Absorption Spectra of Metallofullerenes M@C_{82} of Lanthanoids

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UV/vis/NIR spectra of 10 kinds of M@C_{82} (M = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu) dissolved in toluene were observed and the molar absorption coefficients were determined for each absorption peak. The absorption peak wavelengths were similar among 10 kinds of species and their averages were (630 ± 3), (986 ± 26), and (1406 ± 5) nm. The molar absorption coefficients for the peaks around 630 and 1406 nm were found similar for all the species although those for the peak at 986 nm showed a wider variation among the ten. Oscillator strengths have been derived from the observed data. Those for the 630 nm absorption are in the range of 0.05−0.1 which reveals that the transition is allowed, and they slightly decrease as the atomic number of the encapsulated atom is increased. The oscillator strengths for the 986 and 1406 nm absorption are, however, about 1 order of magnitude smaller, and those for the 986 nm absorption vary appreciably as the degree of filling of the 4f orbital changes.

Introduction

Recently, the arc discharge method and laser ablation method using metal containing carbon rods are mainly employed for production of metallofullerenes. Crude extracts containing metallofullerenes can be extracted from the soot by use of some organic solvent. It is well-known that M@C_{82} are the most abundant metallofullerene species in the mass spectra of these extracts[1,2] and the existence of the species has been confirmed for all the lanthanoid elements. For most lanthanoid M@C_{82} (M = La, Ce, Pr, Nd, Pm, Gd, Tb, Dy, Ho, Er, Lu), an ionized M^{3+}@C_{82}^{3-} state, in which 3 electrons are transferred from the encapsulated metal atom to the C_{82} cage, is suggested by the ESR and XPS study[3−6] while for others (M = Sm, Eu, Tm, Yb) an ionized M^{2+}@C_{82}^{2-} is also suggested.[7−10] The electronic structure of the molecule is determined by the cage structure and the charge of the cages and it is reflected in the absorption spectrum in the UV, VIS, and NIR regions. In the study of fullerenes, the absorption spectrum can be used, therefore, to estimate the cage properties.[11,12]

However, no determination has been reported on the absolute values of the absorption coefficients although qualitative discussion of the similarity of the charge and cage structure of fullerenes has been often made from measurements of their absorption spectra. If absorption coefficients of M@C_{82} were determined quantitatively, various similar absorption spectra can also be discussed in terms of the magnitude of oscillator strength, and besides, they can be used for analyzing the amount of isolated M@C_{82}. For measuring absorption coefficients, removal of any insoluble substance by filtration is required, which still remains even after apparent dissolution of fullerenes in organic solvents. This process of filtration of the insoluble often makes it difficult to determine the concentration of the solute, but this problem can be overcome by some analytical method such as neutron activation analysis.

In this paper, we have observed UV/vis/NIR absorption spectra in toluene of 10 kinds of lanthanoid M@C_{82} (M = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu) in which the encaged atoms are considered taken +3 oxidation state, and attempted to determine the molar absorption coefficient of each absorption peak from which the oscillator strength of the transition was derived.

Experimental Section

The arc discharge method was employed for production of the soot containing metallofullerenes. Carbon rods (ϕ = 6 mm × 100 mm) were fabricated by mixing the graphite powder, lanthanoid metal oxide and graphite binder (Graphi-Bond 551R, Niraco inc.), and by sintering for 3 h at 1200 °C. Atomic ratios of these rods, the number of metal atoms to that of carbon atoms, were approximately M/C = 1/50. Using these carbon rods, arc discharge was carried out under the condition of 400 Torr of He atmosphere with the current of 50 A. The soot produced by this method was recovered and then dissolved into 1,2,4-trichlorobenzene for extraction of fullerenes. This solution was refluxed for 8 h and then, filtered for removing the insoluble substance. After the filtration, the solution was evaporated to dryness and dissolved in toluene. A two-step HPLC column separation using a 5PBB column with toluene and a Buckyprep column with toluene in series was employed for purification of the sample. In the first step, the sample was injected into a 5PBB column (10 mm i.d. × 250 mm, Nacalai Tesque Inc.) with toluene at the flow rate of 6 mL/min. The fraction corresponding to the elution of C_{86} according to the UV monitoring was collected and the fraction volume was reduced by evaporating off toluene for the next purification step. In the second step, this fraction was injected to a Buckyprep column (10 mm i.d. × 250 mm, Nacalai Tesque Inc.) and eluted with toluene at the flow rate of 3.2 mL/min, and then, the fraction corresponding to the elution of M@C_{82} was collected. The purity of the M@C_{82} samples obtained was found to be more than 99% by TOF/MS measurements.

The fraction of the purified sample was diluted by toluene to an appropriate concentration and filtered by a membrane filter for removal of any insoluble substance present. After filtration,

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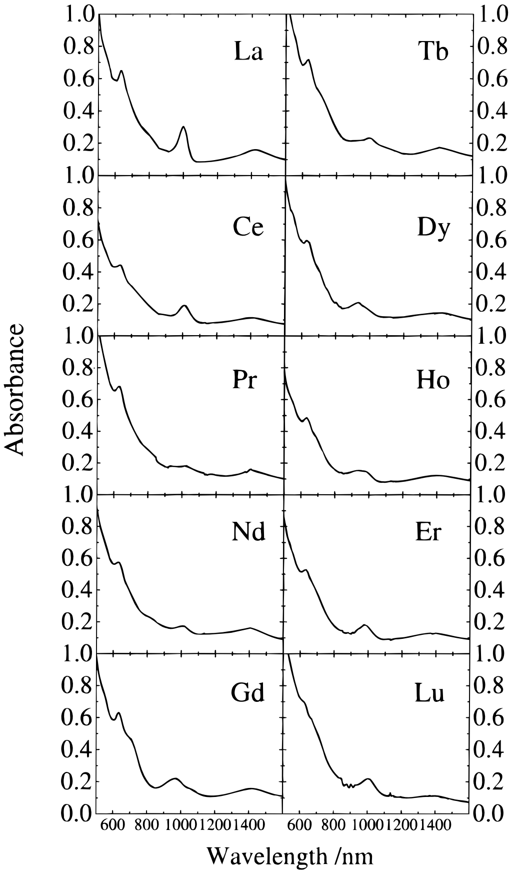

Figure 1. UV/vis/NIR spectra of M@C$_{82}$ UV/vis/NIR spectra of a series of M@C$_{82}$ in 7 × 10^{-5} mol/L solution. These spectra are similar to each other except for the intensity around 1000 nm. The ordinate for each element shows the absorbance plotted in linear scale.

the sample was transferred to a quartz cell of 10 mm light-path length and 2 mm width for the measurement of the absorption spectra. After the absorption measurement, the M@C$_{82}$ sample solution was transferred to a polyethylene vial, weighed for determining the solution weight, and then dried. The samples were, then, irradiated by thermal neutrons in the TRIGA II reactor at St. Paul's University (neutron flux = 1.5 × 10^{12} N/(cm^2 s)) for determination of the amount of the metal in each sample solution by neutron activation followed by γ-ray spectrometry for the determination of each metal by the comparison method standard samples known amount of elements were irradiated together.

Results and Discussion

Figure 1 shows the UV/vis/NIR spectra of the lanthanoid M@C$_{82}$ in toluene normalized to the concentration of 7 × 10^{-5} mol/L for comparison. The spectra show 3 characteristic absorption peaks at the wavelength of around 630, 1000, and 1400 nm. Correlation curves of absorbance vs concentration at each absorption peak were obtained for the La@C$_{82}$ in toluene as shown in Figure 2 by diluting the solution to $^1/_2$, $^1/_5$, $^1/_{10}$, $^1/_{20}$, $^1/_{30}$, and $^1/_{50}$. The linearity of these curves indicates that the species was unaffected by the dilution process e. g. free from dimerization[13] and stable in toluene under the ordinary laboratory environment of air and light at least for the duration of all the procedure (1 day). The molar absorption coefficients determined for each M@C$_{82}$ sample are listed in Table 1. The average wavelengths of the 10 kinds of M@C$_{82}$ are (630 ± 3) nm, (986 ± 26) nm, and (1406 ± 5) nm, and the mean molar absorption coefficients of the corresponding peaks are (9.1 ± 0.8) × 10^3, (3.2 ± 0.7) × 10^3, and (2.2 ± 0.3) × 10^3 M^{-1} cm^{-1} at the peak positions, respectively. The quoted errors show one standard deviations among the 10 species. The variation among the 10 kinds of lanthanoid metallofullerenes is found the largest for the 986 nm absorption both in the peak wavelength (±2.6%) and the absorption coefficient (±22%). Such variation among the lanthanoid elements is better depicted in Figure 3 in terms of oscillator strengths as explained below, and they are apparently related to the degree of filling of the inner 4f electron orbital of the encapsulated metal atom.

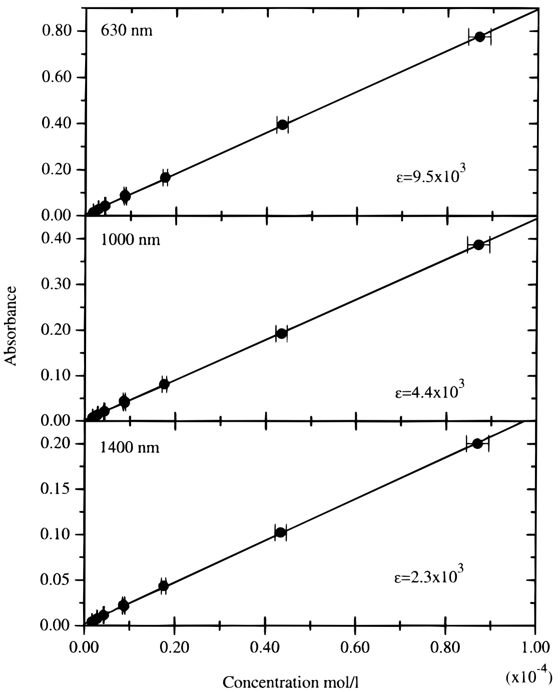

Figure 2. Absorbance vs concentration curve for La@C$_{82}$ dissolved in toluene. A good linear correlation between absorbance and concentration is observed for each absorption peak.

The oscillator strength f of each absorption peak was evaluated from the observed spectra as follows:

$$f = \frac{4m_e c\epsilon_0}{N_a e^2} 2.303E \tag{1}$$

where

$$E = \int \epsilon(\upsilon)\, d\upsilon \tag{2}$$

Here, m_e, c, ϵ_0, N_a, and e represents the electron rest mass, velocity of light, vacuum permittivity, Avogadro's number and electric charge, respectively. The value E was obtained by the least-squares fitting of a Lorentzian curve over the broad absorption peaks. The oscillator strength evaluated are plotted on the ordinate in logarithmic scale against the element in Figure 3. The oscillator strengths for the 630 nm absorption are about 10 times as large as those for the 986 nm and 1406 nm absorptions. For the 630 nm absorption they are about 0.05−0.1 which are within the range for allowed transitions, and show a decreasing tendency as a function of the atomic number as shown by a dotted line in Figure 3a. Those for the 986 and 1406 nm absorptions are about 0.005−0.01 and 1 order of magnitude smaller. The oscillator strength of the 986 nm absorption varies appreciably and the variational trend reveals its dependence on the degree of filling of the 4f orbital, namely,

TABLE 1: Absorption Coefficients and Peak Wavelengths Observed in UV/vis/NIR Spectra of M@C$_{82}$

	ϵ_{max}/wavelength	ϵ_{max}/wavelength	ϵ_{max}/wavelength
La@C$_{82}$	(9.5 ± 1.6) × 10^3/634 nm	(4.4 ± 0.7) × 10^3/997 nm	(2.3 ± 0.4) × 10^3/1416 nm
Ce@C$_{82}$	(9.8 ± 0.7) × 10^3/634 nm	(4.2 ± 0.3) × 10^3/1011 nm	(2.4 ± 0.2) × 10^3/1400 nm
Pr@C$_{82}$	(9.4 ± 0.5) × 10^3/628 nm	(2.6 ± 0.1) × 10^3/1018 nm	(2.3 ± 0.1) × 10^3/1403 nm
Nd@C$_{82}$	(8.3 ± 0.8) × 10^3/626 nm	(2.5 ± 0.2) × 10^3/1004 nm	(2.3 ± 0.2) × 10^3/1404 nm
Gd@C$_{82}$	(9.0 ± 0.3) × 10^3/631 nm	(3.1 ± 0.1) × 10^3/966 nm	(2.3 ± 0.1) × 10^3/1409 nm
Tb@C$_{82}$	(10.0 ± 1.0) × 10^3/631 nm	(3.3 ± 0.3) × 10^3/990 nm	(2.5 ± 0.2) × 10^3/1402 nm
Dy@C$_{82}$	(8.5 ± 0.2) × 10^3/628 nm	(3.0 ± 0.1) × 10^3/934 nm	(2.1 ± 0.1) × 10^3/1404 nm
Ho@C$_{82}$	(9.0 ± 1.0) × 10^3/632 nm	(2.8 ± 0.4) × 10^3/965 nm	(2.5 ± 0.4) × 10^3/1405 nm
Er@C$_{82}$	(7.5 ± 0.3) × 10^3/631 nm	(2.6 ± 0.1) × 10^3/977 nm	(1.9 ± 0.1) × 10^3/1400 nm
Lu@C$_{82}$	(10.0 ± 1.0) × 10^3/629 nm	(3.2 ± 0.5) × 10^3/1001 nm	(1.6 ± 0.2) × 10^3/1413 nm
ave.	(9.1 ± 0.8) × 10^3/986.3 ± 25.7 nm	(2.22 ± 0.28) × 10^3/630.4 ± 2.6 nm	(3.17 ± 0.65) × 10^3/1405.6 ± 5.4 nm
re. error	±8.9%/±0.42%	±20.7%/±2.6%	±12.7%/±0.38%

[a] The unit of ϵ_{max} shown in the table is M^{-1} cm^{-1}. The bottom two columns show averages of absorption coefficients and peak wavelengths at the peaks, and their relative errors.

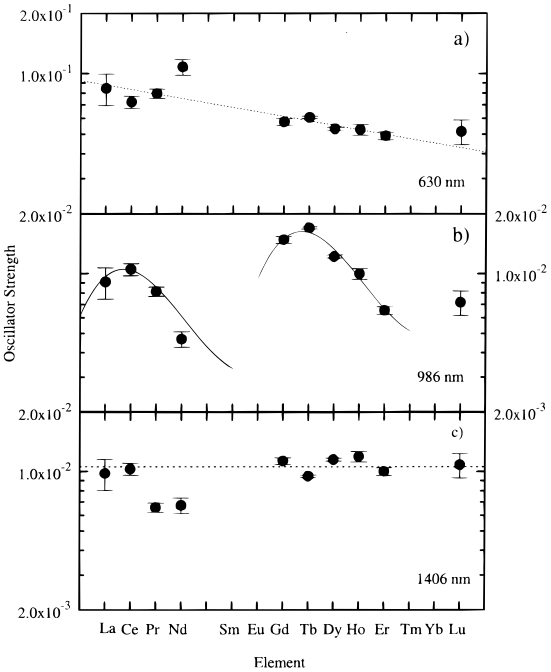

Figure 3. Oscillator strengths of M@C$_{82}$ Oscillator strengths of the absorptions around 630, 986, and 1406 nm are plotted on the ordinates in logarithmic scale for all the 10 elements. The solid curves are explained in the text.

the variational patterns are similar for La, Ce, Pr, Nd (f^0, f^1, f^2, f^3) and for Gd, Tb, Dy, Ho, Er (f^7, f^8, f^9, f^{10}, f^{11}). The solid curve for Gd ~ Er was obtained by a least-squares fitting of a cubic function to the data points, and the shape of this curve is used to fit the data points of La ~ Nd. Those for the 1406 nm absorption are almost the same for most of the species except for Pr and Nd, and the average of eight species is (1.06 ± 0.09) × 10^{-2}.

Conclusion

The results of the present work are summarized as follows:

(1) UV/vis/NIR absorption spectra were observed for 10 kinds of lanthanoid metallofullerenes M@C$_{82}$ (M = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu), and the molar absorption coefficient was obtained for each peak. The absorption wavelengths at peak positions averaged among the 10 kinds of species were found to be (630 ± 3), (986 ± 26), and (1406 ± 5) nm and their corresponding molar absorption coefficients were (9.1 ± 0.8) × 10^3, (3.2 ± 0.7) × 10^3, and (2.2 ± 0.3) × 10^3 M^{-1} cm^{-1}, respectively.

(2) Oscillator strengths of M@C$_{82}$ were evaluated from the observed data. The oscillator strengths of the absorption at 630 nm indicate that the transition is allowed whereas those of the absorptions at 986 and 1406 nm are 1 order of magnitude smaller. Those for the 986 nm absorption show some dependence on the degree of filling of the 4f orbital of the encapsulated atom. Those for the 630 nm exhibit a slight decrease as the atomic number increases while those for the 1406 nm absorption are found the same for eight elements.

This is the first report for the absorption coefficients of M@C$_{82}$, and they can be used for quantitative determination of the amount of M@C$_{82}$ dissolved in toluene.

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References and Notes

(1) 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**, *96*, 7564.

(2) More, L.; Ruoff, R. S.; Becker, C. H.; Lorents, D. C.; Malhotra, R. *J. Phys. Chem.* **1993**, *97*, 6801.

(3) Sueki, K.; Kikuchi, K.; Akiyama, K.; Sawa, T.; Katada, M.; Ambe, S.; Ambe, F.; Nakahara, H. *Chem. Phys. Lett.* **1999**, *300*, 140.

(4) Suzuki, S.; Kawata, S.; Shiromaru, H.; Yamauchi, K.; Kikuchi, K.; Kato, T.; Achiba, Y. *J. Phys. Chem.* **1992**, *96*, 7159.

(5) 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.

(6) Ding, J.; Lin, N.; Weng, L.; Cue, N.; Yang, S. *Chem. Phys. Lett.* **1996**, *261*, 92.

(7) Sueki, K.; Akiyama, K.; Yamauchi, T.; Sato, W.; Kikuchi, K.; Suzuki, S.; Katada, M.; Achiba, Y.; Nakahara, H.; Akasaka, T.; Tomura, K. *Fullerene Sci. Technol.* **1997**, *5*, 1435.

(8) Kikuchi, K.; Sueki, K.; Akiyama, K.; Kodama, T.; Nakahara, H.; Ikemoto, I. In *Fullerenes Volume 4: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials;* Kadish, K. M., Ruoff, R. S., Eds.; Electrochemical Society: Pennington, 1997; p 408.

(9) Kirbach, U.; Dunsch, L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2380.

(10) Xu, Z.; Nakane, T.; Shinohara, H. *J. Am. Chem. Soc.* **1996**, *118*, 11309.

(11) Suzuki, T.; Kikuchi, K.; Oguri, F.; Nakao, Y.; Suzuki, S.; Achiba, Y.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Tetrahedron* **1996**, *53*, 4973.

(12) Ding, J.; Yang, S. *J. Phys. Chem. Solid* **1997**, *58*, 1661.

(13) Shinohara, H.; Kishida, M.; Nakane, T.; Kato, T.; Bandow, S.; Saito, Y.; Wang, X.-D.; Hashizume, T.; Sakurai, T. In *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; Electrochemical Society: Pennington, 1994; p 1361.