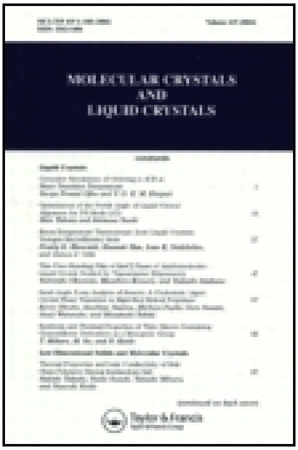

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photoinduced transformation of C_{60} aggregates to Carbon Nanoballs

Keisuke Suzuki [a] , Jeung Sun Ahn [a] , Taisuke Ozaki [a] , Katuyuki Morii [a] , Yoshihiro Iwasa [a] , Nobuo Otsuka [a] & Tadaoki Mitani [a]

[a] Japan Advanced Institute of Science and Technology (JAIST), Tatsunokuchi, Ishikawa, 923-12, Japan

Version of record first published: 04 Oct 2006

To cite this article: Keisuke Suzuki, Jeung Sun Ahn, Taisuke Ozaki, Katuyuki Morii, Yoshihiro Iwasa, Nobuo Otsuka & Tadaoki Mitani (1998): Photoinduced transformation of C_{60} aggregates to Carbon Nanoballs, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 314:1, 221-232

To link to this article: http://dx.doi.org/10.1080/10587259808042482

Mol. Cryst. Liq. Cryst., 1998, Vol. 314, pp. 221–232
Reprints available directly from the publisher
Photocopying permitted by license only

Photoinduced transformation of C_{60} aggregates to Carbon Nanoballs

KEISUKE SUZUKI, JEUNG SUN AHN, TAISUKE OZAKI,
KATUYUKI MORII, YOSHIHIRO IWASA, NOBUO OTSUKA, and
TADAOKI MITANI
Japan Advanced Institute of Science and Technology (JAIST),
Tatsunokuchi, Ishikawa 923-12, Japan

Abstract C_{60} aggregates, which were formed in benzene solution below their freezing points, have been transformed to ball-like nanoscale particles by irradiation of laser light. This transformation has been confirmed by the high-resolution transmission electron microscopy (HRTEM). The size distribution of the photoproducts, carbon nanoball, was directly obtained from the HRTEM images. The characteristics of the transformation from C_{60} molecules to aggregate is well characterized by the photoluminescence spectroscopy.

Keywords: photoluminescence; C_{60}; aggregates; clusters; high-resolution transmission electron microscopy, carbon nanoball.

INTRODUCTION

After the discovery of mass production of fullerenes in 1990[1], many interests have been focused on their unique molecular structures compared with other organic molecules.[2,3] Particularly, the highly symmetric soccer-ball-like structure of C_{60} has attracted much attention since it provides the unconventional electronic states with five and three fold degeneracies in the HOMO and LUMO states, respectively. In its solid forms, the molecular character is maintained, but additional characteristics arise; the strong excitonic effect on the optically-forbidden transitions between the HOMO and LUMO and an appearance of the low-lying CT transitions between the neighboring molecules.[4] These feature lead to unique chemical and photochemical activities, e. g. photo-[5], pressure-[6] and electron-beam-induced[7] polymerization of solid C_{60}, and conversion from C_{60} to superhard and ultrahard carbons under high pressures[8,9]. Considering a small diameter of C_{60} (ca. 0.7 nm), it is possible to control size and structure of the chemical and photochemical products in nanoscale using C_{60} clusters as a starting material. In this sense, the formation of the C_{60} clusters with magic numbers of n=13 and 55 observed in the photoionization time-of-flight mass spectra in vacuum [10], suggests a unique opportunity to stabilize a certain size of particles. Stabilization of a nanometer-size C_{60} clusters in mild experimental conditions is one of our main interests.

In this paper, we report the formation of C_{60} aggregates in solutions of toluene, benzene and carbon disulfide (CS_2) below their freezing points.[11] The photoluminescence spectroscopy has a great advantage to investigate the properties of C_{60} aggregates, since the spectral features associated with the optically forbidden HOMO-LUMO transitions are particularly sensitive to change of the molecular arrangement due to the aggregation. From the spectral analysis, taking account of the confinement of the Frenkel exciton,[12,13] the average size of C_{60} aggregates can be estimated; a typical value in toluene solution is ca. 2.3 nm. When the intensive UV light of pulsed laser is irradiated on C_{60} aggregates, we observed a slight color change of this solutions. The photo-induced products are stable even at room temperature and in air. By the high-resolution transmission electron microscopy (HRTEM), photoproducts were found to be round-shaped nanoscale particles as expected from the luminescence spectroscopy. We name them “carbon nanoballs”. In the following sections, details of the formation of the C_{60} aggregates, the transformation to the carbon nanoballs, and their characterizations will be reported. Our experimental results provide useful information for consistent interpretation of molecular, aggregate and solid forms of C_{60}.

EXPERIMENTAL

C_{60} powder with a purity higher than 99.995% was purchased from Buckey Co. Inc. In addition, the purity of the powder and absence of C_{70} contamination were confirmed by the LD-TOF mass spectrometry. Benzene, toluene, and CS_2 of spectrographic grade were used for solvents. To prevent contamination of oxygen which may affect the photoluminescence spectra, each of the prepared samples were degassed in a 10 mm^2 quartz cell by more than 30 freeze-pump-thaw cycles and sealed under vacuum. Single crystals of C_{60} were prepared by sublimation and were sealed under vacuum. We have checked the oxygen contamination by the near-infrared photoluminescence measurements. Undetectable singlet O_2 luminescence[14] at 1268 nm was a strong evidence for the absence of oxygen contamination. The photoluminescence spectra were measured at temperatures between 115 and 300 K by cooling the samples in a quartz cryostat (Eikoushya EDN-3) with a continuous-flow of cold N_2 gas. Photoluminescence with excitation at 514.5 nm by an argon ion laser was passed through suitable long-pass filters to cut the scattered laser light and imaged onto the entrance slit of a single monochromater (JASCO. Ltd. CT-25GD). To cover the whole luminescence from C_{60} as well as molecular oxygen, a red-sensitivity-enhanced photomultiplier tube (Hamamatsu R5509-41, cooled to 203 K) was used as a detector. The intensity of the excitation beam was kept low enough so that the luminescence intensity is linear against the incident light.

Irradiation of UV-light to C_{60} aggregates in benzene was carried out by using the light source from the third harmonic generator (THG) of Q-switched Nd:YAG laser, which produces pulses of ~ 6 ns duration at 355 nm with a repetition rate of 10 Hz. During the irradiation, the temperature of the sample was controlled at ~ 260 K by using the same cryostat and controller used for the measurements of photoluminescence. After irradiation, the samples were warmed up to room temperature, and then two kinds of specimens for transmission electron microscopy (TEM) were prepared by following methods. Sample A: The solution of sample warmed after UV light irradiation was dropped on a copper grid coated by a perforated amorphous carbon film. And, benzene solvent was evaporated under ambient temperature and atmosphere naturally. Sample B: To separate the unchanged C_{60} from the solution, a filtration was performed by using ultrafilters (Advantec Toyo Co., P0200: 20000 molecular weight cut off) which are anisotropic permselective membranes of poly-m-phenylisophtalamide that separate dissolved solutes at the membranes surfaces on a basis of molecular weight under applied pressure. The benzene solution of the substances remained on the surface of membrane was dropped on the copper grid coated by a perforated amorphous carbon film. High resolution transmission electron microscopy (HRTEM) observations have been performed with a 300 kV electron microscope (Hitachi H-9000NAR) equipped with a high sensitivity TV camera. The spherical aberration constant of the microscope is less than 0.7 mm and the point-to-point resolution is around 0.16 nm at 300 kV. The direct magnification and the electron beam current were 200000 and less than a few A/cm^2 on the sample plane, respectively, in order to minimize irradiation damage.

RESULTS AND DISCUSSION

Photoluminescence spectra of C_{60} dissolved in toluene at three different concentration and C_{60} crystal are shown in Fig. 1. Fig. 1(a) show photoluminescence and absorption spectra of C_{60} toluene solution at concentration of 7 x 10^{-4} M. The concentration of this solution is considerably less than saturated concentration (3.9 x 10^{-3} M)[15] at room temperature. The observed absorption and photoluminescence spectra of this dilute solution are consistent with those previously reported. [16] The spectral shape of photoluminescence at 120 K is essentially the same as that at 300 K, except for the sharper emission profile. In addition, the mirror-symmetry relation approximately holds between photoluminescence and absorption spectra. These spectral features indicate that C_{60} exists in this dilute toluene solution as a isolated molecular form and the weak shoulder structure indicated by an

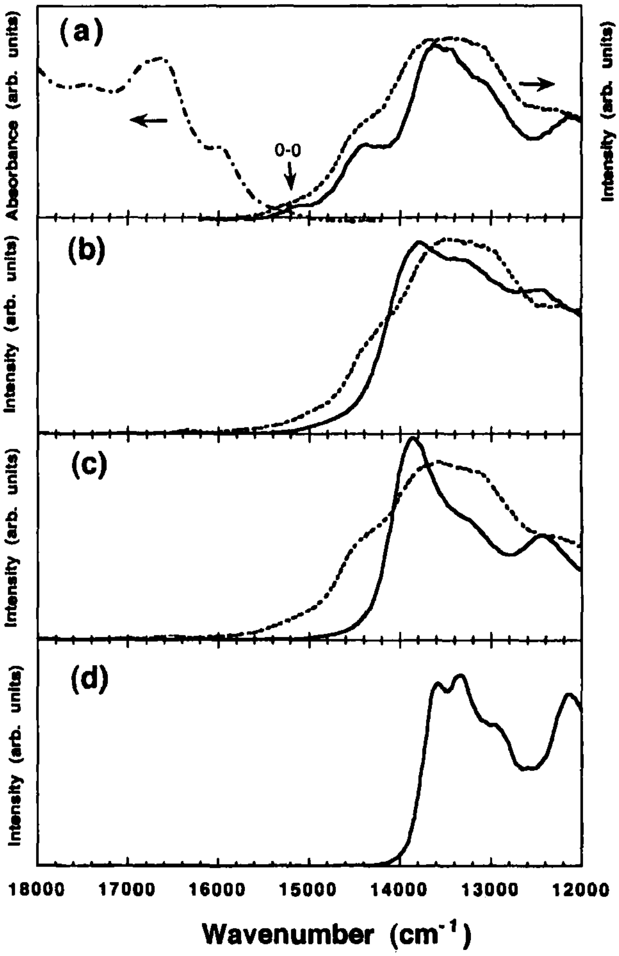

FIGURE 1 Photoluminescence spectra of C_{60} dissolved in toluene at concentrations of (a) 7 x 10^{-4} M, (b) 2 x 10^{-3} M, and (c) 3 x 10^{-3} M near the saturation concentration (3.9 x 10^{-3} M). The solid and dashed lines show the spectra measured at 120 K and 300 K, respectively. The photoluminescence spectrum of the C_{60} single crystals at 120 K is shown in (d). The dash dotted line denotes the absorption spectrum of C_{60} toluene solution at 200 K (7 x 10^{-4} M).

arrow at around 15200 cm^{-1} is assigned to the 0-0 transition component of molecular C_{60}. The photoluminescence spectra of C_{60} toluene solution at concentrations of 2 x 10^{-3} M and 3 x 10^{-3} M are shown in Fig. 1(b) and Fig. 1(c) respectively. The spectral shapes of these concentrated solutions at room temperature are very similar to the same as that of the dilute C_{60} toluene solution, where C_{60} exist as a isolated molecular form at room temperature. On the other hand, the spectral shapes at 120 K are drastically changed. They are rather similar to that of C_{60} crystal at 120 K (see Fig. 1(d)) and the luminescence band related to the 0-0 transition is located in the energy region between those of the C_{60} molecule and the C_{60} crystal. From this similarity and the energy position of the 0-0 component, the drastic shape change in the photoluminescence spectra of the concentrated solutions is attributable to an occurrence of aggregation of C_{60} molecules as discussed below in details.

Fig. 2 shows the photoluminescence spectra of a concentrated C_{60} toluene solution (2 x 10^{-3} M) observed at various temperatures between 115 and 300 K in the cooling and warming processes. In the case of the cooling process, the spectral shape has the molecular feature at temperatures higher than the freezing temperature (ca. 170 K) of the solution and it changes to that of C_{60} aggregates at ca. 170K. In the case of the warming process, the photoluminescence spectra show that the C_{60} aggregates are stable even in the liquid-state solution between ca. 170 K and ca. 210 K and they are decomposed into C_{60} molecules above 210 K. These results indicate that there exists a hysteresis in the transformation from C_{60} molecules to C_{60} aggregates, although the intermolecular coupling inside C_{60} aggregates is considerably weak. The same hysteresis was observed in CS_2 solution between 120 K and the melting point (ca. 160 K) for a concentration of 5 x 10^{-4}M. In benzene, by contrast, we observed the transformation from C_{60} molecules to the aggregates at the melting point (ca. 275 K) without the hysteresis.

The characteristics of the temperature- and concentration-dependent spectra, including the hysteresis, strongly support the model of the transformation from C_{60} molecules to C_{60} aggregates at the freezing

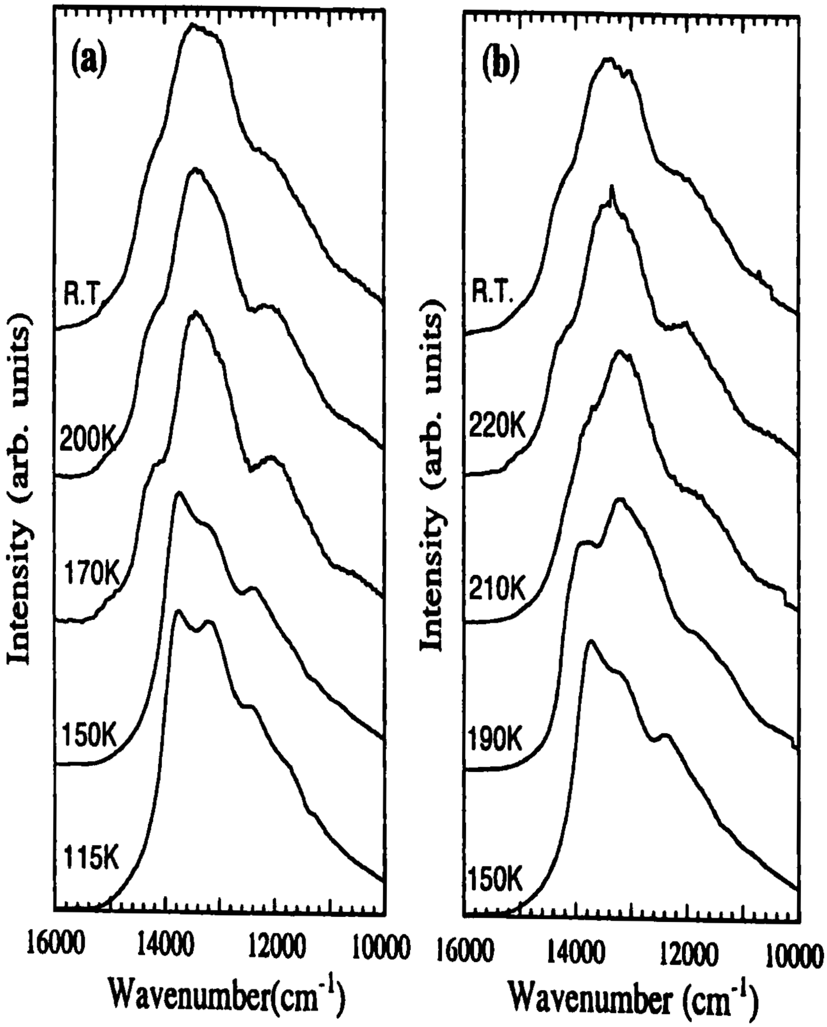

FIGURE 2 Photoluminescence spectra of C_{60} dissolved in toluene at a concentration of 2×10^{-3} M at various temperatures between 300 and 115 K in the cooling(a) and warming processes(b).

temperature. By the formation of aggregates, the 0-0 transition energy of the C_{60} aggregates is red-shifted approaching that of the C_{60} crystal. Since the photoluminescence of C_{60} crystals is attributed to the Frenkel (molecular)-type exciton emission[17], the red shift of the 0-0 band is predominantly due to the confinement in translational motion of the Frenkel excitons. The confined energy (or resonance) of the Frenkel exciton in the 0th-dimension approximation is given by

$$\Delta E = \frac{\hbar^2}{2m^*}\left(\frac{\pi}{d}\right)^2$$

where d and m are the diameter of sample and the translational mass of the exciton, respectively. Since the 0-0 band of the spectra corresponds to the emission from the un-relaxed Frenkel exciton, the size of C_{60} aggregates can be estimated by using the 0-0 transition energies determined from the photoluminescence spectra of molecular, aggregated, and crystalline C_{60}. In this estimation, we considered the difference between the 0-0 transition energies of molecular and crystalline C_{60} as the shifted energy on account of the quantum size effect on the confined excitons in one molecular size. The size of C_{60} aggregates formed in benzene and toluene is estimated as ca. 2.3 nm in diameter, which corresponds to three C_{60} molecules. For the aggregates formed in CS_2 solution, the size was estimated to be about 7 molecules. It is interesting that the estimated 3 and 7 molecules correspond, respectively, to the diameters of the closed shell C_{60} clusters of n=13 and n=147, although more experimental investigations are required to determine the structure of C_{60} aggregates found in this study.

The transformation of the C_{60} aggregates to another new form of carbon was attempted in benzene solution by irradiation of the UV light. The HRTEM images of the samples without the filter-treatment and after the treatment of the filtering (sample A and B, respectively; see the section of EXPERIMENTAL), are shown in Fig. 3 and Fig. 4. In the microscope of the sample A, no distinguishable photoproducts are observed. From the electron diffraction pattern of this sample, we confirmed that it mainly consists of C_{60} powder which remained as the unphototransformed C_{60}. The C60 powder appears to be very sensitive to electron beam irradiation in the TEM observation. During electron beam irradiation, disintegration of C60 powder and structural changes of C60 were observed within a few minutes. In the microscope of the sample B, round-shaped nanoscale carbon particles are clearly observed. The nanoscale carbon particles were quite stable against the electron beam irradiation in comparison with C_{60} powder. From IR measurements of the sample B, it was confirmed that the sample B does not include C60 powder. We call the stable nanoscale photoproducts "carbon nanoballs". Fig. 5 shows the size distribution of carbon nanoballs directly obtained from the HRTEM images of sample B. The carbon nanoballs distribute in a small size less than ca. 10 nm and have discrete sizes of ca. 6 and 8 nm. We could not determine the size distribution in the region of

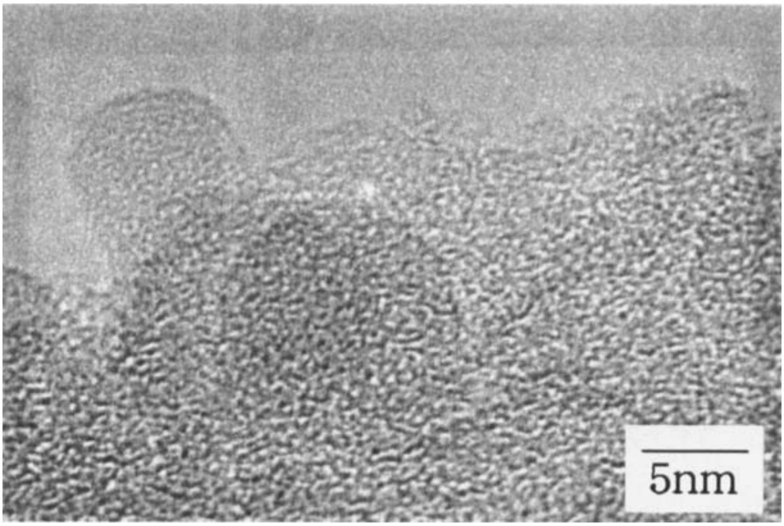

FIGURE 3 HRTEM image of the sample A.

small size (< ca. 5 nm), because the particles of small size were possibly removed from the sample B by the filtration process. Although the structure and the mechanism of formation of carbon nanoballs are not clear yet, they suggest that the C_{60} aggregates before the UV light irradiation transformed to nanoscale C_{60} clusters by photochemical reactions. Also, the shape and the discrete size distribution of carbon nanoballs indicate the presence of some magic numbers of carbon nanoballs.

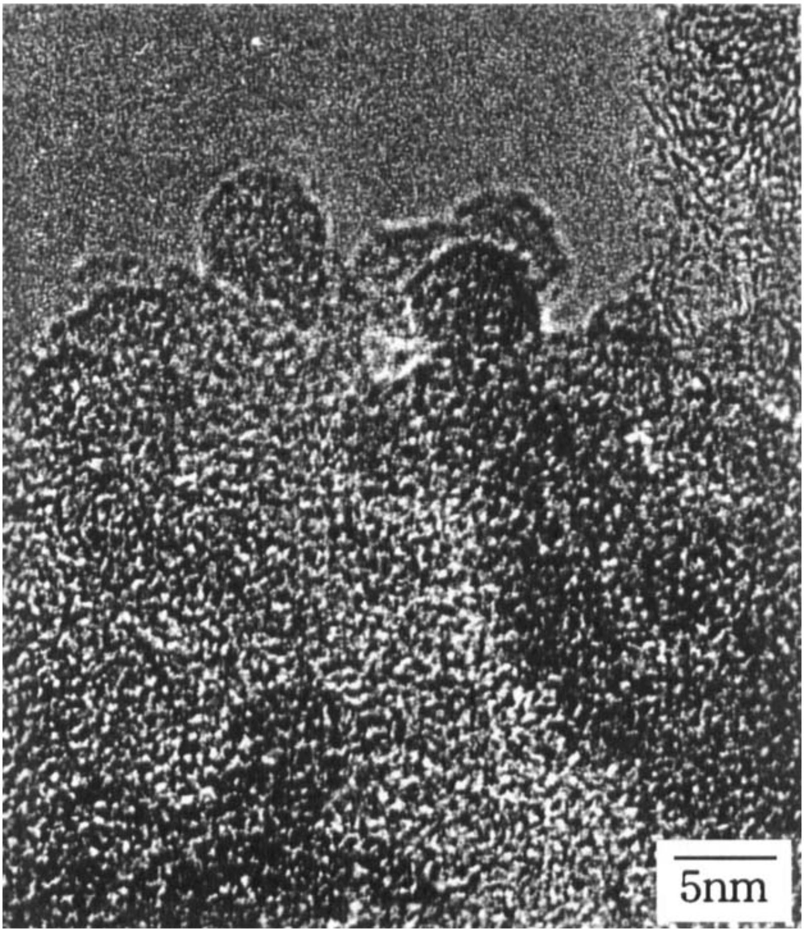

FIGURE 4 HRTEM image of the sample B.

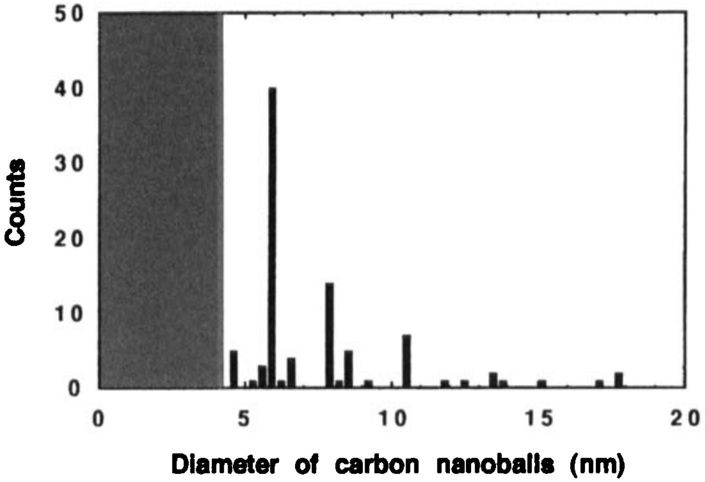

FIGURE. 5 The size distribution of carbon nanoballs observed in the HRTEM images of sample B.

Acknowledgments

The authors are grateful to Dr. A. Q. He of this institute for his experimental assistance and Drs. S. Bandow of the Institute for Molecular Science (IMS), Y. Kanematsu of Osaka University, and H. Kitagawa of this institute for their stimulating discussions. This works has been supported by a grant from the Japan Society for Promotion of Science, from the Ministry of Education, Science, Sports, and Culture, Japan.

References

[1.] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature **347**, 354-358, 1990.
[2.] For a review see M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, Science of Fullerenes and Carbon Nanotrubes, Academic press (1996).
[3.] K. Morii, C. Fujikawa, H. Kitagawa, Y. Iwasa, and T. Mitani, Mol. Cryst. Liq. Cryst., **296**, 357-364 (1997).
[4.] Y. Iwasa, in Opical Properties of Low-dimensional Matewrials, edited by T. Ogawa and Y. Kanemitsu (World Scientific, Singapore, 1995) Chap. 7, p. 340.

[5.] A. M. Rao, P. Zhou, K.-A. Wang, G. T. Hager, J. M. Holden, Y. Wang, W.-T. Lee, X.-X. Bi, P. C. Eklund, D. S. Cornett, M. A. Duncan, and I. J. Amster, Science, **259**, 955-957, 1993.

[6.] Y. Iwasa, T. Arima, R. M. Fleming, T. Siegrist, O. Zhou, R. C. Haddon, L. J. Rothberg, K. B. Lyons, H. L. Carter Jr., A. F. Hebard, R. Tycko, G. Dabbagh, J. J. Krajewski, G. A. Thomas, and T. Yagi, Science, **264**, 1570-1572, 1994.

[7.] T. Toda and T. Kanayama, J. J. Appl. Phys., L63 (1996).

[8.] M. E. Kozlov, M. Hirabayashi, N. Nozaki, M. Tokumoto and H. Ihara, Appl. Phys. Lett., **66**, 1199 (1995).

[9.] V. B. Blank, S.G. Buga, N. R. Serebryanaya, V. N. Denisov, G. A. Dubitsky, Ga. N. Mavrin and M. Yu. Popov, Phys. Lett., **A205**, 208 (1995).

[10.] T. P. Martin, U. Näher, H. Schaber, and U. Zimmermann,Phys. Rev. Lett.,**70**, 3079-3082, 1993.

[11.] K. Suzuki. J. S. Ahn, Y. Iwasa, A. Q. He, N. Otsuka and T. Mitani, Proceeding of IWPNM97, to be published.

[12.] A. I. Ekimov, Al. L. Efros and A. A. Onushchenko, Solid State Commun., **56**, 921-924, 1985.

[13.] T. Itoh, Y. Iwabuchi, and M. Kataoka, Phys. Stat. Sol. (b), **145**, 567-577, 1988.

[14.] J. W. Arbogast, A. P. Darmanyan, C. S. Foote, Y. Rubin, F. N. Diederich, M. M. Alvarez, S. J. Anz and R. L. Whetten, J. Phys. Chem.,**95**,11-12, 1991.

[15.] R. S. Ruoff, R. Malhotra, D. L. Huestis, D. S. Tse and D. Lorents, Nature., **362**,140,1993

[16.] Y. -P. Sun, P. Wang, and N. B. Hamilton, J. Am. Chem. Soc., **114**, 4429-4430, 1992.

[17.] D. J. van den Heuvel, I. Y. Chan, E. J. J. Groenen, M. Matsushita, J. Schmidt, and G. Meijer, Chem. Phys. Lett. **233**, 284-290, 1995.