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Synthesis and Characterization of a Fullerene Derivatives

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Through this paper we are proposing chemically modified fullerol as a fluorescent indicator. We examined the esterification of a fullerol, $C_{60}(OH)_n$, and determined the emission properties which have been directly linked to their chemical structures. As "fullerol" is a mixture of polyhydroxylated fullerenes, the separation of $C_{60}(OH)_n$ and their esters have been attempted by using polyacrylamide gel electrophoresis (PAGE).

Keywords: acetylation; fullerol; PAGE; photoluminescence

INTRODUCTION

Buckminsterfullerene is particularly interesting as it has a unique structure. So far various fullerene derivatives have been reported such

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as water-soluble, halogenated, aminated and methanofullerenes and so on after the discovery of the fullerene [1,2]. Recently, wate-soluble fullerenes have been reported as high functional materials [3,4]. Fullerol is one of the water-soluble fullerene derivatives (polyhydroxylated fullerene) and can be obtained by relatively easy synthesis process (chemical formula of fullerol made from C_{60} is $C_{60}(OH)_n$, and we use "fullerol" for $C_{60}(OH)_n$ hereafter). In one of our previous studies, we have investigated the copolymerization of propylene oxide with carbon dioxide using a fullerol-containing catalyst system, and obtained a fullerol-modified polycarbonate [5]. Also, we reported the luminescence properties of fullerol and showed the possibility of fullerols for the optical applications [6]. It has been reported earlier that the fullerols can be used as a contrast medium using $Gd@C_{82}(OH)_n$ (Gd-containing fullerol) in medical field [7], as a fluorescent coordination compounds of metal ions [8], or as an physiological reagent [9]. If the limitation of solubility of fullerols in the organic solvents is removed or reduced, then fullerols can be used in many fields including use as a fluorescent indicator or marker to biomolecules.

Through this paper we would like to propose the possibility for fullerol as a novel fluorescent indicator which can bind to biomolecules. We have developed the ester by acetylation of fullerol to monitor the change in the emission and absorption properties of fullerol and its ester derivatives, which have been directly linked to their chemical structure. We have also examined two types of fullerols with different numbers of hydroxy group, which were prepared by different methods, separated them with the help of polyacrylamide gel electrophoresis (PAGE) analysis, and compared them with each other.

EXPERIMENTAL

Materials

Fullerenes (99.5%) were obtained from Nakalai Tesque Inc., (Japan). Other chemicals used for chemical modification processes were of reagent grade, and used without further purification. Solvents used for luminescence measurement were purchased from Dojindo Laboratories (Japan). Solvents for fullerols were water (H_2O) or the 1:1 mixture of H_2O and acetonitrile (MeCN) to examine the change in emission wavelength depending on solvent polarity. Solvents in the case of acetylated fullerols were dichrolomethane (CH_2Cl_2), which was not a good solvent for both fullerols and many acetylated fullerols. However we have used CH_2Cl_2 to avoid strong hydrogen-bonding formation between acetylated fullerols and solvent molecules, and

1:1 mixture of CH_2Cl_2 and MeCN to examine the effect of solvent polarity.

Preparation of Fullerols and their Esters

Schemes of synthesis and acetylation processes of fullerols are shown in Figure 1. Two kinds of fullerols (we represent them as "fullerol-A" and "fullerol-B", respectively) were prepared by using fuming sulfuric acid and phosphorus (V) oxide (for fullerol-A) or tetrabutylammonium hydroxide and sodium hydroxide (for fullerol-B) according to the previously reported methods [10,11]. Each fullerol was dried at 105°C for 1 hour under a high vacuum. Acetylated fullerols were obtained by two acetylation methods. In first method an excess of acetyl chloride as an acetylating reagent was added dropwise into tetrahydrofuran (THF) solution (or suspension) of fullerol with a vigorous stirring. After evaporation of the solvent or volatile organic reagents, the solid product was dissolved in dichloromethane or ethyl acetate, and centrifuged at 2430 *G* for 10 minutes. Again after evaporating the solvents used in the centrifuge, the collected products were washed with an excess of *n*-hexane and filtrated with a polytetrafluoroethylene membrane filter (cut-off size is up to $\sim 0.2\,\mu m$). The second acetylation process was carried out with acetic anhydride. Fullerols

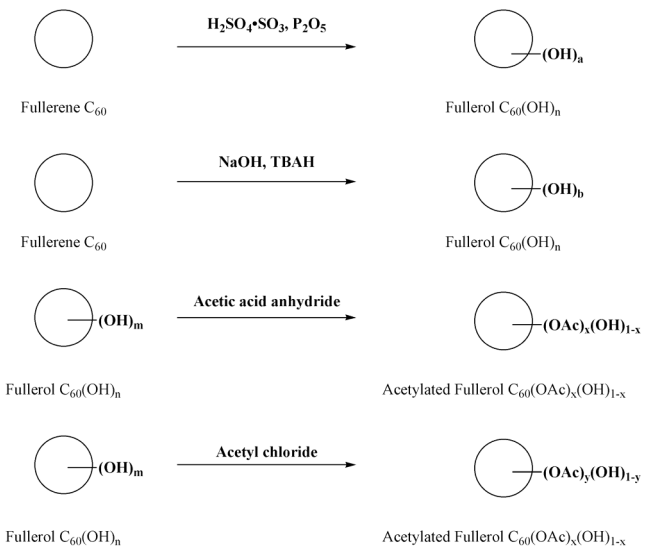

FIGURE 1 Scheme for the syntheses of fullerols and acetylated fullerols.

and acetic anhydride were mixed during stirring in THF at 105°C. After 2 days, the reaction mixture was treated similar to that of the acetylation process used for the acetyl chloride. All products obtained by the acetylation were dried for 1 hour in a vacuum.

Characterization of Fullerene Derivatives

IR spectra were measured on a JEOL JIR-7000 FT-IR spectrometer with KBr pellet. As described in previous reports [9–11], absorption spectra were measured with UV-visible (UV-vis) spectrophotometer (Hitachi: a double beam UV-3200). For fluorescence measurements, an F-4500 fluorescence spectrophotometer (Hitachi) with options for solid samples was used. PAGE analysis was carried out for all sample solutions loaded in each well on a 12% PAGE gel. Loaded sample solutions were 0.25 *N* alkaline solution containing 25 μg samples, 22.3 mM 2-amino-2-hydroxymethyl-1,3-propanediol (Tris) and 22.4 mM Boric acid. Electrophoresis was conducted under the conditions at 100 V for 30 minutes in the TB buffer solution (45 mM Tris and 45 mM Boric acid).

RESULTS AND DISSCUSSION

Syntheses of Fullerol and Acetylated Fullerol

IR spectra for both fullerols of fullerol-A and B (not shown in this article) are similar to the previously reported spectra [10,11]. In IR spectra of the three different kinds of acetylated products (except one IR spectrum of fullerol B treated with acetic anhydride of possible 4 spectrum of fullerol A and B treated with acetic chloride and acetic anhydride), some peaks were seen in the region $1720 \sim 1730\,cm^{-1}$ and $1230 \sim 1240\,cm^{-1}$ which were attributed to ester linkages. However these peaks did not appear in the spectrum of the product prepared from fullerol-B with acetic anhydride. This result suggests that it might be difficult for carbon atom of the carbonyl group in acetic anhydride to attack fullerol B due to the steric hindrance caused by the bulky cage of fullerene (C_{60}) bondings, which has more number of hydroxy groups. The effect of the steric hindrance would be larger for fullerol-B than fullerol-A, as fullerol-B is said to have a larger amount of hydroxyl groups compared to fullerol-A.

Emission Spectra of Fullerols and their Esters in Solution

Emission spectra of fullerol-A, fullerol-B and their esters excited at 340 nm were obtained as shown in Figure 2. We have previously

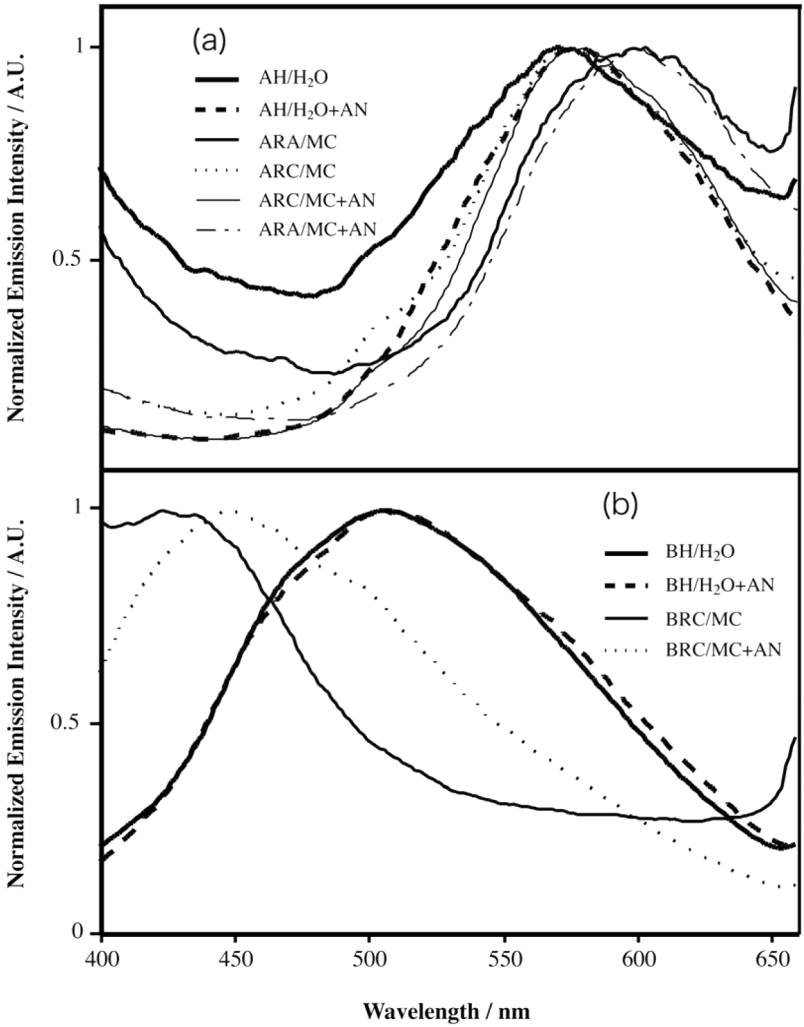

FIGURE 2 Emission spectra of fullerene derivatives. (a) solid line indicates for AH(fullerol-A)/H_2O; dotted line indicates for AH/H_2O + AN(acetonitrile); a broken line indicates for ARA(acetylated fullerol-A obtained with acetic anhydride)/MC; a thin solid line represents ARA/MC(methylene chloride) + AN; a thin dotted line represents ARC(acetylated fullerol-A obtained with acetyl chloride)/MC; a thin broken line represents ARC/MC + AN. (b) solid line, BH(fullerol-B)/H_2O; dotted line, BH/H_2O + AN; a thin solid line, BRC(acetylated fullerol-B obtained with acetyl chloride)/MC; a thin dotted line, BRC/MC + AN.

reported a blue-shift in the emission of maximum wavelength (λ_{Em}) of fullerol-B with decreasing solvent polarity from H_2O to the mixture of H_2O and methanol [6]. Contrary to this effect, λ_{Em} of fullerol-A in Figure 2(a) was slightly red-shifted with decreasing solvent polarity and shows $\sim$30 nm red-shift with acetylation by acetic anhydride. A significant blue-shift of λ_{Em} was observed with acetylation of fullerol-B by having a shift from $\sim$505 to $\sim$450 nm (Figure 2(b)), similar to the previous report [6]. This above mentioned phenomenon of differences in the shift sides between fullerol-A and fullerol-B could be attributed to the number of hydroxyl groups and the bonding positions of hydroxyl groups on the fullerene. Fullerol A with less number of hydroxyl groups might have greater solubility with solvent molecules compared to fullerol B. Solubility of fullerol-A and fullerol-B was also changed by acetylation of fullerol. Acetylated fullerols were easily dissolved in THF, ethyl acetate or other solvents with low polarity.

Polyacrylamide Gel Electrophoresis Study of Fullerene Derivatives

As fullerols are the mixture of fullerols with the different amount of hydroxyl groups, the emission spectra obtained from them were showed a broad nature. Therefore the separation of fullerols and their esters were attempted with the help of PAGE. Absorption and emission spectra of the samples at every 5 mm of the length migrated on the each gel lane were determined. Polyacrylamide-gels shows strong scattering with excitation light at 365 nm with the mercury lamp fitted a U-360 filter, and the resulted luminescence of the gel was shown in Figure 3(a). Absorbance at 300 nm of the sample for each 5 mm of the migration length on each lane was depicted in Figure 3(b).

From Figure 3(b) (Abs/migration length), fullerol-A appeared to be distributed from $0 \sim 2$ cm, and fullerol-B to $1 \sim 2.5$ cm, respectively. The difference of the migration length caused may be due to the difference of ionic charge number of both fullerols. Acetylated fullerol-A's were observed in the range of $0 \sim 0.5$ cm (acetic anhydride method) or $0 \sim 1.5$ cm (acetyl chloride method), shorter than that of the original fullerol-A. On the other hand, the migration length of acetylated fullerol-B was similar to fullerol-B. The reason for this may be due the large amount of hydroxyl groups on the surface of fullerol-B. The ionization tendency of acetylated fullerol-B might be similar to that of fullerol-B. Absorbance of the gel was the highest at 1 cm migration length and the λ_{Em} was $\sim$545 nm. The absorption maximum was moved to 0 cm with acetylation and λ_{Em} were determined to be around $550 \sim 580$ nm.

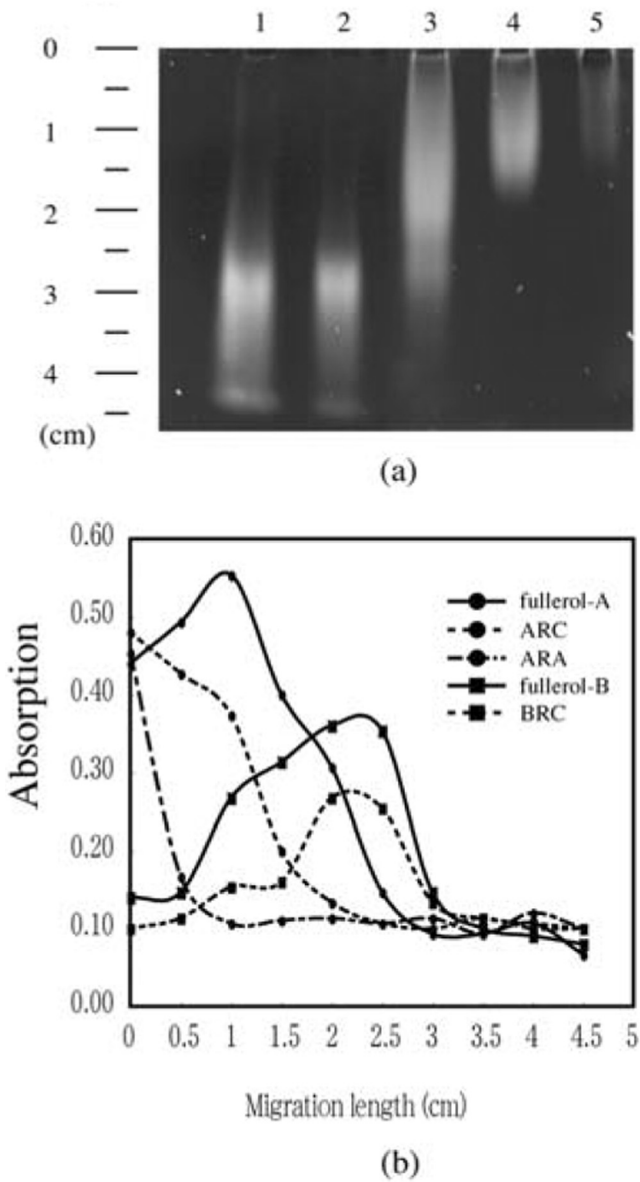

FIGURE 3 Photograph of polyacrylamide gel by electrophoresis shows the distribution of fullerene derivatives in the gel. (a) lane 1, BRC; lane 2, fullerol-B; lane 3, Fullerol-A; lane 4, ARC; lane 5, ARA. Twentyfive micrograms of each sample were loaded per lane. Electrophoresis condition; 100 V; 30 min.; 12%-gel; Tris-Borate buffer solution. (b) This graph shows the absorption intensity of fullerene derivatives, migrated at each region on the gel, for UV at 300 nm (Plot: fullerol-A (–●–), ARC (. . .●. . .), ARA (–●–), fullerol-B (–■–), BRC(. . .■. . .)).

CONCLUSION

Chemical modification of fullerol-A and fullerol-B by using acetic chloride or acetic anhydride gave the three different kinds of acetylated product. The reaction of fullerol-B with acetic anhydride yielded no product because of the steric hindrance of fulerol-B. In the emission analysis, λ_{Em} of fullerol-A was slightly red-shifted with decreasing solvent polarity and $\sim$30 nm red-shifted with acetylation. In the case of acetylated fullerol-B, a significant blue-shift of λ_{Em} from $\sim$505 to $\sim$450 nm was observed. The result obtained by PAGE analysis for fullerene derivatives showed that the migration length for fullerol-A was different from that for acetylated fullerol-A. However migration length of acetylated fullerol-B was similar to fullerol-B. The reason for this may be due the large amount of hydroxyl groups on the surface of fullerol-B. The result obtained from these initial studies regarding the florescent experiments of the fullerene derivatives gives a very good sign for the possibility to use these fullerene derivatives as biomarkers. Our work is progressing very well in this direction.

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