

Design for self-assembled functional dendritic materials

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ABSTRACT

Dendrimers are regularly branched macromolecules with well-predictable three dimensional architectures. The present paper reviews several examples of supramolecular systems in dendrimer chemistry, such as hydrogen-bonding or metal coordination-bonding mediated self-assembly, liquid crystalline dendrimers, and host-guest chemistry in dendrimers.

Key words : dendrimer, self-assembly, functional materials, supramolecules

Introduction

Manipulation of nanometer scale structure have been highly focused on the materials science because nanostructures are playing a dominant role in bring together the fields of biology, chemistry, and physics. In biological systems, nanostructure is the smallest unit of living systems. Proteins, viruses, bacteria, and the other organelles are nanometer scale structure, which are mostly composed of hierarchical self-assembly from smaller units (1). In artificial systems, there are two different ways to approach nanometer scale region. One is the way to break into parts from more large structure, top down strategy, and the other is the way to build up from molecular level using self-assembly, bottom up strategy (2, 3). Either of them are not so easy to perfectly control nano-scale structure construction or manipulation using common materials. Therefore, dendrimers are recently attracting increasing attention, because the dendrimer is a unimolecular nanometric object and have many fascinating properties.

The concept of dendrimer has been proposed by Tomalia in 1985, where the name is originated from its structural shape, comes from 'dendron', means tree in Greek word (4).

Peculiar properties of general dendrimers are described as follows:

1. The synthetic ways of dendrimers are quite different from polymerization of general linear type polymers. Dendrimers are synthesized by repetitions of highly controlled stepwise reaction, including purification steps (5). Therefore, the dendrimers basically have no molecular weight distribution and the molecular weight and size are determined by the times of reaction repetition, as it is called generation.
2. Dendrimers briefly have three componential parts, such as focal core, peripheral functional groups, and branching units (building blocks). Various functional groups can be introduced to the each component in the synthetic step for the modification of completed dendrimers.
3. Dendrimers have densely packed surface and internal low-density cavity around the focal core, because the numbers of branching units are diversely increased from the focal core to periphery. Internal cavity around focal core of dendrimers provides wide application, such as a molecular inclusion, and has a significant potential to use as a site-specific pocket (6).
4. Solution properties of dendrimers are predominantly depending on the peripheral functionalities (7).
5. Because of the densely packed surface, dendrimers are

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hard to entangle or interpenetrate. Thus, dendrimers display relatively lower solution viscosity than linear polymers, even though the two materials have same molecular weight.

Owing to the peculiar properties described above, many application fields have been proposed and various types of dendrimers have been developed (8). On the other hand, there have been many efforts to construct bio-functional materials enough to alternate bio-systems using polymeric systems. However, general linear type polymers are very hard to control their conformation, and difficult to introduce functional groups at designated sites. From this point of view, dendrimers might be promising materials due to the conformational regularity and easiness of modification. Many dendrimer having bio-related functions (9) was practically synthesized and evaluated its physical or chemical properties. In the present paper, I would like to review recent advances of self-assembled functional dendritic materials. It is very important process for the natural system that several subunits hierarchically self-assemble to form large structure mediated by hydrogen bonding, coordination, electrostatic, dipole-dipole interactions, and so on. Dendrimer is nanometer scale macromolecules with well predictable three-dimensional structure and potential building blocks for the construction of organized functional materials. In the biological sense of view, self-assembly of nano-scale dendrimer quite resembles those of biomolecules and is likely to be a powerful method to understand the assembling system

in bio-organism.

Hydrogen-Bonding Mediated Self-assembly

Among the interactions working on the self-assembly in natural systems, hydrogen bonding is one of the most versatile interactions and plays the important roles. For examples, protein folding, complementarity of DNA strands, molecular recognition process of enzymes or antibodies are mostly related to the interactions of hydrogen bonding. In the hydrogen bonding mediated assembly of dendrimers, one of the pioneering examples, reported by Zimmerman et al., the dendron containing two isophthalic acid units covalently attached to rigid aromatic spacer (**Fig 1**; 10). Non-dendritic isophthalic acid derivatives assemble in organic solvents to form either a series of linear aggregates or a cyclic hexamer by hydrogen bonding mediated dimerization of carboxylic acid, whereas the dendritic isophthalic acid derivatives exhibited molecular weight for only species of cyclic hexamer upon the size exclusion chromatography, light scattering, and vapor pressure measurement. Interestingly, it is found that large dendritic wedges can stabilize hexameric aggregates, indicating the influence of van der Waals interaction among the dendritic wedges.

Aida and coworkers have reported hydrogen-bonding-mediated physical gelation of peptide-cored poly(benzyl

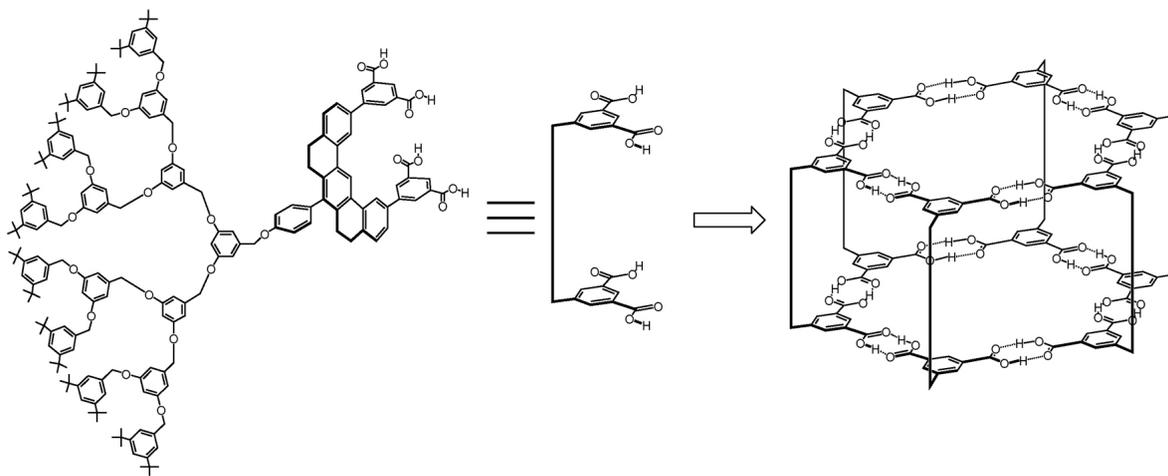


Fig 1.

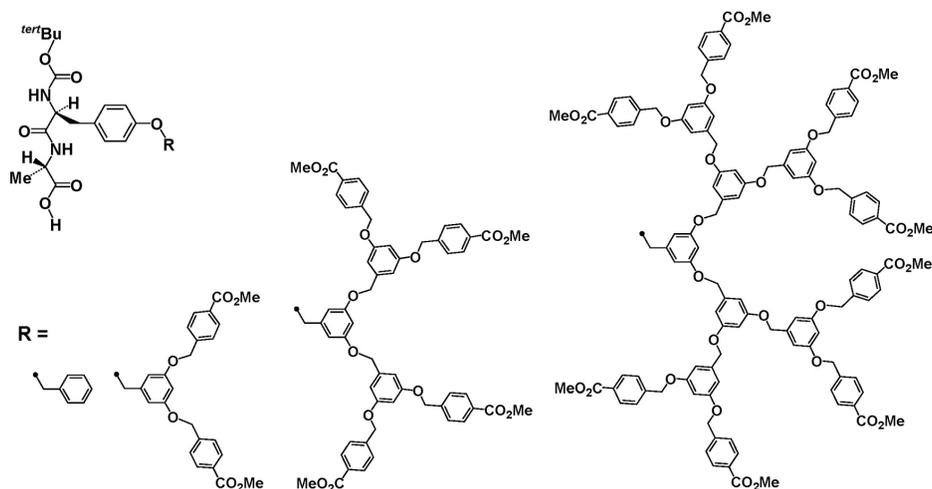


Fig 2.

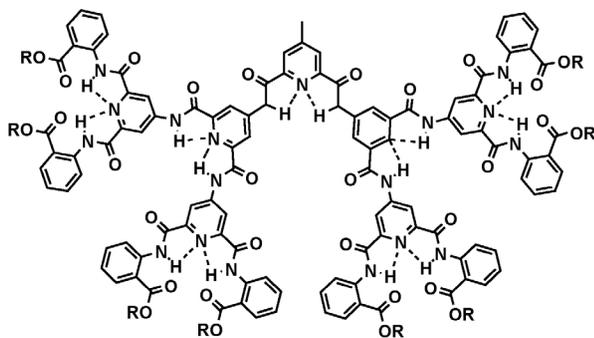


Fig 3.

ether) dendrons, which show significant gelation ability and gel stability in several organic solvents (Fig 2; 11). FE-SEM observation of dried gels reveals a hierarchical fibrous assembly formation. Notably, the gelation of the dendrimers is only observable with dendrimers bearing large dendritic wedge, indicating the participation of van der Waals interactions among the dendritic wedges into the fiber formation. Majoral et al. have reported an organophosphorus dendrimer that functions as an excellent gelator for water (12). Smith and coworkers have developed supramolecular dendritic two-component gels, based on polylysine dendrimers triggered by diamines (13). Kim and coworkers have found that certain polyamine dendrimers form physical gels in organic solvents, but vesicles in aqueous media (14).

On the other hand, intramolecular hydrogen bonding interactions have a potential to control three-dimensional struc-

ture of large dendrimer units. Parquette et al. reported poly (diamido pyridine) dendrimer, which has typically controlled molecular shape by the hydrogen bonding between the amide N-H and N atom of pyridine units (Fig 3; 15). This approach is not a self-assembly for meso-structure construction, but meaningful as a potential tool for molecular recognition or selective inclusion caused by the control of molecular shape.

Metal Coordination-Bondings for Self-assembly of Dendrimers

Metal coordination bonds have versatile properties, such as fluorescent or redox behavior due to the metal-ligand charge transfer, and provide various geometric modes in bonding formation. In biological systems, most active sites of enzymes have metal center, which undertaking highly controlled reactions for sustaining of life. Several kinds of supramolecular type dendrimers having metal coordination in their building blocks were widely researched and demonstrated on their redox or photochemical properties (16, 21). For an example, Reinhoudt et al. synthesized supramolecular type Pd coordinated dendrimers using controlled divergent way (Fig 4; 17). The monomeric building blocks for these Pd coordinated dendrimers have kinetically inert tridentate pincer type ligands and one labile coordinating cyano group. Coordination of

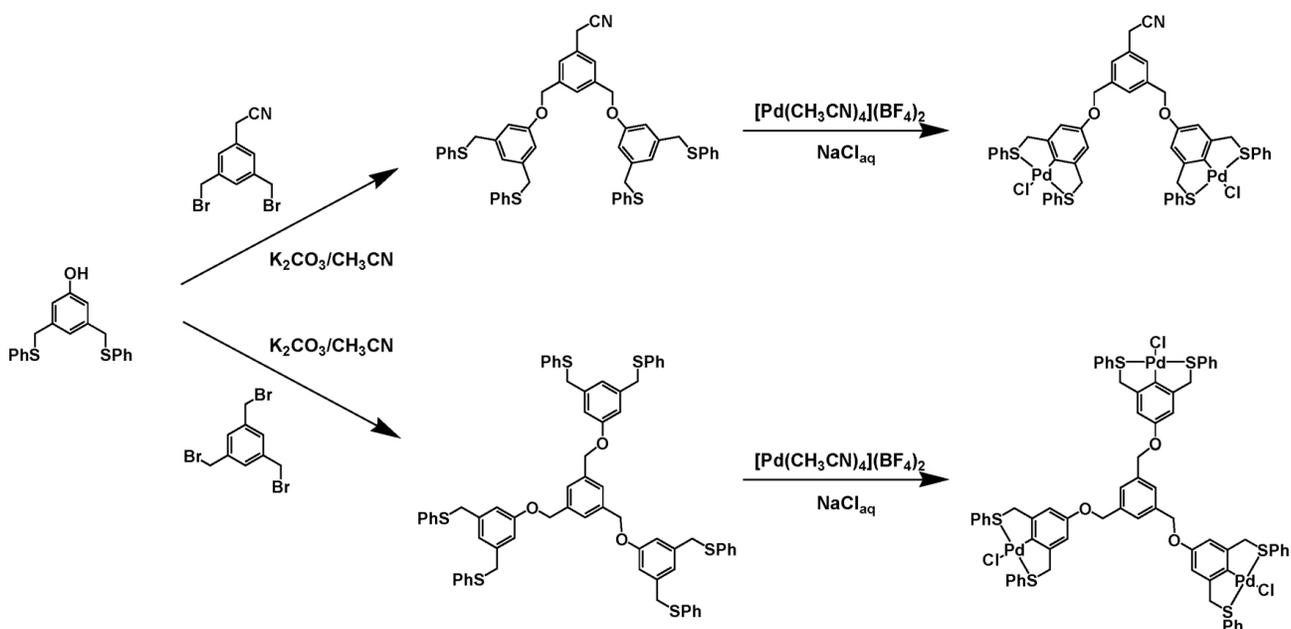


Fig 4.

metal center is temporary protected by a strong coordination of Cl-ion, which can be readily replaced to BF_4^- ion by addition of $AgBF_4$. Subsequent addition of the equivalents of the protected building block yields the next generation dendrimers. These dendrimers were well characterized by FT-IR and MALDI-TOF-MS spectroscopy.

Newkome et al. described the synthesis of dendritic lock and key complexes, which exhibited unique redox behavior (18). Cyclic voltammetry exhibited irreversible redox processes as the increasing of generation number. This irreversible redox behavior is possibly explained by the isolation effect of the redox center from the electrode or destabilization of redox products due to steric hindrance.

Due to the well-controlled three-dimensional shapes and sizes, dendrimers are potential building block for the construction of controlled thin mono or multi-layered films, which provide significant application fields, such as electron-transfer mediators, catalysts, sensors, electronic devices and so on. Abruña et al. synthesized terpyridyl-pendant dendrimers, which gives highly oriented monolayer films on highly oriented pyrolytic graphite surfaces by the interfacial coordination reaction of the dendrimer and bridging ligand 1,4-bis [4,4'-bis (1,1-dimethylethyl)-2,2': 6', 2''terpyridine-4'-yl] benzene with Fe^{2+} or Co^{2+} (19). This monolayer film was electro-

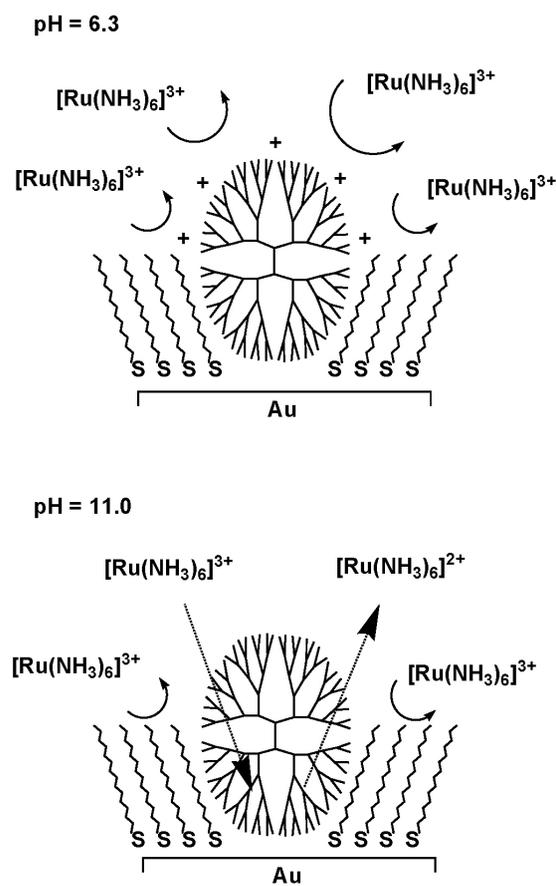


Fig 5.

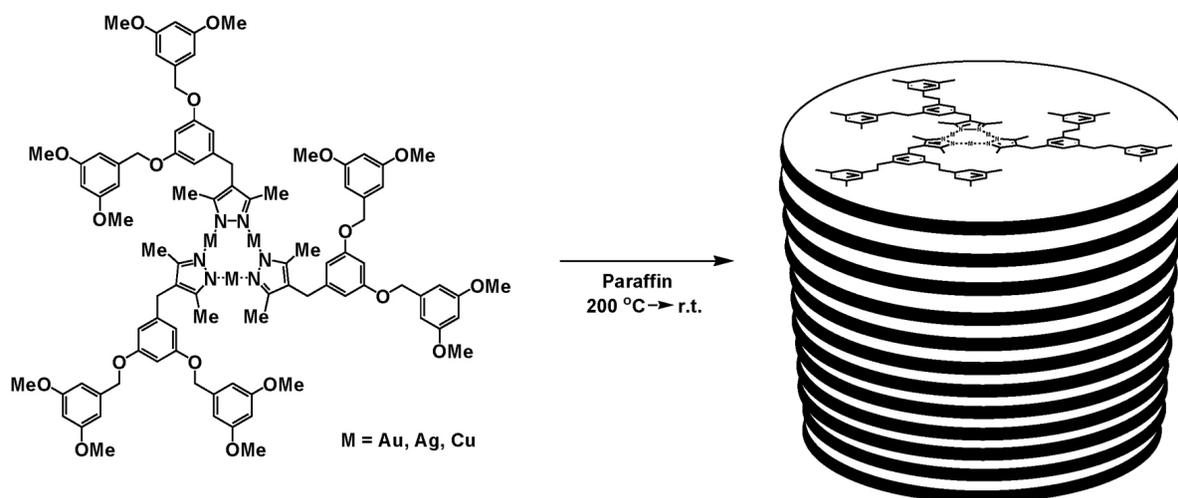


Fig 6.

chemically active and exhibited a reversible wave at a formal potential that corresponds to the respective metal complex.

Crooks et al. reported that the formation of monolayer film of poly(amido amine) on the gold surface using multiple amine/Au interaction (Fig 5; 20). Sequential exposure of hexadecylthiol to the monolayer film compressed the dendrimer structure by additional attachment of hexadecylthiol molecules on gold surface, where this compressed dendrimers played a role of controlled ion gate. At pH 6.3, only negatively charged $[\text{Fe}(\text{CN})_6]^{3-}$ can penetrate a monolayer film, whereas when the dendrimers are fully deprotonated at pH 11, either of $[\text{Fe}(\text{CN})_6]^{3-}$ or $[\text{Ru}(\text{NH}_3)_6]^{3+}$ can penetrate. Metal-metal interactions (21) are also used for the self-assembly of dendritic macromolecules. Recently, hierarchical self-organization of pyrazole anchored dendrimers were reported, where pyrazole is an exobidentate ligand of forming coordination metallacycles with Cu(I), Ag(I), and Au(I). By the coordination reaction with group 11 metal ions, the dendrimers were formed trimeric metallacycles, which further assembled to form fluorescent fibrous assembly due to the metal-metal interaction when a paraffin suspension of these complexes was once heated at 200°C and allowed to cool at room temperature (Fig 6). By replacing the peripheral methyl groups with long alkyl chains such as octadecyl groups, a low-generation dendritic trinuclear Au(I) pyrazolate complex forms a light-emitting organogel in hexane, where the photoluminescence color can be changed synchronously with

the sol-gel transition as a consequence of the reversible formation and disruption of the metallophilic interactions. At the same time, the authors have reported dichroic luminescence from first-generation dendritic trinuclear complexes of Cu(I), Ag(I), and Au(I). When cooled from their hot melts, these trinuclear complexes emit at two different wavelengths, depending on the cooling rate, due to the competition of kinetic and thermodynamic self-assembly events. This unique feature makes them suitable for use as photoluminescent ink for rewritable media for the next-generation security technology for information handling.

Liquid Crystalline Dendrimers

Liquid crystalline dendrimers are widely researched on their self-assembly behavior. Percec et al. synthesized disc or corn shape poly (benzyl ether) dendrimers with long chain alkyl in their periphery, which form rod or sphere type molecular assembly, where the assembly patterns of these dendrimers are significantly influenced on the structure of the parent dendrons (Fig 7; 22). They investigated the polymerization of these liquid crystalline dendrimers with vinyl functionality in their core (23). Of interest, the dendrimers form a random coil cored spherical oligomer in initial polymerization step, which is changed to rod type polymers with helical structure, such like a tobacco mosaic virus, ac-

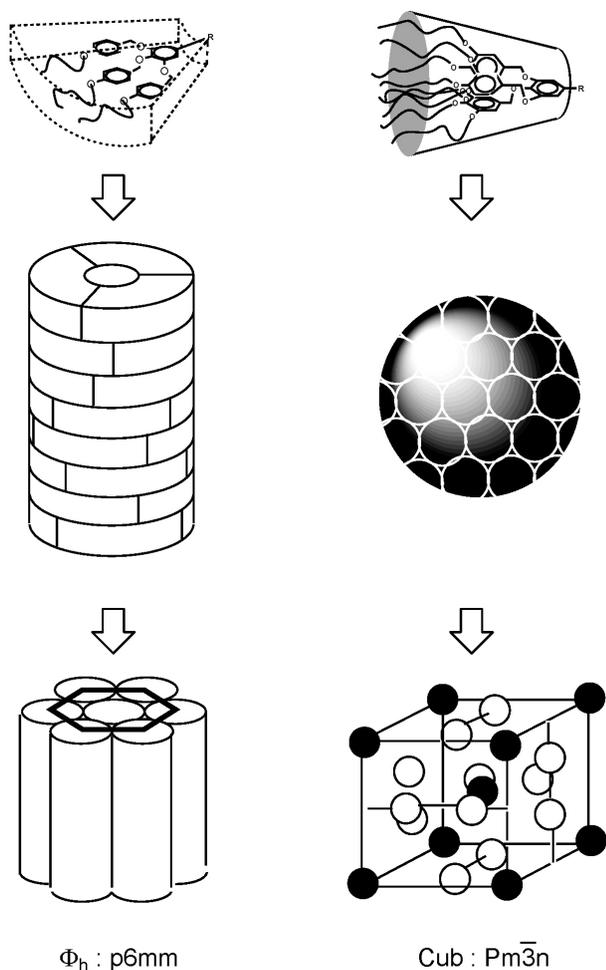


Fig 7.

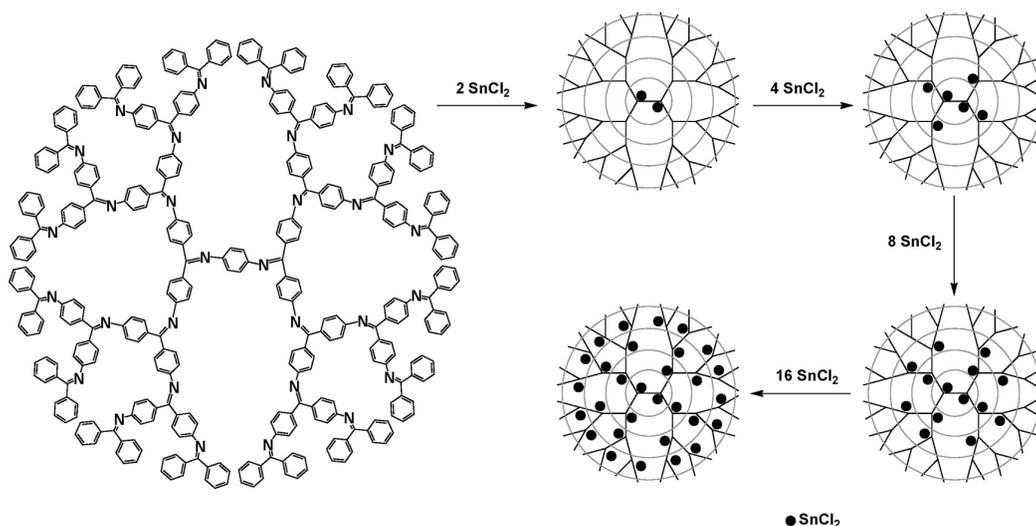


Fig 8.

ording to the increment of degree of polymerization.

On the other hand, several dendrimers with mesogenic surface were synthesized to investigate their self-assembly behaviors (24). For example, Frey et al. reported carbosilane dendrimers with 12, 36, and 108 mesogenic cholesteryl surface groups, first, second, and third generation, respectively (25). When the solution of these dendrimers was cast on the mica film, the dendrimers formed mono or multilayer structure depending on the concentration of the solution. Annealing at 80 - 90°C of the films of first and second generation in the liquid crystalline resulted in the reorientation of the molecules at the surface. Whereas, the third generation dendrimer with densely packed 108 cholesteric end groups behaved differently and did not show any reorientation upon annealing over 150°C. Considering very low glass transition temperature of carbosilane dendrimer, below -100°C, this dendrimeric monolayer film is likely to have drastically different two regions, very hard periphery and soft inner space.

Host-guest Chemistry in Dendrimer

Dendrimers can also accommodate guest molecules in their interior. Meijer et al. have reported a concept of 'dendritic box' with a flexible poly(propyleneimine) dendrimer modified with 64 *t*-Boc-*L*-phenylalanine end groups at its surface. When the

dendrimer is functionalized with *t*-Boc-*L*-phenylalanine, the release of guest molecule occurs extremely slowly due to a steric effect of the bulky *t*-Boc groups on the dendrimer surface. Tomalia have reported that polyamidoamine (PAMAM) dendrimers can host small organic acids due to electrostatic interactions. Fréchet and coworkers have shown that a water-soluble dendrimer can solubilize pyrene in water.

Yamamoto and coworkers have synthesized a series of polyphenylazomethine dendrimers and reported an interesting observation that these dendrimers can complex with metal ions such as Sn²⁺ and Fe³⁺ in a stepwise radial fashion from the core to the periphery (Fig 8; 26). The groups of Crooks and Tomalia have reported that dendrimer-encapsulated metal nanoparticles can be prepared by sequestering metal ions within dendrimers such as polypropyleneimine (PPI) and PAMAM, followed by chemical reduction, where the dimensions and solubilities of the resulting nanoparticles are controlled by those of the dendrimer templates. Such dendrimer-encapsulated metal nanoparticles can be used as catalysts for various reactions (27).

Interlocked molecular assemblies, such as rotaxanes and catenanes, are members of another class of interesting discrete objects formed in solution. One notable example is the pseudorotaxane formation of cucurbituril, which shows high affinity to amino alkanes due to the hydrophobic inner cavity and hydrophilic surface functionality, and the diaminobutane-terminated PPI dendrimer, reported by Kim and coworkers (28).

Conclusion

Throughout the present paper I have briefly reviewed recent progress in self-assembled dendritic materials. As described above, various types of dendrimers have been used as a building block for self-assembled functional materials. The application field of dendrimers has wide spectrum because of their unique characteristics as well as their structure. In many cases, the molecular design of dendrimers is based on mimic of natural concept, as a consequence of the structural similarity of dendrimers to natural biomolecules. I expect that the inspiration from biosystem and continuous investigation will provide us more powerful and sophisticated functional dendritic mate-

rials in the near future.

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