

Investigation of epitaxial arrangement and electronic structure of a La@C₈₂ film grown on an MoS₂ surface

K. Iizumi, Y. Uchino, K. Ueno, and A. Koma

Department of Chemistry, School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

K. Saiki

Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Y. Inada, K. Nagai, Y. Iwasa, and T. Mitani

Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa 923-1292, Japan

(Received 8 March 2000)

Molecular arrangement and electronic structure of a La@C₈₂ film epitaxially grown on an MoS₂ surface have been studied using reflection high-energy electron diffraction and electron energy-loss spectroscopy (EELS). It was revealed that La@C₈₂ molecules form a close-packed hexagonal lattice on a cleaved face of MoS₂ with the intermolecular distance of 1.13 ± 0.03 nm. EELS of the La@C₈₂ film in the valence excitation region indicated seven peaks coming from $\pi \rightarrow \pi^*$ transitions together with the π -plasmon excitation. The absence of a distinct band gap means that the La@C₈₂ epitaxial film is not semiconducting, but metallic or semimetallic. From the EELS result, we propose an electronic structure diagram of the La@C₈₂ epitaxial film.

I. INTRODUCTION

Endohedral metallofullerene La@C₈₂ is an attractive material because of its unique molecular structure and novel electronic properties.^{1,2} Since the discovery of synthesis and separation methods of a milligram-scale amount La@C₈₂,³ various physical and chemical properties have been extensively studied.⁴⁻⁷ To the best of our knowledge, however, the past studies on La@C₈₂ were carried out using a very small bulk single crystal or a deposited amorphous film. If the growth of an epitaxial film of La@C₈₂ is achieved, it becomes possible to investigate in detail such physical and chemical properties as electric conductivity, photovoltaic property, reactivity with various gases, etc., and new application fields will be opened.

In order to prepare a well-ordered thin film of La@C₈₂, molecular beam epitaxy (MBE) is thought to be the most promising method. Actually epitaxial films of not only C₆₀ or C₇₀, but also many other kinds of higher fullerene films have been grown by the MBE method. As the substrate for the epitaxial growth of La@C₈₂, a cleaved surface of such layered materials as MoS₂, GaSe or mica is suitable. They have a two-dimensional lamellar structure, and each unit layer is bound together via weak van der Waals force. This structure results in a cleaved surface without dangling bonds. In previous works, we have reported that C₆₀ and C₇₀ films grow epitaxially on cleaved surfaces of various kinds of layered materials,^{8,9} and that interactions between a C₆₀ molecule and these surfaces are weak.¹⁰ Thus it was expected that La@C₈₂ molecules grow epitaxially on the layered material substrate, too.

In the present work, we have succeeded in growing epitaxial La@C₈₂ films on MoS₂ substrates, and studied the

molecular arrangements of the grown film using reflection high-energy electron diffraction (RHEED). The intermolecular distance of the La@C₈₂ film was compared with that of a bulk single crystal of La@C₈₂. The epitaxial relationship between the La@C₈₂ film and the MoS₂ substrate was also determined.

As for the electronic structure of La@C₈₂, ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy have been measured for amorphous films to know the filled state structure.^{2,6} Few experimental results, however, have been obtained for the electronic structure of the empty state. In this study we measured low-energy electron energy-loss spectroscopy (EELS) for the epitaxial La@C₈₂ film on MoS₂ in order to elucidate both the filled state and the empty state structures. Low-energy EELS measured in the reflection geometry is a powerful technique to study surface electronic structures of various materials, because it can reveal not only optically allowed dipole transitions, but also optically forbidden monopole, quadruple, or spin-flip transitions. It also probes plasmon excitations with a high surface sensitivity.^{11,12} The combination of MBE and low-energy EELS is useful for studying the electronic structure of such materials as endohedral metallofullerene, which could not be prepared with a bulk amount. The EEL spectra of the La@C₈₂ epitaxial film also give information on its electrical character. From the EELS result, we will propose the electronic structure diagram of the La@C₈₂ epitaxial film together with the assignment of energy-loss peaks.

II. EXPERIMENT

La@C₈₂ mixed with soot was produced by an arc discharge of La₂O₃-loaded carbon composite rods under a partial atmosphere (200 torr), followed by a two-step extraction

via refluxing, first in orthodichlorobenzene and then in pyridine. The La@C₈₂ was isolated by a high performance liquid chromatography with toluene as an eluent. La@C₈₂ dissolved in CS₂ solution was transferred into an alumina crucible, and CS₂ was vaporized by heating at 70 °C in the atmosphere. After this process, the crucible was introduced into an ultrahigh vacuum (UHV)-MBE chamber with a base pressure of 3×10^{-8} Pa. It was carefully heated at 300 °C for 24 h in order to remove the residual solvent.

The MoS₂ substrate with a size of $5 \times 10 \times 0.1$ mm³ was cut from a natural molybdenite crystal. It was cleaved in atmosphere just before loading into the MBE chamber, and thermally cleaned by heating at 400 °C for 30 min. Then La@C₈₂ molecules were evaporated from the crucible heated at 430 °C. During the growth of La@C₈₂, the substrate temperature was kept at 200 °C. Surface structures of the substrate and the grown film were monitored by RHEED with an incident electron energy of 20 keV.

The grown film was transferred into an analysis chamber with a base pressure of 8×10^{-9} Pa without breaking UHV. Before the EELS measurement, Auger electron spectroscopy (AES) measurement was carried out in order to check for the absence of contamination and the presence of La atoms. These spectra were measured with a double-pass cylindrical mirror-type electron energy analyzer (ULVAC-PHI model 15-255G). Typical primary electron energies (E_p) for AES and EELS measurements were 3000 and 20 eV, respectively. In the EELS measurement, the full width at half maximum of the elastic peak was as narrow as 0.5 eV. All spectra were obtained by the pulse-counting method, and then the first- and the second-derivative ones were numerically calculated for AES and EELS measurements, respectively.

III. RESULTS AND DISCUSSION

A. RHEED observation

Figures 1(a) and 1(b) show RHEED patterns of the La@C₈₂ film grown on the MoS₂ substrate with about one monolayer equivalent coverage. The incident electron beam was parallel to the $[11\bar{2}0]$ and $[10\bar{1}0]$ axes of the MoS₂ substrate, respectively. Bright streaks in Figs. 1(a) and 1(b) come from the MoS₂ substrate. Since the MoS₂ surface has a sixfold symmetry, the streak interval of the substrate in the $[10\bar{1}0]$ direction [Fig. 1(b)] is $\sqrt{3}$ times larger than that of the $[11\bar{2}0]$ incidence [Fig. 1(a)], and the same pattern appears at every 60° azimuth when the substrate is rotated around the surface normal.

When La@C₈₂ molecules were evaporated from the alumina crucible, new streaks with much narrower intervals appeared between streaks of the substrate, as marked by arrows (\downarrow) in the photograph, which indicates the epitaxial growth of La@C₈₂ molecules. The interval of streaks from La@C₈₂ observed in the $[10\bar{1}0]$ direction is $\sqrt{3}$ times larger than that in the $[11\bar{2}0]$ incidence. This indicates that La@C₈₂ molecules form a close-packed hexagonal lattice with the principal axis parallel to the $[11\bar{2}0]$ axis of the MoS₂ substrate.

The intermolecular distance of the La@C₈₂ epitaxial film grown on the MoS₂ substrate calculated from the streak interval was 1.13 ± 0.03 nm. This value agrees with that of the

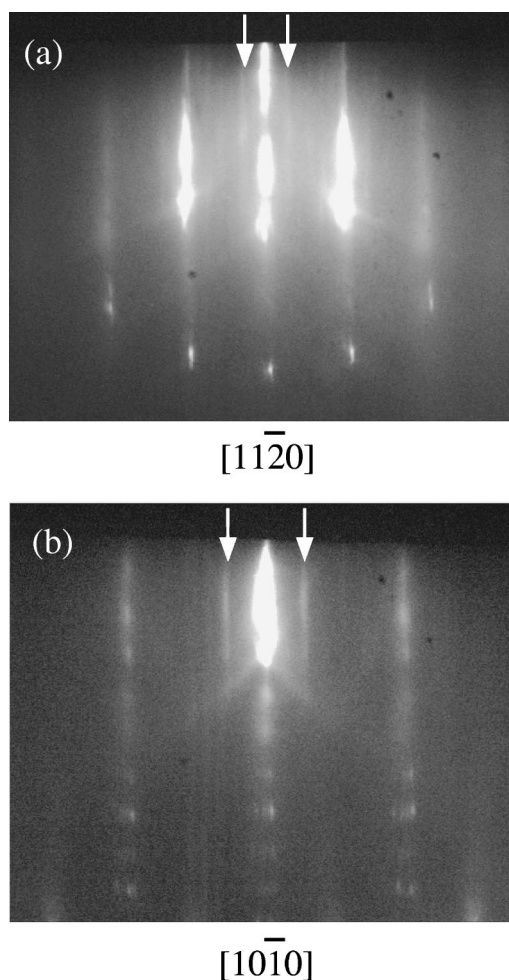


FIG. 1. RHEED patterns of submonolayer La@C₈₂ on the MoS₂ substrate. The incident electron beam is parallel to the $[11\bar{2}0]$ orientation of the MoS₂ substrate in (a), and to the $[10\bar{1}0]$ orientation in (b).

solvent-free hcp bulk La@C₈₂ single crystal; 1.116 nm,¹³ within an error. Therefore the lattice constant ratio of MoS₂ to La@C₈₂ is not close to an integer. Namely, the hexagonal lattice of La@C₈₂ molecules is incommensurate with that of the topmost sulfur atoms of the MoS₂ substrate. The proposed arrangement of La@C₈₂ molecules on the MoS₂ substrate is illustrated in Fig. 2.

In our previous works⁹ it was found that C₇₀ molecules form a hexagonal lattice ($a = 1.08$ nm) on the MoS₂ substrate ($a = 0.316$ nm) with its principal axis rotated by 30° from that of the substrate. In this case two lattices come to have commensurate points ($0.316 \times 2\sqrt{3} = 1.09$). In contrast, C₆₀ molecules form a hexagonal lattice ($a = 1.00$ nm) on MoS₂ with its principal axis parallel to that of the substrate, because no commensurability can be achieved for the rotation around the surface normal. On other layered material substrates such as MoSe₂, GaSe, or InSe,^{9,14} the principal axis of the hexagonal lattice of fullerene molecules was found to rotate from that of the substrate only when it is commensurate with the substrate lattice. In the case of La@C₈₂, no commensurability is achieved with the MoS₂ substrate by the rotation, and it results in the epitaxial growth with the principal axis of the film parallel to that of the MoS₂ substrate.

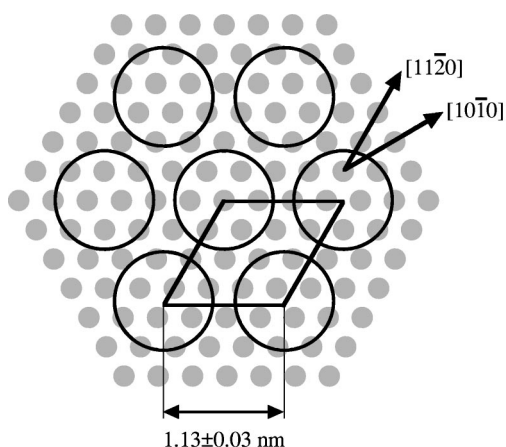


FIG. 2. Suggested arrangement of La@C_{82} molecules on the MoS_2 substrate. Large circles represent La@C_{82} molecules, and small circles are the surface S atoms on the MoS_2 substrate.

B. AES measurement

Figure 3 shows the first-derivative Auger electron spectra of a clean MoS_2 surface (a) and the epitaxial La@C_{82} film on the MoS_2 substrate (b). In the spectrum of MoS_2 , the peak at 149 eV is derived from the S KLL transition, and peaks at 184 and 219 eV come from the Mo MNN transitions. No trace of contamination, such as oxygen or carbon, was detected. In the spectrum of the epitaxial La@C_{82} film, weak signals at 60 and 78 eV and a strong signal at 267 eV were additionally observed, which indicates the existence of lanthanum and carbon atoms. There was no signal of impurity, so that we can conclude that a clean epitaxial film of La@C_{82} was obtained.

C. EELS measurement

Figure 4(a) shows a typical EEL spectrum of the epitaxial La@C_{82} film on the MoS_2 substrate measured with E_p of 20 eV. The probing depth of EELS with E_p of 20 eV is less than 0.5 nm,¹⁵ which is smaller than the diameter of a La@C_{82} molecule. Thus only the information on the electronic struc-

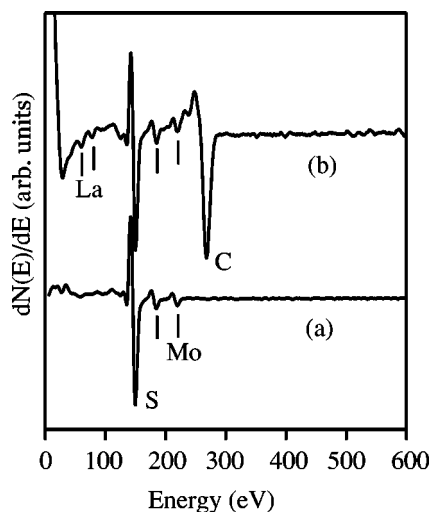


FIG. 3. Auger electron spectra of a clean MoS_2 surface (a) and the epitaxial La@C_{82} film on the MoS_2 substrate (b). Primary electron energy is 3000 eV.

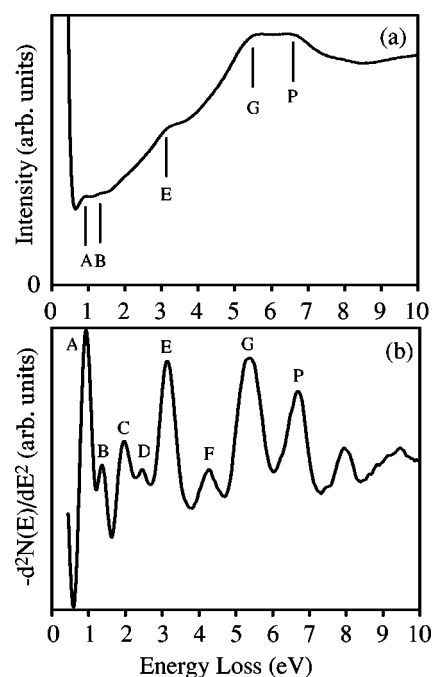


FIG. 4. EEL spectra of the epitaxial La@C_{82} film on the MoS_2 substrate. (a) Intensity and (b) the second-derivative spectra $-d^2N(E)/dE^2$ are shown in the upper and lower parts, respectively.

ture of the La@C_{82} film can be obtained. There are five energy-loss peaks at 0.9, 1.3, 3.1, 5.4, and 6.7 eV, and some shoulders can be seen. No band gap region with small intensity of backscattered electrons is seen in Fig. 4(a), which suggests that the La@C_{82} film has a metallic character. The second-derivative spectrum is shown in Fig. 4(b). Eight energy-loss peaks were found at 0.9, 1.3, 1.9, 2.5, 3.1, 4.3, 5.4, and 6.7 eV in the EEL spectrum. These peaks are labeled $A-G$ and P in the order of the loss energy. The π -plasmon excitation is observed around 6–7 eV in the EELS of the π -electron system such as C_{60} , C_{70} , or graphite.^{16,17} Thus the peak P is considered to come from the π -plasmon excitation. The π -plasmon excitation energy of the La@C_{82} film is slightly higher than those of C_{60} (6.4 eV) and C_{70} (6.3 eV).¹⁷ Peaks $A-G$ are thought to correspond to $\pi-\pi^*$ transitions.

From this spectrum, we propose an energy diagram of the epitaxial La@C_{82} film as shown in Fig. 5, taking account of the theoretical calculation on the molecular orbital of La@C_{82} .^{18,19} Since the energy interval between the lowest-unoccupied molecular orbital and singly occupied molecular orbital is 3.8 eV in Ref. 18, we consider two states L (the lowest-unoccupied molecular orbital) and S (singly occupied molecular orbital, 0 eV), which are separated by 3.8 eV. Energies are taken to be relative to level S , corresponding to the Fermi level. Five peaks with loss energies less than 3.8 eV should be related to level S , while peaks F and G are related to level L . As a result, five occupied energy levels are considered: H (the highest-occupied molecular orbital, -0.9 eV), I (-1.3 eV), J (-1.9 eV), K (-2.5 eV), and M (-3.1 eV). Peaks A, B, C, D , and E can be assigned to $H \rightarrow S$, $I \rightarrow S$, $J \rightarrow S$, $K \rightarrow S$, and $M \rightarrow S$ transitions, respectively. Con-

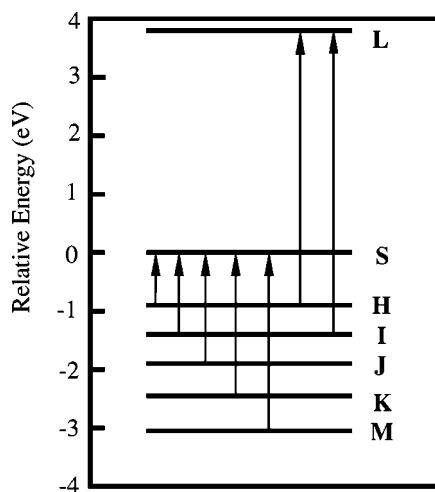


FIG. 5. Energy diagram of the epitaxial La@C₈₂ film proposed from the EELS measurement. Level *S* corresponds to the singly occupied molecular orbital; SOMO and the Fermi level. Energies are taken to be relative to the Fermi level.

sidering the energy between these levels, the weak peak *F* and peak *G* are ascribed to the *H*→*L* and *I*→*L* transition, respectively.

In the UPS result,⁶ we can see peaks at 0.9 eV(α), 1.6 eV(β), 2.1 eV, and 3.3 eV. Reference 6 insists that α and β peaks correspond to SOMO and HOMO, respectively. If SOMO is fixed at 0 eV, other peaks also have to shift by +0.9 eV. Therefore, we should consider the binding energies as follows: 0.0 eV(α), 0.7 eV(β), 1.2 eV, and 2.4 eV. Comparing our energy diagram with the UPS result, it is obvious that *S*, *H*, and *I* states correspond to peaks at 0.0, 0.7, and 1.2 eV in the UPS result, respectively. Because the UPS peak at 2.4 eV is broad, we consider this peak corresponds to *J* and *K* states. As a whole, the energy diagram in Fig. 5 agrees well with the UPS result except the occupied state *M*. This state was not observed by UPS. However, if the *M* state does not exist, the peak *E* cannot be explained. We consider the reason of the absence of the *M* state in UPS as follows: The UPS process is related to the electronic transition excited by ultraviolet photons, so that UPS can observe only dipole allowed transitions. In contrast, EELS can reveal not only dipole transitions but also optically forbidden transitions. If

transitions from the *M* state is optically forbidden, it is not unreasonable that peak *E* appears in EELS in spite of the absence of *M* state in UPS. Therefore EELS is useful to observe the whole electronic structures of the La@C₈₂ film.

In the case of a C₆₀ molecule, we can discuss the selection rules of EELS for some electronic transitions because of its high symmetry (*I_h*). For example, HOMO and LUMO of C₆₀ are indicated *h_u* and *t_{1u}*, respectively. This HOMO-LUMO transition is not a dipole transition but a monopole one. Then optical measurements cannot observe this transition, but EELS can. In contrast with C₆₀, a La@C₈₂ molecule has a lower symmetry (*C₂* as a C₈₂ cage) and the character of its π orbitals is yet unknown. In Fig. 4(b), peaks *A*(*H*→*S*), *E*(*M*→*S*), and *G*(*I*→*L*) are strong versus all the other ones. What makes probabilities of these transitions large is not clear. A detailed theoretical investigation is expected to address this problem.

IV. CONCLUSIONS

We have succeeded in growing a La@C₈₂ epitaxial film on a cleaved MoS₂ surface, and revealed its electronic structure using EELS. From the RHEED observation, it was elucidated that La@C₈₂ molecules form a close-packed hexagonal lattice on the MoS₂ surface with an intermolecular distance of 1.13 ± 0.03 nm, which agrees well with that of the solvent-free bulk La@C₈₂ single crystal. The crystal axis of the epitaxial La@C₈₂ film was found to be parallel to the $[11\bar{2}0]$ axis of the MoS₂ substrate.

A finite band gap was not observed in the EELS of the La@C₈₂ epitaxial film, which indicates that it is not semiconducting but semimetallic or metallic. The π -plasmon transition is observed at the loss energy of 6.7 eV. We have proposed an energy diagram derived from the EELS result, which is consistent with previous works on the UPS observation and on the theoretical calculation.

ACKNOWLEDGMENTS

This work has been supported by the Grant-In-Aid for Scientific Research on the Priority Area "Fullerenes and Nanotube" by the Ministry of Education, Science, and Culture of Japan. Y. Iwasa would like to acknowledge the support by the Japan Society for the Promotion of Science (RFTF96P00104, MPCR-363/96-03262).

¹Y. Chai, T. Guo, C. Jin, R.E. Haufler, L.P.F. Chibante, J. Fure, L. Wang, J.M. Alford, and R.E. Smalley, *J. Phys. Chem.* **95**, 7564 (1991).

²D.M. Poirier, M. Knupfer, J.H. Weaver, W. Andreoni, K. Laasonen, M. Parrinello, D.S. Bethune, K. Kikuchi, and Y. Achiba, *Phys. Rev. B* **49**, 17 403 (1994).

³K. Kikuchi, S. Suzuki, Y. Nakao, N. Nakahara, T. Wakabayashi, H. Shiromaru, K. Saito, I. Ikemoto, and Y. Achiba, *Chem. Phys. Lett.* **216**, 67 (1993).

⁴R.D. Johnson, M.S. de Vries, J. Salem, D.S. Bethune, and C.S. Yannoni, *Nature (London)* **355**, 239 (1992).

⁵J.H. Weaver, Y. Chai, G.H. Kroll, C. Jin, T.R. Ohno, R.E. Haufler, T. Guo, J.M. Alford, J. Conceicao, L.P.F. Chibante, A. Jain,

G. Palmer, and R.E. Smalley, *Chem. Phys. Lett.* **190**, 460 (1992).

⁶S. Hino, H. Takahashi, K. Iwasaki, K. Matsumoto, T. Miyazaki, S. Hasegawa, K. Kikuchi, and Y. Achiba, *Phys. Rev. Lett.* **71**, 4261 (1993).

⁷M. Nomura, Y. Nakao, K. Kikuchi, and Y. Achiba, *Physica B* **208B-209B**, 539 (1995).

⁸M. Sakurai, H. Tada, K. Saiki, and A. Koma, *Jpn. J. Appl. Phys., Part 2* **30**, L1892 (1991).

⁹M. Sakurai, H. Tada, K. Saiki, and A. Koma, *Chem. Phys. Lett.* **208**, 425 (1993).

¹⁰K. Iizumi, K. Ueno, K. Saiki, and A. Koma, *Appl. Surf. Sci.* (to be published).

- ¹¹F. P. Netzer, in *X-ray Spectroscopy in Atomic and Solid State Physics*, Vol. 187 of *NATO Advanced Studies Institute Series B: Physics*, edited by J. G. Ferreira and M. T. Ramos (Plenum Press, New York, 1987), Vol 187, p. 335.
- ¹²K. Saiki, T. Tokoro, and A. Koma, *Jpn. J. Appl. Phys., Part 2* **26**, L974 (1987).
- ¹³T. Watanuki, Ph.D. thesis, University of Tokyo, 1997 (in Japanese).
- ¹⁴K. Ueno, K. Iizumi, K. Saiki, and A. Koma (unpublished).
- ¹⁵G. Ertl and J. Kupperts, *Low Energy Electron and Surface Chemistry* (Verlag Chemie, Weinheim, 1974), p. 7.
- ¹⁶A. Lucas, G. Gensterblum, J.J. Pireaux, P.A. Thiry, R. Caudano, J.P. Vigneron, and W. Krätschmer, *Phys. Rev. B* **45**, 13 694 (1992).
- ¹⁷R. Kuzuo, M. Terauchi, M. Tanaka, Y. Saito, and Y. Achiba, *Phys. Rev. B* **51**, 11 018 (1992).
- ¹⁸S. Nagase and K. Kobayashi, *Chem. Phys. Lett.* **214**, 57 (1993).
- ¹⁹S. Nagase, K. Kobayashi, and T. Asaka, *Bull. Chem. Soc. Jpn.* **69**, 2131 (1996).