Crystal Structure and Physical Properties of Elecrocrystallized Dye-C_{60} Fulleride Compounds

Hiroshi Moriyama[1)], Tokuko Watanabe [2)], Kenzi Yoza[3)]

1) Department of Chemistry Toho University, Miyama 2-2-1, Funabashi, 274-8510 Japan
2) University of Marine Science, Kohnan 4-5-7, Minato-ku, Tokyo, 108-8477 Japan
3) Bruker AXS, Moriyacho 3-9-A, Kanagawa-ku, Yokohama, 221-0022 Japan

Electorcrystallization of the chlorobenzene/ethanol solution containing C_{60} and cationic dye, e.g., brilliant green, crystal violet, and other triphenylmethane dyes resulted in the crystalline C_{60}^- fulleride compounds. Discrete fulleride anions[1)] have drawn much attention, as the electron-accepting ability of C_{60} is its most characteristic chemical properties. The C_{60} ability as electron acceptors leads to intriguing physical properties, such as superconducting of alkali metal doped C_{60} as well as unique ferromagnetic behavior of TDAE-C_{60}. However, there has been rather limited number of well-characterized C_{60} anion radical salts, mainly because of the extreme air sensitivity.

Although three different ways to synthesize (Dye)(C_{60}) compounds were reported, [2)-4)] no single crystals were so far obtained. We have recently succeeded in obtaining the single-crystal C_{60} anion radical salts stabilized by cationic organic dyes. Fig 1. shows the SEM microphotograph of the black-colored needle-type single crystal of C_{60}^- salts of Brilliant Green cationic dye. The profile of the IR spectra of the salts seems to change significantly. Only 526 cm^{-1} and 577 cm^{-1} peaks from C_{60} were observable, however, the peaks between 1000 cm^{-1} and 1300 cm^{-1} based on Brillinat Green were disappeared completely. This means the charge transfer interaction exists in some way, and not the mixture of two components.

ESR spectra of the salts (Fig. 2) under Ar atmosphere demonstrate that the broad signal (g=1.999, ΔHpp=ca. 44 G) superimposed by sharp signal (g=2.001, ΔHpp=ca. 5 G), which is characteristic feature of the ESR of C_{60} anion radicals. The time-course of the ESR spectra shows the degradation, observed by the broad signal disappeared in several weeks. The X-ray crystal structure analysis of (Brilliant Green)$^+$(C_{60})$^-$ definitely confirms 1:1 salts of C_{60}^- and cationic dye, Brilliant Green. (Fig. 3) The preliminary results of the semicondcuting behavior, despite the high resistivity, were obtained for these salts on the basis of the four-probe electronic conductivity measurements.

1) C. A. Reed and R. D. Bolskar, *Chem. Rev.*, **100**, 1099-1105 (2000). 2) H. Moriyama, M. Abe, S. Hanazato, H. Motoki, T. Watanabe, and H. Kobayashi, *Synth. Met.*,**103**, 2374-2375 (1999). 3) X. Wei, Z. Suo, G. Yin, and Z. Xu, *Fullerene Sci. Technol.*, **7**, 781-793 (1999). 4) T. Kitagawa, Y. Lee, and K.Takeuchi, *Chem. Commun.*, 1529-1530 (1999).

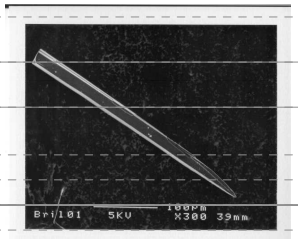

Fig. 1. SEM Micrograph of (Brilliant Green)$^+$(C_{60})$^-$

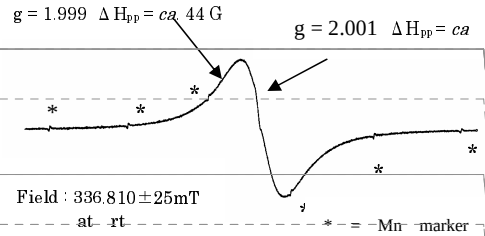

Fig. 2. ESR Spectrum of (Brilliant green)$^+$(C_{60})$^-$ Crystal just after Isolation

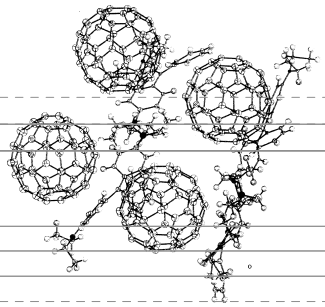

Fig. 3. X-ray Crystallographic Structure of Single Crystal (Brilliant Green)$^+$(C_{60})$^-$

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We thank a grant-in-aid (No. 10126188) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

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