

21 January 2000

Chemical Physics Letters 316 (2000) 381-386

CHEMICAL PHYSICS LETTERS

www.elsevier.nl/locate/cplett

Electronic structure of Eu@C₆₀ studied by XANES and UV–VIS absorption spectra

T. Inoue ^a, Y. Kubozono ^{a, *}, S. Kashino ^a, Y. Takabayashi ^a, K. Fujitaka ^b, M. Hida ^b, M. Inoue ^a, T. Kanbara ^a, S. Emura ^c, T. Uruga ^d

> ^a Department of Chemistry, Okayama University, Okayama 700-8530, Japan ^b Department of Mechanical Engineering, Okayama University, Okayama 700-8530, Japan ^c ISIR, Osaka University, Osaka 567-0047, Japan ^d JASRI, Sayo 679-5198, Japan

> > Received 8 September 1999; in final form 3 November 1999

Abstract

Eu endohedral C_{60} , Eu@C₆₀, has been extracted with aniline from soot prepared by arc-heating of a graphite/Eu₂O₃ composite rod and obtained at high concentration by combining sublimation and repeated high-performance liquid chromatography. The laser desorption time-of-flight mass spectrum showed a pronounced peak of Eu@C⁺₆₀ The UV–VIS absorption spectrum of this sample has a red-shift in the onset (> 900 nm) in comparison with those for C₆₀ and C₇₀, as expected from electron transfer from the Eu atom to the C₆₀ cage. The valence state of the Eu atom in Eu@C₆₀ has been determined to be +2 by Eu L_{III}-edge XANES. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Encapsulation of an atom into the C_{60} cage is an important subject in studies of fullerenes. For example, N@C₆₀ and RG@C₆₀ (RG: rare gas) have been produced by ion implantation and high pressure methods, respectively, and their physical properties have been elucidated [1–5]. The atoms inside the C₆₀ cage in these compounds are electrically neutral, and the cages have no electronic charge. These compounds have basic importance in the chemistry and physics of fullerenes. However, metal endohedral C₆₀ (M@C₆₀, M: alkaline, alkaline-earth, lanthanide metals, etc.) seem to have greater potential for appli-

cations as superconducting or magnetic materials, because the C_{60} cage is expected to be charged as a result of electron transfer from the metal atom. It is in fact known that electron transfer plays an important role in the superconductivity of metal-intercalated C_{60} materials, such as Rb_3C_{60} and K_3C_{60} [6]. However, physical and chemical properties of $M@C_{60}$ have rarely been studied in spite of this potential as new materials, because pure samples could not be obtained.

Recently, we reported the extraction of some $M@C_{60}$ with aniline [7,8] and the enrichment of $Ca@C_{60}$, $Y@C_{60}$, $Ce@C_{60}$, $Pr@C_{60}$, $Gd@C_{60}$, $Nd@C_{60}$ and $Dy@C_{60}$ by high-performance liquid chromatography (HPLC) [9–11]. Furthermore, we reported that the Eu atom in Eu@C₆₀ is inside the C_{60} cage on the basis of the Eu L_{III}-edge XAFS at

^{*} Corresponding author. Fax: +81-86-251-7853; e-mail: kubozono@cc.okayama-u.ac.jp

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295 K of the soot which contained a large amount of $Eu@C_{60}$ [12]. However, no sample of $M@C_{60}$ completely separated from other metallofullerenes has yet been obtained, and the purification of $M@C_{60}$ has remained a target of our continued efforts. The present Letter reports on our attempts aimed at the purification of $Eu@C_{60}$ by combining sublimation and HPLC techniques, by which we have confirmed the valence state of the Eu atom in $Eu@C_{60}$.

2. Experimental

Soot-containing Eu@C₆₀ was prepared by archeating a Eu₂O₃/graphite rod (Toyo Tanso; Eu concentration: 0.8 mole%) at 27 V and 80 A under a 80 Torr He atmosphere. The soot was sublimed at 450°C for 2 h under dynamical pumping at 10^{-6} Torr. The powder obtained by sublimation was dissolved in distilled aniline by applying ultrasonic excitation at $0-5^{\circ}$ C for 2 h, and the aniline solution was filtered with a 0.2 µm membrane filter (Toso: H-25-2). The aniline solution was passed through a semi-preparative HPLC system (Toso: UV-8020 detector; CCPS dual pump) with a Buckyclutcher I column (Regis: 10 mm $\phi \times 250$ mm) using aniline as the eluent. The flow rate of the eluent was 0.75 ml min⁻¹, as detected by UV at 330 nm. The compositions of the samples were checked by a laser desorption time-of-flight (LD–TOF) mass spectrometer at 337 nm (Finnigan: Vision 2000). Eu L_{III}-edge XANES and XAFS spectra were measured in the fluorescence mode at BL01B1 of SPring-8 and in the transmission mode at BL-7C of KEK-PF, respectively. The UV–VIS absorption spectrum was measured with a Hitachi 228 spectrophotometer.

3. Results and discussion

3.1. Characterization of the $Eu@C_{60}$ sample

The LD–TOF mass spectrum of the soot (Fig. 1a) shows a pronounced peak of $Eu@C_{60}^+$ and weaker peaks attributable to other fullerenes (C_{60} , C_{70} , $Eu@C_{70}$, $Eu@C_{70}$, $Eu@C_{74}$...). The fraction of $Eu@C_{60}$ was higher than those in the soots prepared by arc-heating of graphite rods containing other metal



Fig. 1. LD–TOF mass spectra in arbitrary units of: (a) soot; (b) sublimate; (c) aniline extract; and (d) the fraction collected after the second HPLC procedure (F2 in Fig. 2d). See text for symbols I and II.

oxides [7,8]. The powder obtained by sublimation of the soot at 450°C (Fig. 1b) shows three peaks of C_{60}^+ . C_{70}^+ and Eu@C⁺₆₀ with a very weak peak corresponding to Eu@C⁺₇₄; no peak was observed below m/z =600. The mass spectrum of the powder obtained by sublimation below 400°C showed only peaks corresponding to C_{60}^+ and C_{70}^+ , while that observed after sublimation at 500-600°C was identical with that observed at 450°C. No metallofullerene other than $Eu@C_{60}$ was sublimed at temperatures up to 600°C. These findings show that sublimation above 450°C is useful to obtain $Eu@C_{60}$ from the soot by elimination of the other metallofullerenes. On the other hand, empty fullerenes (C_{60}, C_{70}) and higher fullerenes) and metallofullerenes (M@C₆₀, M@C₇₀, $M@C_{76}$, $M@C_{82}$ and $M@C_{90}$) were obtained by sublimation at 450°C from the soots containing Y, Ce, Nd, Tb and Dy endohedral fullerenes [13].

The LD–TOF mass spectrum of the filtered aniline solution (Fig. 1c) exhibits three peaks of C_{60}^+ , C_{70}^+ and Eu@C_{60}^+, and a weaker peak of Eu@C_{74}^+. The peak intensity of Eu@C_{60}^+ relative to that of C_{70}^+ is about six times higher than that in Fig. 1b, showing that aniline is an effective solvent for the extraction of $M@C_{60}$ [7–11].

The HPLC profile of the aniline extract (Fig. 2a) shows two peaks and a shoulder at 14–25 min. The fraction with a very intense peak at 17.5-25 min was assigned to C₆₀ and C₇₀, because the peaks corresponding to pure C_{60} and C_{70} were observed in this region (Fig. 2b and c). When the fraction from 14.1-15.8 min denoted as F1 in Fig. 2a, which exhibited a shoulder, was collected and injected again into the HPLC system, the peaks of C_{60} and C_{70} disappeared (Fig. 2d) and two peaks were observed at 12.5–18 min. The essential component of the first peak around 15 min was assigned to $Eu@C_{60}$. The mass spectrum of the second peak denoted as A showed peaks corresponding to C_{60}^+ , Eu@C $_{60}^+$ and impurities originating from aniline. This mass spectrum suggests the existence of clusters such as $(C_{60})_n (Eu@C_{60})_m.$

The fraction from 12.5–14 min (F2) was then collected to avoid contamination from compounds in the second HPLC peak (A). A dominant peak of $Eu@C_{60}^+$ was observed with very weak peaks corre-



Fig. 2. HPLC profiles of: (a) aniline extract; (b) C_{60} ; (c) C_{70} ; and (d) the collected fraction (F1 in (a)). See text for symbols A and F2.

sponding to C_{60}^+ and C_{70}^+ in the mass spectrum of the fraction F2 (Fig. 1d). The peaks of C_{60}^+ and C_{70}^+ were weaker than 8% of that of Eu@ C_{60}^+ . Very weak peaks denoted as I and II were assigned to impurities produced by laser irradiation. Very recently, Ogawa et al. reported the purification and isolation of Er@ C_{60} by a similar technique [14,15].

3.2. Electronic structure

The Eu@C₆₀ powder sample was obtained by evaporating the anline from the fraction F2. This sample, hereafter denoted as S1, was used for the measurement of the Eu L_{III}-edge XANES spectrum (Fig. 3a). Since Eu L_{III}-edge XANES is unaffected



Fig. 3. Eu L_{III} -edge XANES spectra of: (a) Eu@C₆₀ sample S1; (b) Eu₂O₃; and (c) EuS.

by a trace of C_{60} and C_{70} in the sample, it can selectively give information on the electronic properties of Eu@C₆₀. The inflection point E_0 of the Eu L_{III} -edge, which is 6 eV lower than that for Eu_2O_3 (6979 eV) (Fig. 3b), is close to that for EuS (6971 eV) (Fig. 3c); the valences of Eu atoms are +3 in Eu_2O_3 and +2 in EuS. It is further shown from the Eu L_{III}-edge XANES spectra that the E_0 for the Eu^{2+} compound is 7 eV lower than that for the Eu^{3+} compound [16]. We conclude that the valence of the Eu atom in $Eu@C_{60}$ is +2. The XANES peaks are assigned to the $2p_{3/2}$ -5d transitions of Eu^{2+} and Eu^{3+} . Recently, Kikuchi et al. concluded that the valence of the Eu atom in Eu@C₈₂ was +2from the similarity of UV-VIS-near IR absorption spectra for $Eu@C_{82}$ to those for $Yb@C_{82}$ and Tm@C₈₂ [17]; Yb and Tm atoms have the valence state of +2. The stability of Eu²⁺ in Eu endohedral fullerenes can be associated with that of the $4f^7$ state as in the $4f^0$ and $4f^{14}$ states.

The UV–VIS absorption spectrum of the aniline extract (Fig. 4a) is nearly identical with that for C_{60} (Fig. 4b), but it has no clear similarity to that of C_{70} (Fig. 4c). This is consistent with the LD–TOF mass spectrum (Fig. 1c) which exhibits a pronounced peak corresponding of C_{60}^+ . The spectrum of the aniline solution of the Eu@C₆₀ sample S1 showed a structureless pattern different from those for C_{60} and C_{70} (Fig. 4d) but similar to that recently observed for the aniline solution of Er@C₆₀ [15].

The onset of the absorption spectrum of the Eu@C₆₀ sample, S1, shows a clear red-shift. This red-shift may be attributed to the $t_{1u}-t_{1g}$ transition due to the electron transfer from the Eu atom to the C₆₀ cage. Though intense peaks due to the $t_{1u}-t_{1g}$ transition were observed for $C_{60}^{-}-C_{60}^{4-}$ [18], no corre-



Fig. 4. UV–VIS absorption spectra in arbitrary units of the aniline solutions of: (a) extract; (b) C_{60} ; (c) C_{70} ; and (d) $Eu@C_{60}$ sample S1.

sponding peaks were observed for Eu@C₆₀ as in the case of Er@C₆₀ [15]. Consequently, there is no characteristic feature that makes this spectrum resemble those of M@C₈₂ (M²⁺), Ca@C₇₂ and Ca@C₇₄ (Ca²⁺) [17,19,20].

The reason for the structureless pattern observed in the absorption spectrum presents an unsolved problem. It may originate from the formation of $Eu@C_{60}$ -aniline complex in the aniline solution or the existence of isomers resulting from a lowering of symmetry of the C_{60} cage caused by the encapsulation of the Eu atom. Furthermore, an exohedral adduct may also be produced by the reaction of $Eu@C_{60}$ with aniline in the aniline solution, as in the case of the photochemical reaction of La@C₈₂ with a disilirane derivative [21]. We found that the $Eu@C_{60}$ sample, S1, was insoluble in CS₂; this suggests that $Eu@C_{60}$ has a small bandgap as is the case for C₇₄, which is insoluble in common organic solvents such as toluene or CS₂ [22]. Such a smallbandgap structure may facilitate the formation of exohedral adducts with aniline in the aniline solution.

The Eu L_{III}-edge XAFS of the soot, which contains a large amount of Eu@C₆₀, was measured at 50 K to determine the Eu–C distances for Eu@C₆₀ with thermal fluctuation of Eu and C atoms suppressed. The distances were 2.384(6) Å for the first-neighboring C atoms and 2.90(1) Å for the second-neighboring C atoms, which is within a standard deviation of those measured at 295 K [12]. This result supports the assignment of an endohedral structure of Eu@C₆₀ in the soot.

Acknowledgements

The authors are grateful to Professor Hisanori Shinohara of Nagoya University, Professor Yoshihiro Iwasa of JAIST, Dr. Kenji Ishii of the University of Tokyo, Professor Tunehiro Tanaka of Kyoto University and Professor Takeshi Akasaka of Niigata University for their valuable discussion. The XANES and XAFS studies were performed under a proposal of SPring-8 (1998A0048-CX-np) and a proposal of KEK-PF (98G-289), respectively. This work is supported by a Grant-in-Aid (11165227) from the Ministry of Education, Science, Culture and Sports, Japan.

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