi, M.; Ando, Y. *J. Phys. Chem.* **1992**, *96*, 3571. (e) Suzuki, S.; Kawata, S.; Shiromaru, H.; Yamauchi, K.; Kikuchi, K.; Kato, T.; Achiba, Y. *J. Phys. Chem.* **1992**, *96*, 7159. (f) Bandow, S.; Kitagawa, H.; Mitani, T.; Inokuchi, H.; Saito, Y.; Yamaguchi, H.; Hayashi, N.; Sato, H.; Shinohara, H. *J. Phys. Chem.* **1992**, *96*, 9609. (g) Kato, T.; Suzuki, S.; Kikuchi, K.; Achiba, Y. *J. Phys. Chem.* **1993**, *97*, 13425.

(5) (a) Soderholm, L.; Wurz, P.; Lykke, K. R.; Parker, D. H.; Lytle, F. W. *J. Phys. Chem.* **1992**, *96*, 7153. (b) Park, C.-H.; Wells, B. O.; DiCarlo, J.; Shen, Z.-X.; Salem, J. R.; Bethune, D. S.; Yannoni, C. S.; Johnson, R. D.; de Vries, M. S.; Booth, C.; Bridge, F.; Pianetta, P. *Chem. Phys. Lett.* **1993**, *213*, 196.

(6) (a) Kikuchi, K.; Suzuki, S.; Nakao, Y.; Nakahara, N.; Wakabayashi, T.; Shiromaru, H.; Saito, K.; Ikemoto, I.; Achiba, Y. *Chem. Phys. Lett.* **1993**, *216*, 67. (b) Yamamoto, K.; Funasaka, H.; Takahashi, T.; Akasaka, T. *J. Phys. Chem.* **1994**, *98*, 2008.

(7) Shinohara et al. also isolated Sc_2@C_{74}, Sc_2@C_{82}, and Sc_2@C_{84} by HPLC. Shinohara, H.; Yamaguchi, H.; Hayashi, N.; Sato, H.; Ohkochi, M.; Ando, Y.; Saito, Y. *J. Phys. Chem.* **1993**, *97*, 4259.

(8) Suzuki, T.; Maruyama, Y.; Kato, T.; Kikuchi, K.; Achiba, Y. *J. Am. Chem. Soc.* **1993**, *115*, 11006.

(9) (a) Hino, S.; Takahashi, H.; Iwasaki, K.; Matsumoto, K.; Miyazaki, T.; Hasegawa, S.; Kikuchi, K.; Achiba, Y. *Phys. Rev. Lett.* **1993**, *71*, 4261. (b) Poirier, D. M.; Knupfer, M.; Weaver, J. H.; Andreoni, W.; Laasonen, K.; Parrinello, M.; Bethune, D. S.; Kikuchi, K.; Achiba, Y. *Phys. Rev. B* **1994**, *49*, 17403.

(10) Retention times for Y@C_{82}: 482 (CS_2) and 9.4 min (toluene).

(11) The electronic absorption spectrum of the minor La@C_{82} isomer (La@C_{82}-B) is quite different from that of La@C_{82}-A, probably due to the different cage structures. Yamamoto, K.; Funasaka, H.; Takahashi, T.; Akasaka, T.; Suzuki, T.; Maruyama, Y. *J. Am. Chem. Soc.*, submitted for publication.

0002-7863/94/1516-9367$04.50/0

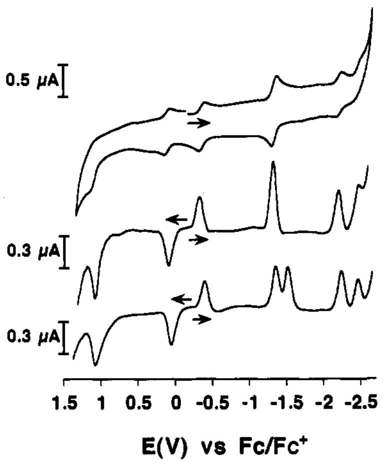

Figure 3. CV (a) and DPV (b) of Y@C_{82}-A at 20 mV/s in 1,2-dichlorobenzene containing 0.1 M (n-Bu)$_4$NPF$_6$. The rest potential is –0.07 V. (c) DPV of La@C_{82}-A under the same conditions.

mV/s. By DPV (Figure 3b), the peak current intensity of the second reduction is twice that of each of the other redox peaks; the shape of the current voltage curve suggests a simultaneous two-electron transfer, not an overlap of two one-electron transfers.

In comparison with the electrochemistry of the major (A) and minor (B) isomers of La@C_{82} (Table 1),[8,11] we would like to point out the following. (1) Each of the metallofullerenes has a remarkably small potential difference between the first oxidation and the first reduction (Y@C_{82}-A, 0.44 V; La@C_{82}-A, 0.49 V; La@C_{82}-B, 0.40 V).[12] This may suggest that the HOMO of Y@C_{82}, originally the LUMO+ of the C_{82}, is singly occupied (i.e., SOMO), as proposed for La@C_{82}.[13] Therefore, the oxidation state of the yttrium is close to that of the lanthanum, likely 3+.[14] (2) Although the second reduction of La@C_{82}-B is also a two-electron process, the redox potentials of Y@C_{82}-A are rather close to those of La@C_{82}-A (Table 1 and Figure 3). (3) The first oxidation and reduction potentials of Y@C_{82}-A are anodically shifted by 30 and 80 mV, respectively, relative to those of La@C_{82}-A (Table 1). These relatively small shifts are in agreement with the ab initio calculations, which predict that the ionization potential and the electron affinity of Y@C_{82} (6.22 and 3.20 eV, respectively) are almost the same as those of La@C_{82} (6.19 and 3.22 eV, respectively).[14]

Table 1. Redox Potentials of the Isolated Metallofullerenes[a]

compd	$^{ox}E2$	$^{ox}E1$	$^{red}E1$	$^{red}E2$	$^{red}E3$	$^{red}E4$	$^{red}E5$
Y@C_{82}-A	+1.07[b,c]	+0.10	–0.34	–1.34[d]		–2.22	–2.47[c]
La@C_{82}-A	+1.07[b,c]	+0.07	–0.42	–1.37	–1.53	–2.26	–2.46[c]
La@C_{82}-B	+1.08[b,c]	–0.07	–0.47	–1.40[d]		–2.01	–2.40[c]

[a] Half-cell potentials unless otherwise stated. Values are in volts relative to ferrocene/ferrocenium couple. Conditions: 0.1 M (n-Bu)$_4$NPF$_6$ in 1,2-dichlorobenzene; working electrode, Pt disk (1-mm diameter); counter electrode, Pt wire; reference electrode, Ag/0.01 M AgNO$_3$ and 0.1 M (n-Bu)$_4$NClO$_4$ in CH$_3$CN. CV: scan rate, 20 mV/s. [b] Irreversible. [c] Values were obtained by DPV: pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV/s. [d] Two-electron process.

In conclusion, the electronic structure of the major Y@C_{82} isomer, examined by the electronic absorption spectra and the electrochemistry, is almost identical to that of the major La@C_{82} isomer, although the ionization potentials and ionic radii of the metals are different. This indicates that Y@C_{82}-A would have a cage structure and an oxidation state of the metal similar to those of La@C_{82}-A. These "fullerenolanthanides" are new kinds of organolanthanide compounds stabilized by the delocalization of the negative charges on the fullerene cages and the protection of the lanthanide metals by spherical carbon ligands.[15] We are currently producing and separating other fullerenolanthanides, such as Sc@C_{82} and Ce@C_{82}, to expand this new field between fullerene chemistry and organometallic chemistry.

Acknowledgment. We would like to thank Profs. S. Nagase and T. Kato for helpful discussions and Prof. T. Nogami for lending his facility for soot generation. This work was supported by the Ministry of Education, Science and Culture of Japan (No. 06224230).

---

(12) Such ease of both oxidation and reduction has been observed for metallophthalocyanine radicals such as bis(phthalocyaninato)lutetium (ΔE = 0.48 V in CH$_2$Cl$_2$). Turek, P.; Petit, P.; André, J.-J.; Simon, J.; Even, R.; Boudjema, B.; Guillaud, G.; Maitrot, M. *J. Am. Chem. Soc.* **1987**, *109*, 5119.

(13) (a) Laasonen, K.; Andreoni, W.; Parrinello, M. *Science* **1992**, *258*, 1916. (b) Nagase, S.; Kobayashi, K.; Kato, T.; Achiba, Y. *Chem. Phys Lett.* **1993**, *201*, 475. (c) Nagase, S.; Kobayashi, K. *Chem. Phys Lett.* **1993**, *214*, 57.

(14) The ab initio calculations predict that the charges on the lanthanum, yttrium, and scandium metals are 2.92+, 2.59+, and 2.16+, respectively. Nagase, S.; Kobayashi, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1837.

(15) "All organolanthanide compounds are *markedly* sensitive to oxygen and moisture." Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1988; p 968. As expected from the low oxidation potentials, La@C_{82} and Y@C_{82} are gradually oxidized by air to give insoluble materials. Moisture-sensitivity is not observed.