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Separation, Detection, and UV/Visible Absorption Spectra of Fullerenes; C_{76}, C_{78}, and C_{84}

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New kinds of fullerenes were separated by HPLC with benzene from carbon soot. At least four fractions were well separated. Mass analysis confirmed the separation of C_{60}, C_{70}, C_{84} and the mixture of C_{76} and C_{78}. Absorption spectra of C_{76}, C_{78}, and C_{84} were measured for the first time.

The efficient macroscopic preparation of C_{60} and C_{70} by the arc vaporization of graphite in He atmosphere has demonstrated many interesting aspects, possibly reflecting their peculiar form, "soccer ball structure".[1)] Among many attractive information reported so far, the recent finding of superconductivity in K-doped C_{60} films is of particular interest, because a new type π conjugated system (three dimensional) seems to play an essential role on appearance of the conduction behavior.[2)] After the first report by Kraetschmer et al.,[3)] it has been shown that C_{60} and C_{70} are separable major products from carbon soot.[4)] However, it has been also suggested that the crude benzene-soluble material from carbon arc apparatus contains small amounts of some other fullerenes as well.[4)] Here we describe a new HPLC technique suitable for the separation of fullerenes with high separation ability as well as high yield. We also describe preliminary results on UV/visible spectra of pure C_{76}, C_{78}, and C_{84} fullerenes.

The soot-like material containing C_{60}, C_{70}, and other fullerenes was prepared by arc heating of graphite (99.997%) under about 100 Torr He condition. Crude benzene-soluble products were extracted from the carbon soot using hot benzene. A preparative HPLC (Model LC-908 with JAIGEL 2H, 2H, Japan Analytical Industry Co.) was used to separate several kinds of fullerenes from very concentrated extract. An eluted solution was benzene and its flow rate was 5 ml/min. Since the fullerenes are generally less soluble in hexane, chloroform, or THF, the use of benzene as an elute is very versatile to satisfy the requirements for separation of these fullerenes from crude materials.

As shown in Fig. 1, there appears at least four fractions by detecting refractive index. The retention times for these four fractions were 75, 84, 91, and 98 min, respectively. The first two components, namely, F-1 and F-2 in Fig. 1 were found to be attributed to C_{60} and C_{70}, respectively. About 7 mg of C_{60} and 3 mg of C_{70} were obtained by 3 ml injection each.

In order to identify the chemical species appearing in the F-3 and F-4, we further carried out mass spectroscopic experiments. The mass spectra obtained for the F-3 and F-4 are shown in Fig. 2(a) and (b), respectively. A fast atom bombardment (FAB) mass spectrometer (JEOL HX 110) was used for this purpose. The resulting mass spectra indicate that the F-4 portion consists of a single mass component, C_{84}, while the F-3 contains at least two mass peaks, attributable to C_{76} and C_{78}.

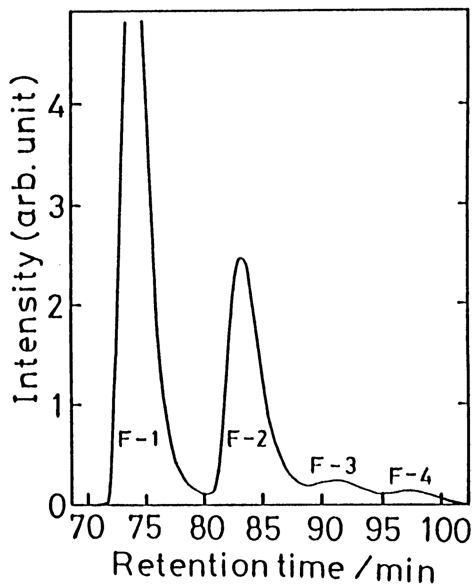

Fig.1. The result of the separation of fullerenes by a preparative HPLC. The intensity of F-1 is about 1/3 of F-2.

Absorption spectrum of C_{84} in benzene is shown in Fig. 3(a). Absorption onset of C_{84} is located at around 1000 nm, while those for C_{60} and C_{70} are at 635 nm and at 650 nm, respectively.[4,5] The onset of absorption for C_{60} (1.95 eV) and C_{70} (1.91 eV) is known to correspond to HOMO-LUMO energy gap,[6] and the C_{60} crystal shows semiconductor character.[7,8] The observed onset for C_{84} here, thus, indicates that if C_{84} is also a closed shell in its electronic structure, the energy gap is only 1.2 eV. This small energy gap in a free molecule would possibly result in the appearance of metallic character in crystalline form.

In order to clarify two mass peaks observed for F-3, the portion of F-3 was further divided into three in accord with the retention time. The F-3 fraction was recycled over 4 times prior to the separation. The absorption spectra thus obtained are shown in Fig. 3(b)-(d). Here, Fig. 3(b) is absorption spectrum obtained by collecting all part of the F-3, while the spectra of Fig. 3(c) and (d) are those obtained by careful

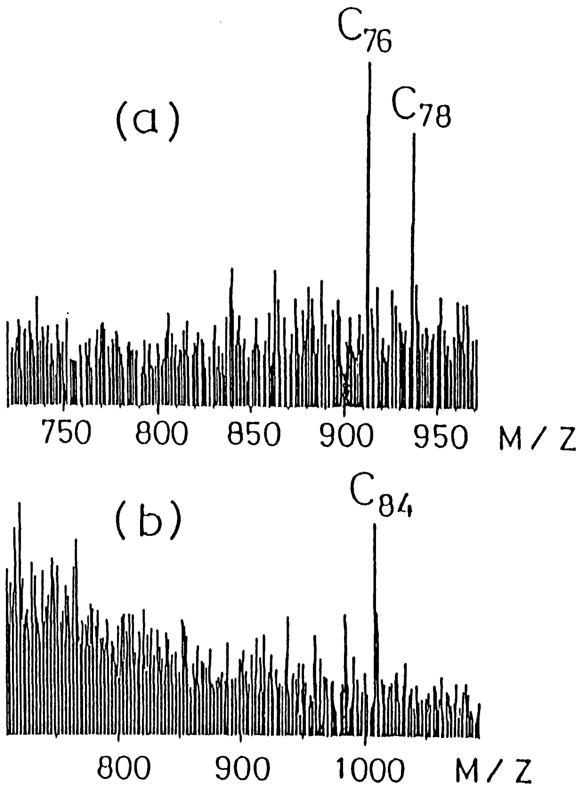

Fig.2. The FAB mass spectra obtained for fullerenes; (a) is obtained for the F-3 and (b) is obtained for the F-4 component of Fig.1.

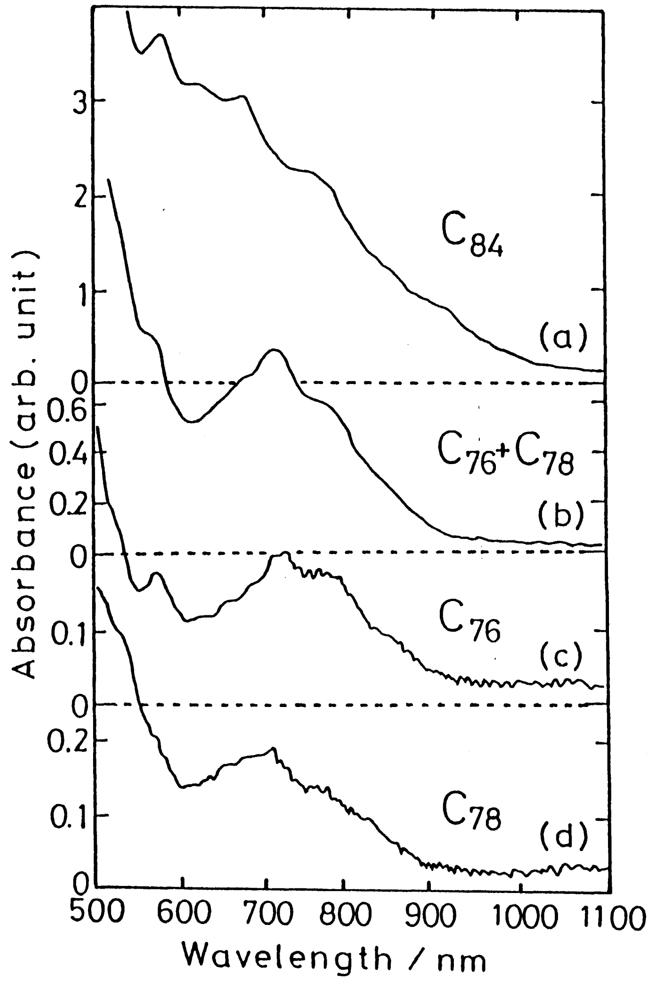

Fig.3. (a) The absorption spectrum of the F-4 of Fig.1: (b) The absorption spectrum of the F-3 of Fig.1: (c) The absorption spectrum obtained by collection of the first 1/3 part of the F-3: (d) The absorption spectrum obtained by collection of the last 1/3 part of the F-3.

collection of the first 1/3 part and the last 1/3 part of the F-3, respectively. By comparing these spectra, it is noticed that the spectrum of Fig. 3(b) is reproduced by adding the spectrum of Fig. 3(c) to that of Fig. 3(d). This fact strongly indicates that the C_{76} and C_{78} are separable by the present technique. Finally, considering the results deduced by both mass spectrum and the retention time expected for C_{76} and C_{78} in the present system, it is strongly suggested that the spectra shown in Fig. (c) and (d) are those of C_{76} and C_{78}, respectively.[9]

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