

論文内容の要旨

論文題目 : Solution and Electron Microscopic Studies of Chemically-Modified Carbon Nanoclusters

(化学修飾された炭素ナノクラスターの
溶液中および電子顕微鏡下における研究)

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1. Introduction

Studies of carbon clusters and their self-organization have been attracted much attention in these decades due to their potential application in the field of material and biological science. From the view point of synthetic chemistry, fullerene and carbon nanotube are widely studied because of the reactive π electron rich surface, which can be easily modified by chemical reactions. Chemical modification of carbon clusters bestows them functionality for application use. The modification can be observed by electron microscopic analyses even for single molecular level, which is due to the high stability of carbon cluster under electron beam. In this work, I will report the preparation, characterization and properties of chemically modified fullerene vesicles, which are assembly of anionic fullerene amphiphiles. The chemically modified vesicles display highly hydrophobic environment even in water to serve as a nanoscopic scaffold for non covalently anchoring organic molecules.

2. Preparation, Characterization and Properties of Fullerene Vesicles with Fluorous Surface

Potassium salt of highly fluorinated fullerene **1** was synthesized via pentaaddition reaction of C_{60} . The fullerene **1** features a nonpolar/polar/nonpolar ternary motif, which is far different from the widely accepted amphiphilic molecules, featured as a polar head/nonpolar tail for constructing of assembled structure in water. The unique amphiphilic fullerene **1** was found to dissolve in water to form vesicles with an average diameter of 36 nm determined by dynamic light scattering (DLS) measurement.

The membrane structure of fullerene vesicle was confirmed by DLS and static light scattering (SLS) measurement. The SLS measurement shows the vesicle has a hollow spherical shape with interdigitated monolayer membrane structure with its nonpolar fluoruous chains facing to the aqueous environment (Figure 1a). Unlike lipid vesicles that easily loose their structural integrity when removed from aqueous solution, the vesicle of **1** is very robust and retains the spherical shape even on a solid substrate under high vacuum (Figure 1b).

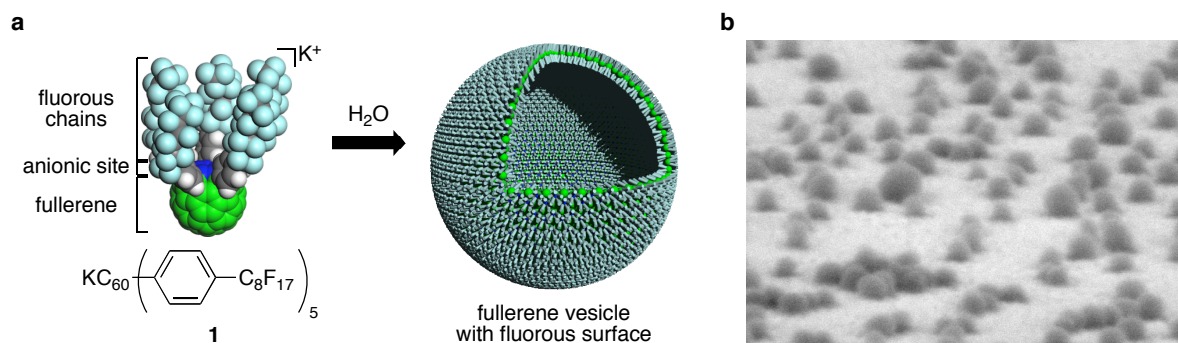


Figure 1. (a) Schematic illustration of the vesicle from fluoruous fullerene amphiphile **1** and (b) SEM image of the vesicles on an ITO surface.

SLS study of the vesicle of **1** showed the vesicle has a room on its fluoruous surface, which can be utilized for molecular accommodation. The vesicle solution was found to dissolve C₈F₁₈, which is completely insoluble in water. The solubilization of C₈F₁₈ in aqueous solution of fluoruous vesicle of **1** was studied by ¹⁹F NMR (Figure 2). One broad peak at δ -86.2 ppm due to the terminal CF₃ group (signal i, Figure 2a) was observed for the mixture of C₈F₁₈ in fluoruous vesicle solution. At 80 °C, broad signals due to the three CF₂ groups appeared (signals ii, iii, iv, Figure 2b). From the integrated area of the CF₃ signal, the concentration of C₈F₁₈ in the vesicle solution to be approximately 1.9 g/L (i.e., 3.2 molecules of C₈F₁₈ per molecule of **1**) and the solubility is 1,000,000 times larger than that in water.

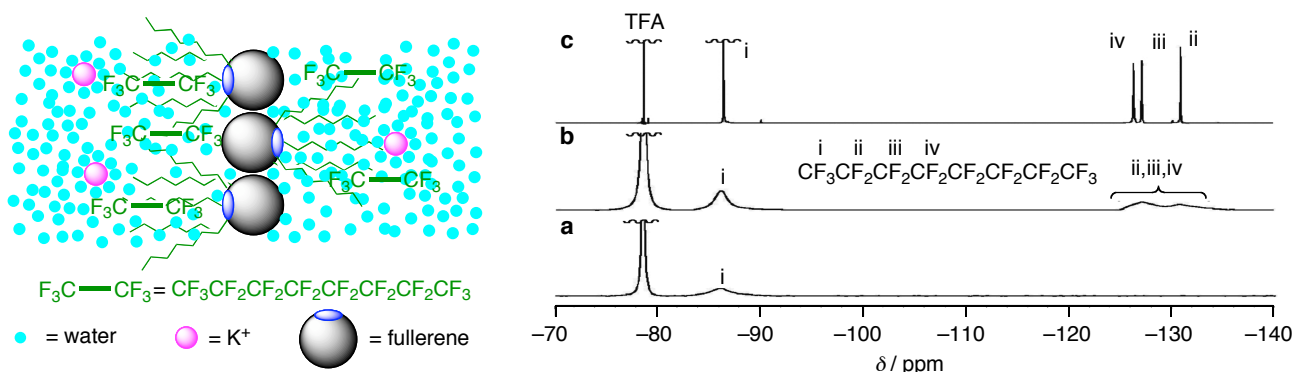


Figure 2. Solubilization of C₈F₁₈ on the surface of vesicle of **1** in water. ¹⁹F NMR chart of (a) C₈F₁₈ in a D₂O solution of vesicle of **1** at 25 °C, (b) at 80 °C, (c) neat C₈F₁₈ at 25 °C.

3. Effect of Surface Modification of Vesicle on the Membrane Property and Vesicle-covered Substrate

Formation of fluoruous vesicle of **1** shows the high stability of fullerene vesicle, even after chemical modification and open the way for further study of the substituent effect on vesicle. Fullerene amphiphiles bearing different linear substituents at *para* positions of phenyl groups (**2–6**) were designed and synthesized to study the effect of (i) chain length and (ii) polarity on structure and property of the vesicles. Introduction of hydrophobic alkyl chains in different length (**2–5**) or hydrophilic diethylene

oxide chain (6) did not hamper the formation of fullerene vesicle. DLS measurements of the aqueous solution of vesicle of 2-6 showed the sizes of the vesicles were controlled in the range of 20–45 nm regardless of the side chain components, without any separatory methods (Figure 3).

Properties of surface-modified vesicles are highly affected by the substituents both on solid substrates and in solution. The effect of substituents on vesicle surface was observed in wettability of vesicle-coated substrates. Figure 4 shows water contact angle of vesicle-covered mica surface. Contact angle increases according to the length of alkyl substituents (2<3<4<5) or hydrophobicity of substituents with the similar chain length (6<3<1).

This result shows the bulk property of a substrate can be controlled by modification of fullerene molecules. In solution, water permeability through fullerene membrane was measured by ^{17}O NMR method. The permeability of fullerene membranes 2-5 (Figure 5a), which have alkyl chains on its surface in different length, showed the water permeation through the membrane was suppressed by long alkyl chains, especially the membrane made of fullerene 5 was found to be the least water-permeable membrane. As for the comparison between vesicle 1, 3 and 6, which have similar chain length in different polarity, water permeability decrease as the polarity of side chain decrease. Thermodynamic study of water permeability showed the substituents on vesicle affect the packing structure of fullerene moiety in the membrane. These tendency of water permeability of fullerene vesicle is well corresponding with the tendency of water contact angle of vesicle coated surface (Figure 4). The surface modification of fullerene vesicle affects both the repellency of bulk water and permeation of water molecules.

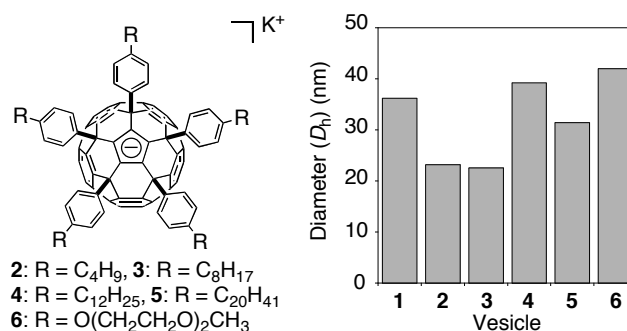


Figure 3. Diameters of fullerene vesicles of 1–6 in water measured by DLS.

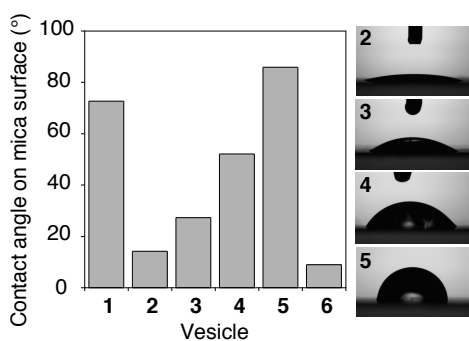


Figure 4. Contact angle of water on vesicle-covered mica surface.

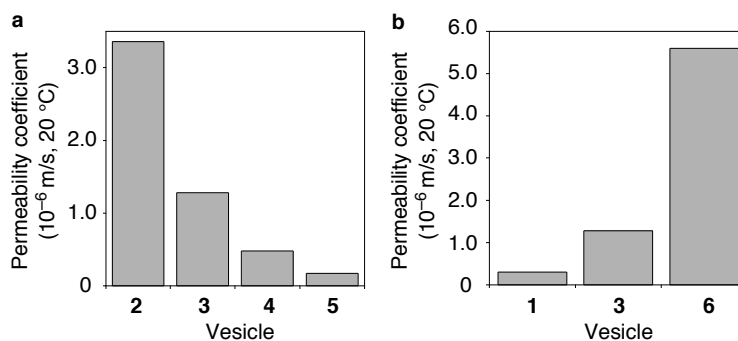


Figure 5. Permeability coefficients of water through (a) fullerene membrane 2–5 and (d) fullerene membrane 1, 3, 6 measured at 20 °C.

4. Highly Watertight Fullerene Vesicles on Solid Surfaces

The fullerene vesicle shows water-tightness also on a solid substrate. Fullerene vesicle of 1 showed strong contrast inside under scanning transmission electron microscopy (STEM) measurement and the contrast did not change after 10 minutes of electron irradiation (Figure 6a). This strong contrast indicates water is encapsulated in the vesicle, which forms via noncovalent interaction, under 10^{-5} Pa.

Interestingly, decrease of inner contrast of the vesicle was observed by the addition of 1% C_8F_{18} (Figure 6b). After 2 minutes of exposure to electron beam, only the shell structure of the vesicle was observed. These results indicate the addition of fluorine molecule loosens the membrane structure to release the inner water. Fullerene vesicle of **1** was found to keep water inside under high vacuum and the water can be released by the addition of fluorine molecules.

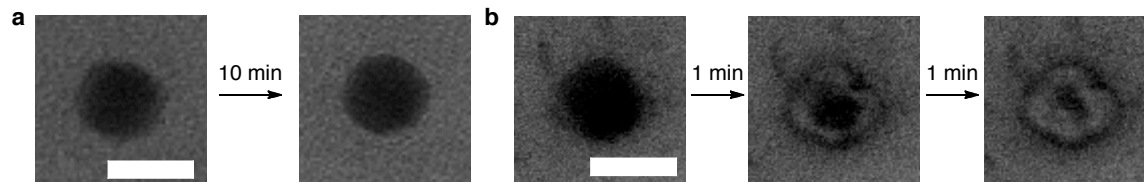
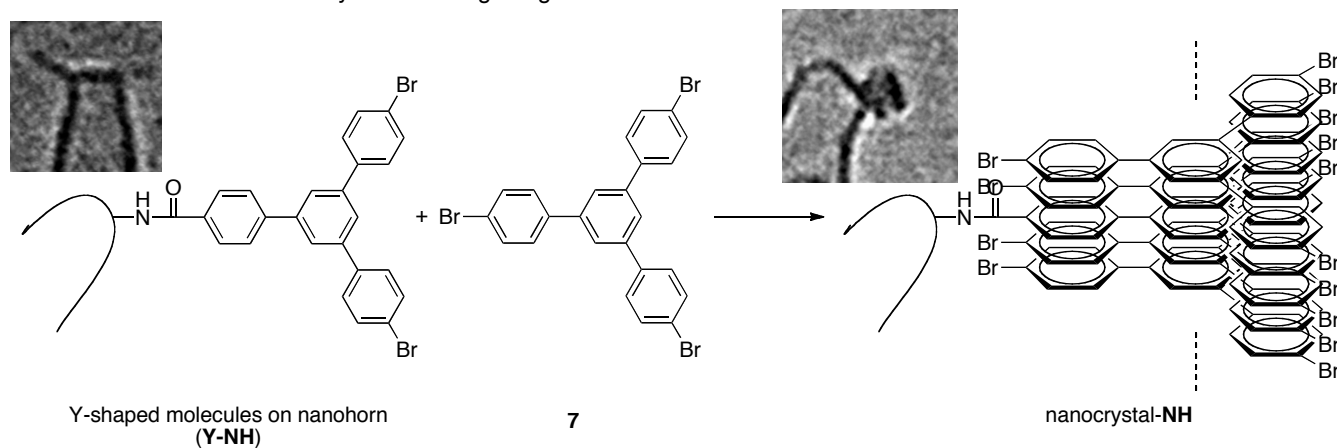


Figure 6. STEM images of (a) vesicle of **1** and (b) vesicle of **1** containing 1% of C_8F_{18} . Inner content was rapidly lost under electron irradiation for sample b. Scale bars represent 50 nm.

5. Transmission Electron Microscopic Study of Crystal Growth on Single Organic Molecule

Transmission electron microscopic (TEM) study of Y-shaped molecule attached on nanohorn (Y-NH) made it possible to visualize two fundamental properties of organic molecules (Scheme 1). One is the C-C bond rotation. From the TEM image of Y-NH, I estimate the rotation speed is 4.8 rpm, and the speed did not change by cooling the sample to 4 K. Another interesting image was obtained by the addition of tribromide **7** to Y-NH. Nanometer-sized crystalline objects were observed on NH. The TEM image of the nanocrystal was reproducible by the simulation image of tribromide molecules stacking on Y-shaped molecule on NH.

Scheme 1. Formation of nanocrystal on a single organic molecule on nanohorn.



6. Conclusion

Water-soluble self-assembly with hydrophobic surface was prepared and the characteristic properties were studied. The properties of fullerene vesicles were changed according to the bulkiness or hydrophobicity of substituents, which were observed in contact angle of water and water permeation. Vesicle of **1** shows fluorine environment in water to accommodate fluorine molecules on surface and the membrane property was also changed to release the inner contents under STEM condition. TEM can be also utilized for the study of single organic molecule and crystal growth. From the TEM studies, the speed of C-C bond rotation and initial state of crystal growth were visualized for the first time.