論文 / 著書情報
Article / Book Information

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Title(English)	Construction and Unique Host Capability of Polyaromatic Micelles with Anthracene Rings
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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Water mediates various phenomena in nature. A huge number of natural products are soluble in water and wide-ranging chemical reactions are carried out under mild aqueous conditions. Interestingly, hydrophobic biomolecules are also dissolved in water upon encapsulation by aqueous protein assemblies with hydrophobic cavities. In contrast, most of synthetic compounds are insoluble in water and thus synthetic processes are usually performed in organic solvents. Inspired by the biological host-guest system, various water-soluble artificial hosts are developed and a great number of aqueous host-guest composites are reported. However, the development of new aqueous hosts capable of encapsulating a variety of functional organic compounds as well as more convenient and practical solubilizing methods are required from the viewpoint of material science through aqueous media.

Through this thesis I report the construction novel polyaromatic micelles for the purpose of dissolving various aromatic molecules in water and exploring the photophysical properties of the resultant host-guest composites. As new amphiphilic molecules for the preparation of the polyaromatic micelles, I designed V-shaped amphiphiles composed of two anthracene panels connected by a benzene ring at *meta*-position to make a bent polyaromatic framework. In addition, two hydrophilic groups were attached to the convex side of the benzene ring. Spontaneous and quantitative formation of the polyaromatic micelles occurred by assembly of the V-shaped amphiphiles in aqueous solutions via hydrophobic effects and aromatic-aromatic interactions. The size and shape of the product was revealed by AFM and DLS analyses. The polyaromatic micelle provides a spherical shell with an average diameter of about 2 nm with narrow distributions. The polyaromatic micelle is a dense molecular cluster of anthracene fluorophores and exhibited unusual fluorescence behavior. Upon irradiation at the anthracene panels, a methanol solution of the amphiphile showed typical blue anthracene-like fluorescence. On the other hand, an aqueous solution of the polyaromatic micelle showed unusual pale green fluorescence. This fluorescence also indicates the presence of aromatic-aromatic interactions between the anthracenes. The miceller structures provided flexible polyaromatic frameworks and thereby could encapsulate various size and shape of aromatic guest molecules in water. The polyaromatic micelle accommodated fluorescent dyes and the resultant host-guest nano-composites exhibited strong fluorescence from the encapsulated guest through efficient energy transfer from the host shells to the guests.

The shell-functionalization of the polyaromatic micelles was accomplished by attaching various functional groups to the anthracene panels of the V-shaped amphiphile and the subsequent quantitative self-assembly in aqueous solutions. As functional groups, I chose small electron-withdrawing groups and linear π-conjugating groups and then synthesized new amphiphilic subunits. The shape and size of the functionalized polyaromatic

micelles remain similar to the original, but the fluorescence intensities increase significantly by attaching π-conjugating groups. Furthermore, the shell-functionalization drastically enhanced the host-guest photophysical properties in the cavities of the polyaromatic micelles, as estimated by fluorescence intensities from the encapsulated fluorescent dyes.

The structural flexibility and large polyaromatic panels of the bent molecular framework enable the polyaromatic micelles to successfully encapsulate a variety of nanocarbons such as spherical fullerenes, planar nanographenes, and cylindrical carbon nanotubes, in water through simple grinding (and sonicating) protocols. The polyaromatic surfaces of the bent amphiphiles effectively surround polyaromatic surfaces of the nanocarbons through multiple aromatic-aromatic interactions, rendering the resultant nanocarbon composites readily soluble in water at room temperature. Aqueous composites of photo reactive nanocarbons exhibited enhanced stability toward light irradiation due to the shielding effect of the polyaromatic frameworks of the polyaromatic frameworks. Furthermore, the simple casting and washing protocols of the aqueous nanocarbon composites gave rise to pure nanocarbon films on glass plates.

The V-shaped amphiphilic molecule also acted as a solubilizing reagent for metallo-phthalocyanine and its derivatives in water through a simple grinding protocol. The obtained aqueous nanocomposites were composed of the core of the metallo-phthalocyanines and the shell of the V-shaped amphiphiles. The nanocomposites were stable enough in aqueous solutions for more than one week at room temperature. In addition, large planar metallo-phthalocyanine polymers could be dissolved in water by the same way. Casting the aqueous solutions of the nanocomposites on glass plates followed by a washing protocol gave rise to thin metallo-phthalocyanine films.

Through above works, I have developed a new class of micelle-like molecular capsules possessing expandable polyaromatic frameworks. I realized that the water-soluble capsules are able to encapsulate various size and shape of aromatic compounds such as linear and planar dyes as well as spherical, planar, and tubular nanocarbons. These results would contribute to the design of a new type of dye, sensor, probe, and photosensitizer and the development a new process for producing organic materials compatible with green chemistry.