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Electrical and Optical Properties of a Potassium-doped Film of a Long Alkyl Chain-linked C₆₀

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Electrical and optical properties of a potassium (K) -doped film of a hexadecyl chain-linked C₆₀ (**C60-C16**) were evaluated by electric conductivity, UV-visible near-IR and Raman spectra. The conductivity of the pristine film ($3 \times 10^{-7} \text{ S cm}^{-1}$) largely increased to 0.1 S cm^{-1} after doping. The absorption band of **C60-C16** anion was observed around 900 nm in the K-doped film. As a result of Raman spectra measurement, it was confirmed that tri- and/or tetra-anions of **C60-C16** are formed in the film.

Keywords: C₆₀; alkyl chain; doping; two-dimension; cast film; electric conductivity

INTRODUCTION

The films with two-dimensional (2-D) C₆₀ arrangement, which were fabricated by self-assembled monolayers, Langmuir-Blodgett or casting techniques, have attracted much attention from the viewpoints of the fundamental and practical study.^[1] We reported that a long alkyl chain-linked C₆₀ via a phenyl ring takes a layer structure and forms the

2-D arrangement of C₆₀ moieties in the cast film.^[2] In this work, we investigated potassium (K) -doping effect on a cast film of a hexadecyl chain-linked C₆₀ via *para* position on a phenyl group (**C60-C16**) as shown in Figure 1.

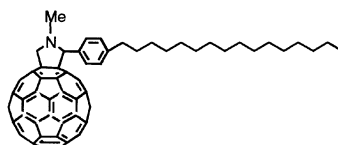


FIGURE 1. Molecular structure of **C60-C16**.

EXPERIMENTS

C60-C16 was synthesized according to a similar route in the previous report.^[2,3]

For the electrical and optical measurements of the K-doped **C60-C16** film, apparatus shown in Figure 2 was used. The film was prepared by dropping carbon disulfide solution of **C60-C16** on an amorphous carbon-coated glass substrate. For the electrical measurement of the cast film by dc two-probe method, a pair of 100-nm-thick Au electrodes (gap width: 1 mm, length: 5 mm) was deposited on the substrate prior to the film preparation. A quartz cell, in which the sample was inserted, was set in a UV-vis-NIR spectrophotometer (Shimadzu UV-3100PC). Under vacuum (about 10⁻⁵ Torr) the temperature of the heater was raised slowly. When resistance of the film started to decrease, the temperature was fixed.

X-ray diffraction (XRD) measurement of the cast film was carried out on a RIGAKU RU-300 using Cu K_α radiation in the 2θ-θ scan mode. The Raman spectra were measured by JASCO NRS-2100 Laser Raman spectrophotometer and taken with the 514.5-nm Ar-ion line.

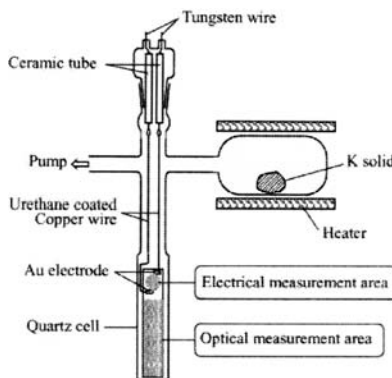


FIGURE 2. Doping apparatus.

RESULTS AND DISCUSSION

To evaluate a structure of the pristine **C60-C16** film, XRD

measurement was performed. As a result, 00 l reflections were observed up to the fifth, and then no other reflection was observed. These indicate that the **C60-C16** film takes the well-ordered layer structures. The d -spacing calculated by Bragg's equation is 25.3 Å.

Figure 3 shows time dependence of the electric conductivity of the K-doped **C60-C16** film during exposure to K vapor in vacuum at room temperature. The time when the conductivity started to increase was defined as zero. The conductivity of the pristine **C60-C16** film was $3 \times 10^{-7} \text{ S cm}^{-1}$. The conductivity increased rapidly to $10^{-2} \text{ S cm}^{-1}$ for several minutes and attained 0.1 S cm^{-1} after 30 minutes. As from 30 minutes the conductivity didn't change until 120 minutes.

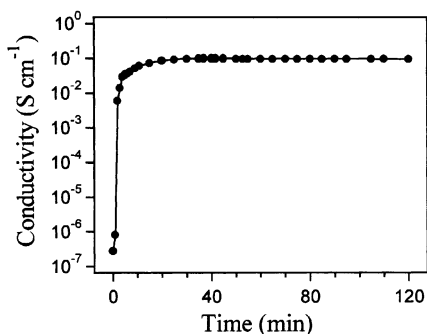


FIGURE 3. Time dependence of the electric conductivity of the K-doped **C60-C16** film during exposure to K vapor.

Figure 4 shows UV-visible near-IR spectra of the pristine and the K-doped films of **C60-C16**. The pristine film didn't exhibit the optical absorption in the near-IR region. On the other hand, a new broad absorption band appeared around 900 nm in the K-doped film. From the result of C_{60} ,^[4] it is considered that the appearance of the new absorption band is a evidence of the electron transfer from K to C_{60} moiety to form the **C60-C16** anions.

Figure 5 shows Raman spectra of the pristine and the K-doped films of **C60-C16**. In the pristine film, a sharp Raman line at 1462.5 cm^{-1} associated with the $A_g(2)$ pentagonal pinch mode of C_{60} (1469 cm^{-1})^[5] was observed. This line shift of **C60-C16** (from 1469 to 1462.5 cm^{-1}) is regarded as influence on addition of a substituent to C_{60} . In the K-doped film, the pentagonal pinch mode shifted by about 21 cm^{-1}

(from 1462.5 to 1442 cm^{-1}) and broadened. To characterize the stoichiometry x of K_xC_{60} samples, the amount of a downshift of the $A_g(2)$ pentagonal pinch mode is often used. It is found that the downshift is $\sim 6 \text{ cm}^{-1}/\text{K atom}$ for the mode.^[6,7] From the result of K-doped C_{60} , it was confirmed that three and/or four K atoms per one **C60-C16** are intercalated and that tri- and/or tetra-anions of **C60-C16** are formed in the film.

In conclusion, K-doping effect on a cast film of a hexadecyl chain-linked C_{60} was investigated. We succeeded in constructing a high conducting film of C_{60} derivative by K-doping. In addition, it was found that three and/or four electrons transfer to one C_{60} moiety.

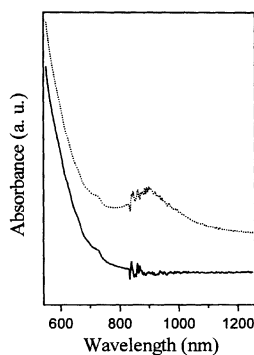


FIGURE 4. UV-visible near-IR spectra of the pristine (solid line) and the doped (dotted line) films.

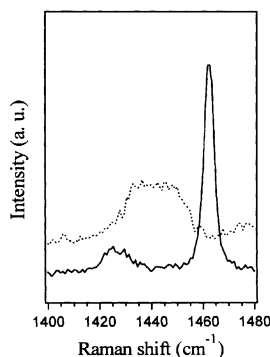


FIGURE 5. Raman spectra of the pristine (solid line) and the doped (dotted line) films.

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