

Abstract

Title: The Synthesis and Supramolecular Assemblies of Fullerene Amphiphiles

[両親媒性フラーレンの合成と超分子集合体]

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Amphiphilic fullerene derivatives, which have a carbonaceous structure as a hydrophobic part of the molecule, have shown a wide range of physical and chemical properties that make them attractive for the preparation of supramolecular assemblies and new materials. Thus, methods for preparation of assembled materials as well as methods of synthesis of amphiphilic fullerenes are currently drawing much scientific interest. In this thesis, I report that fullerene vesicles can be transformed into a two-dimensional material. Besides, I have developed a new method for the synthesis of hydrophosphorylated fullerenes by mixing [60]fullerene (C_{60}) in a mixed solvent. These hydrophosphorylated fullerenes become fullerene amphiphiles after basification. The contents of each chapter of this thesis are summarized below.

In chapter 1, the background of fullerene amphiphiles is described. Fullerene amphiphiles have a carbonaceous structure as a hydrophobic part and functional group(s) as a hydrophilic part of the molecule. The approaches of fullerene amphiphiles are on introduction of hydrophilic function(s) by chemical modification of C_{60} through two main pathways: nucleophilic additions, and

cycloadditions. When fullerene amphiphiles dissolve into water, they form supramolecular aggregates. The formations of supramolecular assemblies include rods, tubes, vesicles, and films.

Chapter 2 describes that the fullerene bilayer vesicle can be transformed to thin film under appropriate conditions. Our group discovered that an amphiphilic fullerene, fullerene cyclopentadienide (Fig. 1), spontaneously forms a spherical bilayer vesicle when the molecules are dissolved in water. The vesicle has a bilayer membrane where the molecules are stacked in a head-to-head fashion, and is expected to be an ideal precursor for assembled materials of other morphologies. Fullerene thin films are obtained by freezing this fullerene vesicle solution. Transmission Electron Microscopy (TEM) image reveals flat plane supramolecular structures

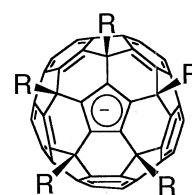


Fig. 1

(Fig. 2), which size ranges from several hundred to over one thousand nanometer. Structural studies on the thin film by TEM show that the thin film is composed of the crystalline membrane of amphiphilic fullerene. The packing parameters of thin films suggest hexagonal packing with AB stacking of the layers.

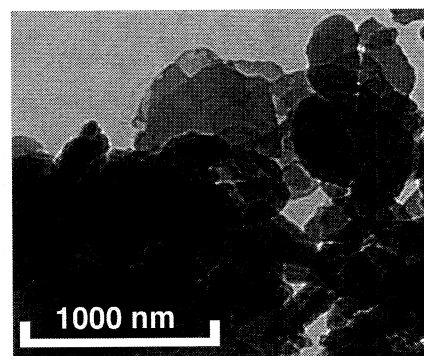
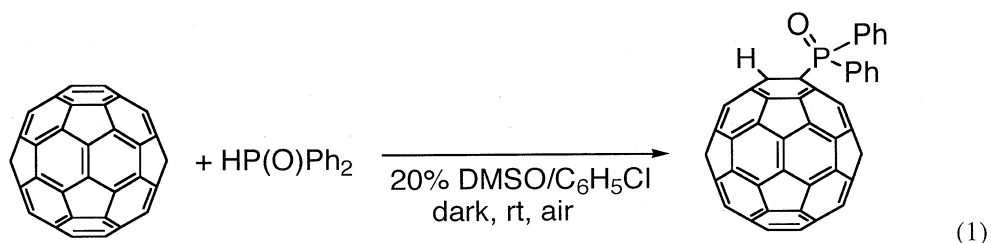


Figure 2. TEM images of fullerene thin films

The morphological change of vesicle was related to the concentration of THF. The Dynamic Light Scattering (DLS) analysis of a size change of vesicle in the volume of 30% THF showed that the size of the particles increase gradually for the first one hour; after two hours of mixing, the distribution of the particles became bimodal, and the size of the larger particles precipitously were over 800 nm at this time; the distribution of the larger particles finally increased to 1200 nm. The change in the particle size accompanied the change in the morphology. Atomic Force Microscope (AFM) images showed that the particles retained the spherical form for the first one hour; however, the particles I observed after eight hours were mainly thin films. Both DLS studies and AFM images on the thin film formation were concluded a plausible mechanism: upon increasing the amount of THF, the molecule intercalates in the fullerene membrane; by

absorbing the small molecule, the fullerene membrane gains the fluidity and vesicles start to fuse to grow in size, and start to collapse to give the thin film finally. The particle shape analysis indicated that the thin films was formed in solution, and supported by themselves.

In chapter 3, the synthesis of hydrophosphorylated fullerene in neutral conditions is shown. The amphiphilic fullerene bearing phosphorous groups has great potential in bioactive system. However, the methodology of fullerene phosphorous compound is quite rare. Recently, our group reported oxoamination reaction of C_{60} which promote by dimethylsulfoxide (DMSO). Following this lead, we gain a simple access to phosphorous fullerene derivatives. The synthesis of hydrophosphorylated C_{60} achieved just by mixing equimolar of C_{60} and secondary phosphine oxide in 20% DMSO/clorobenzene (C_6H_5Cl) without extraneous reagents in moderate to good yield (Eq 1). It undergoes a 1,2-addition addition to give fullerene-substituted phosphine oxide. The procedure is very simple and the synthesis can be carried out on a gram scale. The phosphorous oxides include dialkyl, alkylaryl, and diaryl phosphine oxides bearing alkoxy-, bulky alkyl- and fluorosubstituents. The use of excess phosphorous reagent or longer reaction time does not improve the yield because of the formation of multiadducts. We also obtained fullerene-substituted phosphine by mixing a Ph_2PH and C_{60} in 20% DMSO/ C_6H_5Cl . This product, however, is exceedingly sensitive to oxidation in air owing to the photoactivity of the fullerene moiety, and isolated as the corresponding phosphine oxide



Not only DMSO promotes the hydrophosphorylation of fullerene, but also hexamethylphosphoramide (HMPA) and *N,N*-dimethylformamide (DMF) accelerates the reaction. No reaction takes place in the absence of DMSO and 100% of C_{60} is recovered. The role of C_6H_5Cl is just

to dissolve C_{60} . The reaction rate is in an order of $DMF < DMSO < HMPA$, which follows that of the donor number of each solvent. This order is similarly to the oxoamination and reduction of C_{60} . The key role of DMSO suggests that the reaction takes place through a charge transfer or an electron transfer complex by interaction between phosphine and C_{60} . The complex then undergoes C-P bond formation to generate a diradical intermediate. Rapid isomerization of the diradical intermediate to finally produces the product. In phosphine oxide case, tautomerization should be considered. The reaction takes place via a hydroxyl phosphine form rather than the phosphine oxide form.

Accordingly, hydrophosphorylation of fullerene is run under neutral conditions, the tolerance of functional groups is high, and a variety of phosphorous fullerene could be synthesized. Phosphinate and phosphonate are less reactive and does not undergo the hydrophosphorylation reaction under room temperature as the one used for phosphine oxide. However, both phosphinate and phosphonate reacted with C_{60} at higher temperature in presence of excess amount of phosphorous nucleophiles.

The hydrophosphorylated fullerenes are precursors of fullerene amphiphiles. Basification of hydrophosphorylate fullerene can generate the corresponding phosphorylated fullerene anion (Fig. 3). Dilution of the THF solution of with water forms a stable homogeneous solution. This aqueous solution has the characteristic UV/VIS/NIR spectra with a broad peak in the visible region, which was attributed to aggregation of fullerene in water.

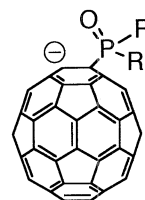


Fig. 3

In chapter 4, I summarized the all results including the transformation of fullerene vesicles into thin films and synthesis of fullerene amphiphiles bearing phosphorous moiety. I also have an outlook for the application of fullerene amphiphiles in materials and bioactivity.