EXAMINATION OF THE SOLUTION BEHAVIORS OF THE GIANT INORGANIC-ORGANIC AMPHIPHILIC HYBRIDS

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Presently, the self-assembly behaviors of traditional small surfactants and amphiphilic block copolymers are fairly well understood. In comparison, rather little is known about the self-assembly behaviors of the giant inorganic-organic amphiphilic hybrids in solution. It remains a wide open field to explore. Giant inorganic-organic amphiphilic hybrids, consisting of nanoscale inorganic clusters and organic functional groups, represent a novel class of functional hybrid materials. They have unique physical and chemical properties and potential applications in catalysis, electronic, optics, magnetic materials, medicine and biology. Therefore, as emerging building blocks, they have promising prospects in the advanced materials. In this PhD work, several representative giant inorganic-organic amphiphilic hybrids (triangular-shaped polyoxometalate (POM)-organic hybrids, POM-containing fluorosurfactants hybrids, POM-containing peptide hybrids POM-peptide hybrids and polyhedral oligometric silsesquioxane (POSS)-polystyrene (PS)) are chosen for studying their self-assembly behaviors in solution. Based on the knowledge of the physical chemistry, colloid and polymer science, we focus on the mechanism of the self-assembly process, and the morphology control of the superstructures through the internal and external conditions, such as the composition of the giant amphiphilies, molecular architectures, solvent nature, temperature, concentration, and extra added salts. It is found that the counterion-mediated interactions dominate the self-assembly of triangular-shaped hybrids in acetone/water mixed solutions, due to the highly dominant hydrophilic portions; the solvent-swelling effect, instead of the charge effect, dominates the whole self-assembly
process of the POM-containing fluorosurfactants; the analogy between small surfactants and giant amphiphiles hydroxyl groups functionalized POSS-PS allows a rough assessment of the possible morphologies of the superstructures, and the particular values of the molecular packing parameter can be translated via simple geometrical relations into specific shape of the equilibrium superstructures.

For the experiments, laser light scattering (LLS) technique is used to monitor the entire self-assembly processes. The morphology and size of the superstructures are determined by using dynamic light scattering (DLS) and static light scattering (SLS). Electron microscopy (TEM, SEM and AFM) is used to confirm the assembly structures and size. The stability of the assembly solution system is characterized by zeta potential
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CHAPTER I

INTRODUCTION

Traditional amphiphiles including small surfactants and linear block copolymers are able to self-assemble into varieties of hierarchical superstructures in selective solvents due to their chemically distinct hydrophobic and hydrophilic components. The self-assembly behaviors of these two traditional amphiphiles have been well studied due to their extensive applications. With the advancement of technology, traditional amphiphiles could not meet the higher requirements of the materials scientists. Recently, one unique type of giant amphiphilic molecules are designed and successfully synthesized. Such giant amphiphilic molecules consist of nanoscale hydrophilic particles as polar heads and organic groups. The pure hydrophilic nanoparticles can self-assemble into hollow spherical black berry superstructures due to counterion-mediated interactions, if they carry proper charge density. For the traditional amphiphilies small surfactants and block copolymer, the solventphobic interactions are the main driving forces for the self-assembly process. The solution behaviors of the above two types of building block have been studied very well. There are lacks of systematic and clear study about the solution behaviors of such giant amphiphilic molecules.

In Chapter II of this dissertation a broad overview to hydrophilic nanoclusters and giant amphiphilic hybrids will be presented. The unique solution behaviors of the hydrophilic nanoclusters and the traditional small surfactants are discussed, and the
driving forces will be discussed in detail to show how they contribute to the self-assembly process. The background will also give a detailed description on how to control the superstructure size.

In Chapter III all the experimental techniques that were used in the experiments provided in this dissertation will be discussed with a major focus on light scattering technique. Dynamic light scattering (DLS) and static light scattering (SLS) were mainly used to monitor the self-assembly process and study the morphologies of the superstructures. The information of the particles shape extracted from these techniques will also be discussed by comparing the hydrodynamic radius \( R_h \) and the radius of gyration \( R_g \). Meanwhile, the morphologies of the superstructures will also be characterized by the electron microscopy (TEM, SEM and AFM). The stability of the superstructures solution will also be characterized by zeta potential.

In Chapter IV, the solution behaviors of two triangular-shaped POM hybrids are discussed. It is found that the counterion mediated-interactions mainly contribute such giant amphiphilic compounds to self-assemble into large, hollow, spherical “blackberry” superstructures in mixed solvents MeCN/water, although such hybrids consist of three large polar POM head groups and a central relatively hydrophobic organic component within one molecule unit, and are expected to be amphiphilic in nature. The self-assembly process is similar to the self-assembly process of hydrophilic macroions, which is distinct from the solvophobic interactions dominating the self-assembly of dumb-bell shaped hybrids. The reason is that the hydrophilic portions are more dominant than in conventional amphiphilic compounds, making them similar to giant hydrophilic POM macroions.
In Chapter V, the self-assembly behaviors of two novel POM-containing fluorosurfactants are investigated. They can self-assemble into hollow, double-layer vesicle structures. It is found that the vesicle sizes demonstrate dynamic change over different solvent composition: the vesicle sizes increase with the increase of the organic solvent content. This trend is opposite to traditional surfactants’ behaviors in solution. The main reason could be the solvent-swelling of the fluoro-chains. The repulsion among the polar heads plays negligible roles during the self-assembly process.

In Chapter VI, a series of giant amphiphilic macromolecules (nDPOSS-PS$_{96}$, n=1,2,3,4) consisting of nanosize polyhedral oligometric silsesquioxane clusters functionalized by dihydroxy groups (DPOSS) as hydrophilic component and polystyrene (PS) as hydrophobic component, were studied in solution. In polar solvent, these giant amphiphiles are found to readily undergo microphase separation and self-assemble into various ordered morphologies, like micelles, cylindrical micelles, vesicles, and reverse micelles. Furthermore, the sensitivity of the resulting superstructures to molecular topology is observed. The particular values of the molecular packing parameter can be translated via simple geometrical relations into specific shape of the equilibrium superstructures.

In Chapter VII, the self-assembly of a series of POM-peptide hybrids are also discussed. Considering the complex compositions of the hybrids, multiple driving forces are involved in the self-assembly of the POM-peptide hybrids, including counterion-mediated interactions, hydrogen bonding, pi-pi interaction, hydrophobic interactions. In this dissertation, the studies of solution behaviours of several representative giant inorganic-organic hybrids show that the driving forces of the self-assembly process depend on the compositions of the giant amphiphiles. The morphologies of
the superstructures can be controlled by the solvent nature, the type of counter ions, the compositions of the amphiphilic hybrids.
CHAPTER II

BACKGROUND

2.1 Overview of Inorganic-Organic Hybrid Materials

In this dissertation, inorganic nanoscale clusters refer to shape and volume-persistent nano-objects with well-defined molecular structure, modifiable functionality, and specific symmetry.

2.1.1 Inorganic Nanoscale Clusters

Nanoscale inorganic clusters have their own advantageous to develop novel nano materials with relatively rigid three-dimensional molecular structures and fixed geometric shapes, and high catalysis efficiency due to large surface area, unique electronic and optical properties. However, because of their poor solubility in organic media and highly symmetric structure of these inorganic supramolecular clusters, which limits their application as nano-materials in real life. At this stage, typical nanoscale inorganic clusters include polyhedral oligomeric silsesquioxane (POSS), fullerene (C\textsubscript{60}), and polyoxometalate (POM), metal-ligand nanocage.

2.1.2 Inorganic-Organic Hybrids

It is desirable to combine well organized inorganic structures with organic molecules into one compound, forming new functionalized hybrids. Such novel strategy not only
affords to combine the properties of inorganic and organic compounds into one unit, but also show synergistic properties. Therefore, it is of great interest to develop advanced materials building using the inorganic-organic hybrid materials as building blocks. This is a new path in technology and provides state-of-the-art tools in the designing new advanced materials. However, this hybrid concept was not mentioned until the development of polymers and new materials. Currently, the study of inorganic-organic hybrid materials has drawn extensive attentions in different fields in recent years. Various POM, POSS, C_{60}, quantum dots, and other inorganic nanoparticles containing hybrid materials have been synthesized in the past decades via different approaches. The organic-inorganic hybrid materials can be classified into two large different families depending on the nature of the bonds between the organic and inorganic part. The first family corresponds to hybrid materials where weak or secondary bonds are presented between the organic and inorganic interface such as hydrogen bonds, electrostatic interactions and Van der Waals forces. The second family corresponds to hybrid materials where covalent or primary bonds are attached to the organic part with the inorganic molecule. Although it is relatively easy to synthesize the first class of hybrid materials through non-covalent bonding, they are not stable due to external changes such as temperature, ion strength and pH value et al. Therefore, the second family of hybrids with covalent interactions attracts more attention because they are chemically stable. In this dissertation, I will focus on the second family of hybrids with covalent interactions.

Because inorganic/organic hybrids are composed of two chemically distinct parts: hydrophobic and hydrophilic components, they belong to amphiphilic materials. These immiscible components can drive them to self-assemble into a wide variety of complex
structures with hierarchical structures and special functions. The self-assembly behaviors of the traditional amphiphilic materials including small surfactants\textsuperscript{11} and amphiphilic diblock copolymers, \textsuperscript{12} have been well studied and extensively reviewed in the literatures. However, there is no systematic study about the self-assembly behaviors of the giant amphiphilic hybrids.

2.2 Polyoxometalates (POM) Containing-Organic Hybrids

Recently, more studies have been focused on decoration and functionalization on the surface of POM nanoclusters with organic functional motifs to process them into inorganic-organic amphiphilic materials for more applications.

2.2.1 Polyoxometalates (POMs)

POMs represent a large group of structurally well-defined, giant macroanions assembled from multiple transition metal oxides, which are linked through shared oxygen atoms. Owing to the tunable valence and coordination geometry of the central metal ions, various POMs with different sizes, shapes and charges have been synthesized.\textsuperscript{13} Due to the structural diversity, electronic, optical and magnetic properties of POMs, they have been widely used for many different applications including: molecular magnetism, protein sequencing, solar cells, stimuli responsive materials, catalysis, medicine and storage devices. As a result of those applications and the advancement of modern techniques, more scientists from different fields are paying more attentions to these molecules.\textsuperscript{14} Therefore, the field of POMs has been rapidly expanding from isopolyoxometalates to heteropolyoxometalates, from early transition metal POMs (Mo, V, Cr, Fe, W, Mn, etc.) to late transition metal POMs (U, Nb, Au, Pd, etc.), and from pure inorganic molecular clusters to hybrid clusters. Figure 2.1 gives several representative examples of well-
characterized POM molecular clusters. Most of the POMs are negatively charged because of their oxo ligands. The surface charge density of POMs can be readily tuned by substituting the central transition metals, changing the oxidation state of the metal ions, or simply changing the solution pH. Because of the nanoscale of the POMs, when they have appropriate charge density, they can self-assemble into superstructures with black-berry structure. The detailed solution study of POMs type macro-anions had been studied by our group’s previous work.\textsuperscript{15}

![Figure 2.1 The structures of some typical large polyoxometalate molecular clusters.](image)

2.2.2 Polyoxometalates (POMs)-Containing Organic Hybrids

Although POMs have more potential applications, as typical inorganic compounds, they have their own drawbacks such as high crystalline energies (hard to be processed for material scientists), poor solubility in organic media and low recyclability in aqueous media (low catalysis efficiency), which seriously limit their applications.\textsuperscript{16} Such inorganic-organic molecular hybrids are expected to render amphiphilic properties to the POMs and consequently improve their applications by expanding their compatibility in organic media. Furthermore, these organic ligands not only can be applied to improve the compatibility
and processibility of POM materials in organic media while maintaining the functional properties of the POMs, but also adjust some important features of POMs, including electronic and luminescent properties. Exploring the amphiphilic nature of such hybrids and understanding their self-assembly behavior in solution would be important initial steps for scientists.

2.3 Polyhedral Oligometric Silsesquioxane (POSS) Containing-Organic Hybrids

The specific functionalities on a POSS molecule can impart unique thermal, mechanical, optical, rheological, solubility, and diffusivity properties to materials, thereby rendering them as potential candidates for a variety of applications such as photonic materials and catalysis. Recently, various synthesis protocols have been developed to modify POSS molecules and integrate them into various architectures such as POSS-containing hybrid polymers, with applications in electronics, light-emitting diodes (LEDs), catalysis, as well as super-hydrophobic and antimicrobial coatings.

2.3.1 Polyhedral Oligometric Silsesquioxane (POSS)

POSS are structurally well-defined, cage-shaped silica molecular clusters with nanometer size, which have many immense potential applications owing to their nontoxic, biocompatible, chemically inert, and mechanically stable features and the low dielectric constant of POSS materials makes them good thin-film insulators. Among of them, octa-silsesquioxane, as a typical POSS molecule, consist of silicon and oxygen atoms linked into a well-defined, cubic inorganic cage with silicon atoms at the corners and oxygen atoms interspersed along the edges with a roughly spherical shape and eight corner groups,
2.3.2 POSS Containing-Organic Hybrids

POSS nanoparticles, especially the octa-silsesquioxane, have attracted more attention recently due to the ease of which these particles can be incorporated into polymeric materials and the unique capability to reinforce polymers. The salient feature of this particular nanosize building blocks (0.87 nm maximum diameter) is the ability to functionalize the silicon corners with a variety of organic substituents, including block copolymers, olefins and epoxides, mesogenic groups, and biological molecules such as peptides and carbohydrates. (See Figure 2.2) Meanwhile, in the context of the self-assembly, POSS chemistry provides a promising means for precisely manipulating the topology and architecture of the POSS-containing hybrids to control the self-assembly of the molecules into specific structures, yielding hybrid materials with tailored properties. For example, experimental studies on liquid crystalline POSS molecules reveal that covalently attaching mesogenic and rigid nonmesomorphic substituents to the POSS core enables the POSS-containing hybrids to form liquid crystalline phases that the substituents themselves do not exhibit and thereby demonstrate that direct attachment of the relatively rigid POSS cubes influences the types of structures formed and increases the variety of self-assembled structures possible. Specifically, the bottom-up self-assembly technique that has attracted considerable attention is the incorporation of functional macromolecule units into amphiphiles in preparation for optical materials, advanced nano-devices and so on. This is a promising research area for the preparation of multi-function composites.
Figure 2.2 Molecular structure of polyhedral ologomeric silsesquioxane POSS $R_8\text{Si}_8\text{O}_{12}$ (where R may be a hydrogen atom or an organic functional group).

2.4 The Self-Assembly Behaviors of Hydrophilic Macroions and Amphiphiles

In this section, the self-assembly behaviors of pure inorganic hydrophilic macroions and inorganic-organic amphiphiles will be briefly discussed in term of their mechanism.

2.4.1 Blackberry Formation for POMs Solutions

The solution behaviors of the pure inorganic nanoscale cluster POMs will be described and the self-assembly counter-mediated interaction mechanism will be discussed.

2.4.1.1 The Solution Behaviors of the POMs

Large, hydrophilic polyoxoanions with high solubility in water and/or other polar solvents demonstrate unique solution behavior by self-assembling into single layer, hollow, spherical “blackberry” structures, which is obviously different from small, simple ions. These macroions cannot be treated as insoluble colloidal suspensions because they form stable “real solutions”. Counterion-mediated attraction is considered as the main driving force for the self-assembly behavior. The size disparity between the macroions and their
counterions results in macroion–counterion pairing which leads to the inter-macroanionic attraction. The blackberries, with robust membranes semi-permeable to cations, can adjust their size accurately and reversibly in response to the change of solvent polarity and charge density of individual macroions.

2.4.1.2 The Driving Forces for the Blackberry Formation

Hydrophilic macroions represents a transition stage between simple ions and large colloids, which was a previously missed link among simple ions, colloids and polyelectrolytes in solution (see Figure 2.3). It is found that such macroions have completely different solution behaviors from the other two systems and could represent a previously missing intermediate region between them. Soluble inorganic ions are expected to distribute homogeneously in dilute solutions. However, this widely accepted concept might not hold for some giant, highly soluble, hydrophilic macroions carrying moderate amount of charges. These macroions, represented by polyoxometalate (POM) anions and metal-organic cations, tend to self-associate into hollow, spherical, single-layer, vesicle-like blackberry-type structures in dilute solutions. This unique phenomenon has been explored by our group. The macroions cannot be described by the Debye-Hückel Theory because they cannot be treated as point charges, while on the other hand they are still soluble and form “real solutions”, which distinguishes them from colloids.

POMs, as introduced early, are a large group of nanometer-scaled inorganic metal-oxide molecular clusters such as polyoxomolybdates, polyoxotungstates and their derivatives, with well-defined molecular structure, uniform size, shape, mass and (in certain range) adjustable charge density. The cationic nanocages are formed by interacting transition metal cations with special organic ligands to form well-defined
structures. They contain separated hydrophobic organic domains on their surface. Quite a few types of POMs are hydrophilic in nature and are very soluble in polar solvents, mainly due to their surface water ligands coordinated to the metal centers, and their inherent charges. The POM clusters can be categorized into two groups depending on the nature of their charges: strong electrolytes and weak electrolytes. The first group carries inherent charges in crystals which are balanced by multiple small cations. In solution, the majority part of the clusters usually exists as macroanions. The second group is represented by \{\text{Mo}_{72}\text{Fe}_{30}\} and \{\text{Mo}_{72}\text{Cr}_{30}\} (detailed see below).

Let us take \{\text{Mo}_{132}\} solutions as one example to understand the self-assembly mechanism of the giant hydrophilic macroions.\textsuperscript{28} \{\text{Mo}_{132}\} macroions exist as single ions in dilute aqueous solution due to their high charge (-42) and exist as soluble, uncharged molecules in dilute acetone solution. However, they form blackberries in the water/acetone mixed solvents containing 3- 65 vol% acetone.\textsuperscript{29} The interesting fact is that the POM clusters are still soluble and stay as discrete clusters when not carrying any charge, and tend to attract each other when carrying certain negative charges due to the addition of

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Figure 2.3 (left) Hydrophilic macroions represents a previously missed link among simple ions, colloids and polyelectrolytes in solution. (right) A self-assembled blackberry type structure formed by \{\text{Mo}_{154}\} macroions in aqueous solution, representing a typical solution behavior of macroions. Adapted with permission from ref 15. Copyright 2009 American Chemical Society.
water, even with monovalent counter-ions such as H\(^+\), Na\(^+\) or NH\(_4^+\). The conclusion is that the van der Waals forces are not the major attractive forces for the self-assembly. Also, we have excluded the possible contributions from hydrophobic interaction and chemical interaction. Instead, we believe that the counterion-mediated attraction and hydrogen bonding are important.

Furthermore, in the blackberry region, the average blackberry size decreases with increasing water content. Together with theoreticians, we found a linear relationship between the blackberry size and 1/\(\varepsilon\), with \(\varepsilon\) being the dielectric constant of the solvent, suggesting that the blackberry formation is a charge-regulated process. Other similar POM macroions and metal-organic cage macrocations also follow this rule (Figure 2.4). A general equation was developed to describe all the parameters which controls the blackberry size. The phase transition between the single macroions (or molecules) to the blackberries, or the transition between the blackberries with different sizes, can be achieved by changing the solvent content (see the case of Mo\(_{132}\) Figure 2.4 right) for strong electrolyte-type POMs, and by changing the solution pH for weak electrolyte-type POMs (see the case of \{Mo\(_{72}\)Fe\(_{30}\}\) below in Figure 2.4 right), suggesting that the blackberry phase is thermodynamically stable.

Weak electrolyte type POMs, such as Keplerates \{Mo\(_{72}\)Cr\(_{30}\}\) and \{Mo\(_{72}\)Fe\(_{30}\}\), are almost neutral clusters in single crystals, and become macroanions due to the partial deprotonation of their water ligands attached to the non-Mo centers in solution. For example, \{Mo\(_{72}\)Fe\(_{30}\}\) has 30 potential deprotonation sites. When dissolved in water for a 1.0 mg/mL solution, 7–8 protons are released from each \{Mo\(_{72}\)Fe\(_{30}\}\) cluster. The cluster can be treated as a weak acid with its degree of deprotonation increases with increasing
solution pH. As shown in Figure 2.5, at pH<2.9, uncharged \{Mo_{72}Fe_{30}\} clusters stay as soluble molecules. When pH>2.9, \{Mo_{72}Fe_{30}\} clusters are more charged. Self-assembly occurs with the blackberry size decreasing with increasing pH. Similar behavior has been observed in other weak-acid type of POMs, such as \{Mo_{72}Cr_{30}\}.

By using synchrotron SAXS, it is demonstrated that the counterions (even small monovalent ions) can associate around single macroions, which is also confirmed by simulations. The degree of association increases with increasing macroionic concentration and/or decreasing solvent polarity. (see Figure 2.6) The counterion-mediated attraction is found to be responsible for the blackberry formation, together with hydrogen bonding among the macroions. The macroions are “smart” – they can distinguish different monovalent ions and choose the ones with smaller hydrated sizes.
2.4.2 Blackberry Formation for Nanocage Solutions

Similar blackberry formation processes have also been observed in macrocations solutions. For example, $M_6L_4(NO_3)_{12}$ (with $M$ = ethylenediamine Pd(II), $L$ = 2,4,6-tris(4-pyridyl)-triazine)\textsuperscript{33} (stay as $\{M_6L_4\}^{12+}$ macrocations in solution) and $M_{12}L_{24}$ ($M$ = Pd, $L$ = 2,6-bis(4-pyridylethynyl)toluene) (stay as $\{M_{12}L_{24}\}^{24+}$ macrocations in solution) metal-organic nanocages can both self-assemble into blackberry type structures (Figure 2.7).\textsuperscript{34} The relation between the blackberry size and the solvent content (in dielectric constant) is consistent with our earlier observations on macroanions solutions (a charge-regulated process). The conclusion is the blackberry formation is a universal phenomenon for large cations, not only for macroanions. For example, similar phenomenon occurs in another hydrophilic macrocation system. A viral capsid type vesicle self-assembled from $M_{12}L_{24}$ metal-organic hybrid nanocages show the similar self-assembly behavior when the size and charge of such complex nanoparticles are in proper ranges.
Figure 2.7 The {M₆L₄}¹²⁺ cationic cages also form blackberry structures (left), as confirmed by light scattering and TEM (middle) techniques, and the process is also charge regulated (right). Adapted with permission from ref 33. Copyright 2010 American Chemical Society.

2.4.3 Blackberry Formation for a Hydrophilic Carboxylic Acid-capped Fullerene in Solutions

A hydrophilic carboxylic acid-capped fullerene (AC₆₀) with 12 carboxylic acid groups shelled on the periphery shows the behavior of macroions by self-assembling into single-layer “blackberry” structures. (See Figure 2.8) Without involvement of hydrogen-bounding, its solution behavior is different from previous amphiphilic fullerenes. There is an inverse relationship between the size of the superstructures with the polarity of the solvent. It is also confirmed that the counterion-mediated attraction is the major driving force for the self-assembly process. It is a new way to assemble fullerene derivatives into ordered vesicular structures with tunable sizes and narrow size distribution and might afford a feasible strategy to the design and preparation of single-layered structures based on fullerene and their derivatives.³⁵
2.4.4 Blackberry Formation for POSS Solutions

Both positively and negatively charged polyhedral oligomeric silsesquioxane (see Figure 2.9 POSS 1a and 1b, respectively) ions were also observed to self-assemble into blackberry-type supramolecular structures in water/acetone mixed solvents, driven by the counterion-mediated attraction. DLS results reveal that the sizes of the blackberry structures increase with increasing acetone content. The charge-regulated process is illustrated in Figure 2.10. Interestingly, studies on the two oppositely charged POSS macroions with identical charges and similar sizes show the discrepancy between positively and negatively charged POSS macroions: POSS 1b can self-assemble in polar solvents and forms fewer supramolecular structures relative to POSS 1a. The discrepancy in solution behaviors of the oppositely charged macroions can be related to different counterions, different ionic domains of macroions, the ionic strength in solution, and the water-bridged hydrogen bonding between macroions.\textsuperscript{36}
Figure 2.9 Chemical structures of POSS macroions: (a) negatively charged (b) positively charged POSS. Reprinted with permission from Ref 36. Copyright 2015, Wiley InterScience.

Figure 2.10 Transmission from discrete macroions (molecules) to blackberries, then to discrete macroions owing to the change of solvent content for 1.0 mg mL\(^{-1}\) POSS 1a in water/acetone mixed solvents. Reprinted with permission from Ref 36. Copyright 2015 Wiley InterScience.

2.4.5 The Influencing Factors to the Self-Assemblies of the Hydrophilic Macroions in Solution

In this section, the influencing factors, such as the components of the macroions, the solvent nature, and the counterions will be discussed in the following paragraphs.

2.4.5 (1) Effect of the Macroion Components on the Self-Assemblies

Two types of “Keplerate” clusters (abbreviations \{Mo\(_{72}Fe_{30}\}\) and \{Mo\(_{72}Cr_{30}\}\), respectively, see Figure 2.11), which have almost identical size and same surface structures,
but different central metal, are chosen to study their self-assembly behaviors in solutions. To compare the different self-assembly behaviors of both types of macroanion, aqueous solutions containing both types of POMs (1:1 mass ratio, up to 0.5 mg/ml each) were prepared and then maintained at 30°. The CONTIN analysis of the DLS results show the presence of two differently sized large species (see the red curve in Figure 2.12 A). That means that such two types of clusters demonstrate self-recognition by forming two types of homogeneous blackberries instead of mixed ones in their mixed aqueous solution (See the Figure 2.12). The explanation is the different degree of deprotonation of the clusters with the same pH value. The charge difference between the two macroions is believed to be the major reason, suggesting that the long-range, delicate electrostatic interaction is essential and critical for self-recognition behavior.37

![Figure 2.11](image-url) (a)comStructure of the spherical, 2.5-nm-diameter \{Mo_{72}M_{30}\}-type clusters (M is Fe^{3+} or Cr^{3+}; ball-and-stick representation)(b) The unique identical surface structures of the two Keplerates(c) The cartoon of the self-recognition process of the mixed Mo_{72}Fe_{30} and Mo_{72}Cr_{30}. Reprinted with permission from Ref 37. Copyright 2011, Science.
A study about the self-assembly behaviors of two macroions \([(C_4H_9)_4N)_7 (Mo_6O_{18}NC(OCH_2)_3XMo_6O_{18}(OCH_2)_3CNMo_6O_{18}) (X = Mn^{III} (1), Fe^{III} (2))]\), with almost identical charge densities and morphologies except for their different encapsulated central metal atoms has also been reported. Time-resolved static and dynamic light scattering, transmission electron microscopy, and energy-dispersive X-ray spectroscopy were utilized to analyze the self-recognition behavior between the two macroions. Density functional theory calculation and kinetic monitoring of the disassembly process of the formed blackberry superstructures in the individual solutions of the two macroions and their mixture solution, respectively, were combined to uncover the mechanism for their self-recognition behavior. It is observed that the two macroions also self-assembled into two different size superstructures in their mixed solutions, demonstrating a self-recognition behavior between two highly similar macroions during their assembly process, as
confirmed by DLS, SLS, and TEM/EDS analysis. This self-recognition behavior can be explained by the slightly different charge distributions of the macroanions resulting from their different central atoms (confirmed by theoretical DFT calculations and dissociation experiments). Meanwhile, this work also confirms that the long-range counterion-mediated electrostatic attraction is sensitive to the small difference in macroions and consequently offers the possibility for delicate selectivity and preference among different macroions.\(^{38}\)

![Figure 2. 13 Model of the self-recognition during the self-assembly of two molecular rods in their mixed solution (polyhedra code: blue, MoO\(_6\) or MoO\(_5\)N; purple, MnO\(_6\); yellow, FeO\(_6\)). Reprinted with permission from Ref 38. Copyright 2014 American Chemical Society.](image)

2.4.5 (2) Effect of the Solvent Nature on the Self-Assemblies

Two representative macroanions Mo\(_{72}\)Fe\(_{30}\) and Mo\(_{132}\) with hollow spherical shape, but chemically different components, are chosen to study charge control for the self-assemblies, as shown in Figure 2.14. The self-assembly sizes are determined by dynamic light scattering technique and plotted with the inverse relative dielectric constant of the solvent medium. (See Figure 2.15) It is found that there is a linear relationship between the equilibrium size and the inverse of the dielectric constant of the medium, which means that this relationship can be used to predicate the size of the assemblies linearly with the inverse of the dielectric constant of the medium.\(^{29}\)
Figure 2. 14 Polyoxometalates (POMs) Mo$_{72}$Fe$_{30}$ (top, left) and Mo$_{132}$ (bottom, left) and a cartoon of their shell-like superstructure where the size range refers to the situation in aqueous solutions. Reprinted with permission from Ref 29. Copyright 2007 Physical Review Letter.

Figure 2.15 Shell radius as determined by dynamic light scattering as a function of the inverse relative dielectric constant of the solvent for two different polyoxometalates: Mo$_{72}$Fe$_{30}$ and Mo$_{132}$. Reprinted with permission from Ref 29. Copyright 2007 Physical Review Letter.
2.4.5 (3) Effect of the Counterions on the Self-Assemblies

In the Debye-Hückel theory, both small cations and anions can be treated as point charges, while the large colloidal particles are able to attract substantial amount of counterions around them to decrease their net charge density greatly. Although the macroions are in the middle between the small ions and the colloidal particles, they are large enough to demonstrate the size disparity between small ions and macroions. Therefore, the interaction between macroions and counterions might be important. The study on counterion-macroion interaction was initiated over a decade ago, when inorganic chemists contemplated the role of counterions and their interaction with macroions POMs on the catalytic properties of POM clusters. Small-angle X-ray scattering (SAXS) is a powerful technique to explore this interaction. The POM macroions are uniform molecular clusters whose scattering curve can be calculated based on their form factors in dilute solution. The scattering curve will change if counterions closely interact with the POM macroions. For the first SAXS experiment, dilute solutions of \{Mo_{72}V_{30}\} are used. Several peaks can be identified from the SAXS curve obtained from 0.1 mg/mL (0.013 mM) aqueous solution of \{Mo_{72}V_{30}\} (Figure 2.16). The \(R_g\) value obtained from the Gunier plot (10.8 ± 0.5 Å) suggests that there is no counterion association around the macroions. In Figure 2.16 (top), the p(r) curves show that for \{Mo_{72}V_{30}\} in dilute aqueous solutions, there is just discrete \{Mo_{72}V_{30}\} clusters (a core shell spherical particle with a maximum linear dimension of ~ 26 Å), no counterion association around macroions. On the other hand, when the \{Mo_{72}V_{30}\} concentration is > 0.052 mM, or a certain amount of acetone is introduced into the solution, another distant peak appears (centered at ~30 Å and extends the effective distribution to ~ 34 Å) in the p(r) plot (Figure 2.16, bottom). Meanwhile, the
original distribution remains unchanged, suggesting that the macroions still exist as
discrete ions (the self-assembly process is slow; see below). This additional peak suggests
that some counterions are closely associated with the macroions and distribute in the range
of 0.2-0.9 nm to the surface of macroions. The peak due to the associated counterions
becomes more and more significant with increasing POM concentration or acetone content.
Meanwhile, Gunier plots indicate that the average $R_g$ value of the $\{\text{Mo}_{72}\text{V}_{30}\}$ macroions
also increases accordingly. The appearance of the peak due to associated counterions is
consistent with the appearance of the blackberry structures, indicating the direct connection
between these two issues and the role of counterions on the blackberry formation.
Compared to nanosized POM macroions, the large blackberry structures are much more
powerful in attracting counterions. As estimated from zeta potential analysis, in aqueous
solution, $>99\%$ of the effective charge on the blackberries has been neutralized by the
closely associated counterions.$^{32}$

A simple theoretical approach based on a mean-field model confirms the above
experimental results regarding the interaction between two macroions in salt-free solutions
with medium dielectric constant $\varepsilon$, with the aim to address the attraction of two like-charge
macroions. All small counterions are categorized into two groups: free and bound cations.
The formation of a bound cation is assumed due to strong electrostatic attraction with
macroions, dictated by a free energy gain $\Delta\mu_{bm}$ relevant to the equilibrium ratio of bound
and free cations.
Figure 2. Top: Distance distribution functions based on calculated and experimental scattering data for \([\text{Mo}_{72}\text{V}_{30}]\) obtained by using an indirect Fourier transform of the primary SAXS data. (○): 0.052 mm \([\text{Mo}_{72}\text{V}_{30}]\), (●): 0.013 mm \([\text{Mo}_{72}\text{V}_{30}]\), (c): \([\text{Mo}_{72}\text{V}_{30}]\) calculated. Bottom: Experimental distance distributions for 0.26 mm \([\text{Mo}_{72}\text{V}_{30}]\) in water and acetone/water mixed solvents with various acetone content (in vol%). (—): 75% acetone/water, (○): 65% acetone/water, (– – –): 45% acetone/water, (……): 10% acetone/water, (□): in pure water. Reprinted with permission from Ref 32. Copyright 2009 Wiley InterScience.
2.4.6 The Driving Forces for the Self-assembly Process of the Inorganic-Organic Hybrids in Solutions

The bottom-up self-assembly is a controllable technique at the nanoscale level, which provides fascinating perspectives in the field of molecular materials design through varieties of noncovalent intermolecular forces, (i.e. hydrophobic interaction, van der Waals force, hydrogen bonding, electro static force).

2.4.6.1 Hydrophobic Interaction

Hydrophobic word means "water-fearing," and hydrophobic substances tend to aggregate together rather than distribute themselves in water medium (see figure 2.17). Hydrophobic word describes the segregation and apparent repulsion between water and nonpolar substances. The mixing hydrophobes and water molecules is not spontaneous, however, hydrophobic interactions between hydrophobes are spontaneous. When hydrophobes come together and interact with each other, enthalpy increases (ΔH is positive) because some of hydrogen bonds that form the clathrate cage will be broken (See figure 2.17 bottom left). Tearing down a portion of the clathrate cage will cause the entropy to increase (See figure 2.17 bottom right), ΔS is positive), since the forming of the clathrate cage decreases the entropy. According to the formula: ΔG = ΔH−TΔS, ΔH = small positive value, ΔS = large positive value, ΔG is negative and hence hydrophobic interactions are spontaneous. Hydrophobic interactions are relatively stronger than other weak intermolecular forces (i.e., van der waals interactions or hydrogen bonds). The strength of hydrophobic interactions depend on several factors including (in order of strength of influence) (a) Temperature: As temperature increases, the strength of hydrophobic interactions increases as well. However, at an extreme temperature, hydrophobic
interactions will denature. (b) Number of carbons on the hydrophobes: Molecules with the greatest number of carbons will have the strongest hydrophobic interactions. (c) The shape of the hydrophobes: Aliphatic organic molecules have stronger interactions than aromatic compounds. Branches on a carbon chain will reduce the hydrophobic effect of that molecule and linear carbon chain can produce the largest hydrophobic interaction. This is because carbon branches produce steric hindrance, so it is harder for two hydrophobes to have very close interactions with each other to minimize their contact to water.\(^ {39,40}\)

Figure 2.17 (top) Hydrophobic effect (bottom left) The image above indicates that when the hydrophobes come together, they will have less contact with water. They interact with a total of 16 water molecules before they come together and only 10 atoms after they interact.
2.4.6.2 Electrostatic Interaction

Electrostatic interaction universally exists between charged particles (cations or anions), which can be described by Coulomb's law. The interactions can be either attractive or repulsive, depending on the signs of the charges. Like charges repel. Unlike charges attract. The magnitude of the electrostatic interaction between two point charges is directly proportional to the scalar multiplication of the magnitudes of charges and inversely proportional to the square of the distance between them. The magnitude can be stated by the below simple mathematical expression.\(^{41}\)

$$\text{Force} = \frac{k_e q_1 q_2}{\varepsilon r^2},$$  \hspace{1cm} \text{Equation 2.1}

\(k_e\) is Coulomb's constant \((k_e = 8.9875517873681764 \times 10^9 \text{ N.m}^2\text{C}^{-2})\), \(q_1\) and \(q_2\) are the signed magnitudes of the charges, \(r\) is the distance between the charges (meters), \(\varepsilon\) = the dielectric constant of the medium (unitless). The dielectric constant reflects the tendency of the medium to shield charge from each other. \(\varepsilon\) is 1 in a vacuum, around 4 in the interior of a protein and 80 in water. Water is very efficient at shielding charges, reducing electrostatic forces between ions.

2.4.6.3 Van der Waals Interactions

In physical chemistry, the Van der Waals forces (or Van der Waals' interaction), is the sum of the attractive or repulsive forces between molecules (or between parts of the same molecule)\(^{42}\) The resulting van der Waals forces can be attractive or repulsive.\(^{43}\) Van der Waals interactions occur between all neighboring atoms in structures and interfaces, but are not significantly different from those made by the same atoms with solvent, which includes: (1) force between two permanent dipoles; (2) force between a permanent dipole
and a corresponding induced dipole; (3) force between two instantaneously induced dipoles (London dispersion force).\textsuperscript{44} It is also sometimes used for the totality of intermolecular forces. Van der Waals forces are relatively weak compared to covalent bonds, but play a fundamental role in fields as diverse as supramolecular chemistry, structural biology, polymer science, nanotechnology, surface science, and condensed matter physics. Van der Waals forces define many properties of organic compounds, including their solubility in polar and non-polar media. The main characteristics of van der Waals forces are:\textsuperscript{45} (1) They are weaker than normal covalent ionic bonds; (2) Van der Waals forces are additive and cannot be saturated; (3) They have no directional characteristic; (4) They are all short-range forces and hence only interactions between nearest need to be considered instead of all the particles. The greater is the attraction if the molecules are closer due to Van der Waals forces. (5) Van der Waals forces are independent of temperature except dipole - dipole interactions.

2.4.6.4 Hydrogen Bonding

Hydrogen bonding is a type of electrostatic attraction between polar molecules that occurs when a hydrogen (H) atom bound to a highly electronegative atom such as nitrogen (N), oxygen (O) or fluorine (F) experiences attraction to some other nearby highly electronegative atom. Figure 2.18 below gives the illustration of the features of generic hydrogen bonding. An atom (Acceptor) with a basic lone pair of electrons can interact favorably with a hydrogen atom (H) covalently bound to a donor atom (Donor). Hydrogen bonding requires that atoms A and D are both electronegative. H-D must have acidic properties. In the donor part, the electron cloud from around the hydrogen nucleus of the donor is decentralized by the attracting from the electronegative atom, resulting in the H
atom with a positive partial charge. The resulting charge, though only partial, represents a large charge density, because of the small size of hydrogen relative to other atoms and molecules. The lone pair of electrons from another heteroatom then becomes the hydrogen-bond acceptor. The highly electronegative atoms, such as fluorine, oxygen, or nitrogen usually are donor, because the hydrogen atom attached to the relatively electronegative atom plays the donation role for the hydrogen bonding.  

![Diagram of the Hydrogen Bond](image)

**Figure 2.** Illustration of the forming of hydrogen bonding, including the acceptor and donor, the ion pair and the proton H.

Hydrogen bonding can occur between molecules (intermolecular) or within different parts of a single molecule (intramolecular). The magnitude range of hydrogen bonding is from 5 to 30 kJ/mole, stronger than a van der Waals interaction, but weaker than covalent or ionic bonds. This type of interaction can occur in inorganic molecules (like water) or in organic molecules (like DNA and proteins). The higher boiling point of water (100 °C) is due to intermolecular hydrogen bonding, compared to the other hydrides that have no hydrogen bonds, and the secondary and tertiary structures of proteins and nucleic acids is
mainly contributed by the intramolecular hydrogen bonding. The hydrogen bonding also plays an important role in the structure of polymers, both synthetic and natural.

The hydrogen bonding has some features of covalent bonding: it is directional and strong, produces interatomic distances shorter than the sum of the van der Waals radii, and usually involves a limited number of interaction partners, which can be interpreted as a type of valence. Hydrogen bonding can vary in strength from very weak ($1\sim2\text{ kJ mol}^{-1}$) to extremely strong ($161.5\text{ kJ mol}^{-1}$ in the ion HF$_2^-$). In fact, the hydrogen bonding is often a kind described as an electrostatic dipole-dipole interaction.$^{47}$

The hydrogen bonding between water molecules is the most ubiquitous and perhaps simplest example. One water molecule has two hydrogen atoms and one oxygen atom. For the simplest system, only two water molecules are often used as a model (the water dimer). Two water molecules can form hydrogen bonding between them. When more molecules are present, as is the case with liquid water, more hydrogen bonding are possible because the oxygen of one water molecule has two lone pairs of electrons, each of which can form a hydrogen bond with a hydrogen on another water molecule. This can repeat such that every water molecule is H-bonded with up to four other molecules (two through its two lone pairs, and two through its two hydrogen atoms). Hydrogen bonding strongly affects the crystal structure of ice, helping to create an open hexagonal lattice. The density of ice is less than the density of water at the same temperature; thus, the solid phase of water floats on the liquid, unlike most other substances.

Hydrogen bonding also plays an important role in determining the 3D structures of the proteins and nucleic acids. In these bio-macromolecules, hydrogen bonding between different parts of the same macromolecule cause it to fold into a specific shape, which
determines the physiological or biochemical properties of the molecule. For example, the double helical structure of DNA is due largely to hydrogen bonding between its base pairs, as well as pi stacking interactions, which link one complementary strand to the other and enable replication.

Hydrogen bonding can also strengthen many polymers in their main chains. The best known example is the synthetic polymers nylon, where hydrogen bondings occur in the repeat unit and play a major role in crystallization of the material. The hydrogen bondings between carbonyl and amine groups in the amide repeat unit, can effectively link adjacent chains to create crystals, reinforcing the material. The effect is greatest in aramid fibre, where hydrogen bonding stabilizes the linear chains laterally. The chain axes are aligned along the fibre axis, making the fibres extremely stiff and strong. Hydrogen bonding is also important in the structure of cellulose and derived polymers in its many different forms in nature (like wood) and natural fibres (like cotton and flax).  

2.4.6.5 π–π Stacking

π–π stacking is one type of noncovalent, attractive interactions between aromatic rings. A benzene dimer is taken as a prototypical system to study pi stacking (See the figure 2.19). Three possible geometries possibility occur: sandwich, parallel displaced and T-shaped. The parallel displaced and T-shaped are two most stable conformations with energy minima. In contrast, the sandwich configuration is least stable, and represents an energetic saddle.

Experimentally, for a benzene dimer, the bound energy is by 8–12 kJ/mol (2–3 kcal/mol) in the gas phase with a separation of 4.96 Å between the centers of mass for the T-shaped dimer. The small binding energy makes the benzene dimer difficult to study
experimentally, and the dimer itself is only stable at low temperatures and is prone to cluster. Other evidence for pi stacking comes from X-ray crystal structures. Perpendicular and offset parallel configurations can be observed in the crystal structures of many simple aromatic compounds. Similar offset parallel or perpendicular geometries were observed in a survey of high-resolution x-ray protein crystal structures in the Protein Data Bank. 49

The relative binding energies of these three geometric configurations of the benzene dimer can be explained by a balance of quadrupole/quadrupole and London dispersion forces. While benzene does not have a dipole moment, it has a strong quadrupole moment. The local C-H dipole means that there is positive charge on the atoms in the ring and a correspondingly negative charge representing an electron cloud above and below the ring. The quadrupole moment is reversed for hexafluorobenzene due to the electronegativity of fluorine. The benzene dimer in the sandwich configuration is stabilized by London dispersion forces but destabilized by repulsive quadrupole/quadrupole interactions. By offsetting one of the benzene rings, the parallel displaced configuration reduces these repulsive interactions and is stabilized. The T-shaped configuration enjoys favorable quadrupole/quadrupole interactions, as the positive quadrupole of one benzene ring interacts with the negative quadrupole of the other. The benzene rings are furthest apart in this configuration, so the favorable quadrupole/quadrupole interactions evidently compensate for diminished dispersion forces.
2.4.7 The Solution Behavior of the Traditional Amphiphilies (Small Surfactants and Block Co-Polymers)

In this section, the solution behaviors of the traditional amphiphiles, including the small surfactants and block copolymers will be discussed. The molecular packing parameter will be briefly reviewed.

2.4.7.1 Molecular Packing Parameter (P)

The concept of molecular packing parameter (P), as a very important term in surfactant science, is widely invoked in the literature to explain, rationalize and even predict molecular self-assembly in small surfactant solutions. The molecular packing parameter is defined as

\[ P = \frac{v}{l \times a_0} \]  

Equation 2.2

where \( v \) is the surfactant tail volume, \( l \) is the tail length, and \( a_0 \) is the equilibrium area per molecule at the aggregate surface. A particular value of the molecular packing parameter can be translated via simple geometrical relations into specific shape of the equilibrium superstructure (see table 2.1), which is the predictive application of the concept of

Figure 2. 19 Three different representative conformations of benzene dimers.
molecular packing parameter, as discussed in the literature. The formation of various micelle structures is thus characterized by the value of P. If \( P < 1/3 \), spherical micelles are formed; if \( 1/3 < P < 1/2 \), cylindrical micelles are favored; if \( 1/2 < P < 1 \), bilayer vesicles are produced; if \( P \) approaches 1, bilayer planers are expected; while if \( P > 1 \), reversed micelle structures are constructed.\(^{50}\)

Table 2.1 The molecular packing parameter values of the traditional small surfactants correspond to the morphologies of the superstructures.

<table>
<thead>
<tr>
<th>P = v/(a* l)</th>
<th>P ≤ 1/3</th>
<th>1/3 &lt; P &lt; 1/2</th>
<th>1/2 &lt; P &lt; 1</th>
<th>P &gt; 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>morphology</td>
<td>spherical</td>
<td>cylinder</td>
<td>bilayer</td>
<td>reverse micelle</td>
</tr>
</tbody>
</table>

Because the conventional surfactants usually have one polar head group covalently linked with one or several hydrophobic tails, the molecular packing parameter (P) of a surfactant’s geometrical parameters, can be used to predict the assemblies of the surfactants in polar and nonpolar solvents.

The molecular packing parameters show that the self-assembly behavior is determined by the size of polar head and the length of carbon chains. Therefore, it is necessary to figure out the effect of the length and number of alkyl chains and the size of POM polar head to the self-assembly behavior of the amphiphiles. As a new effect, charges of POM head groups should be considered since the interaction between POMs polar heads is not negligible due to the close distance between the polar heads in the formed aggregates and high negative charges of the polar heads. Moreover, the numbers of negative charges of POM heads can be tuned by electro-chemical reduction or direct reduction by reducing agents, such as hydrazine. What is more, mixed aggregates will be obtained when different
common surfactants are mixed in solution. However, the theory might not been applicable for the novel amphiphiles. Therefore, it is quite reasonable to test whether the giant amphiphiles with different POMs head can recognize each other or just mix with each other. Different from the self-assembly of macroions into blackberry structures, the self-assembly of amphiphilic hybrid POMs is more complicated than the self-assembly of common amphiphilic surfactants, the study of the assembly of hybrid POMs needs to take the counterion effect and the bulky, charged polar head group into account besides the effects of molecular topology, solvent polarity, concentration, and hydrophobicity of the organic ‘tails’.
CHAPTER III

EXPERIMENTAL DETAILS

The properties of the individual giant amphiphiles and the information of their assembled superstructures in solution, such as the shape, size, charge density, are characterize by light scattering technique, zeta potential analyzer, and electronic microscopy.

3.1 Laser Light Scattering Techniques

Light Scattering Theory

The principle of light scattering is shown in figure 3.1. The sample is a solution in a cuvette which is usually cylindric. A monochromatic light source (i.e. a light source emitting light of only one wavelength, usually a laser) shines light on the sample. The intensity or the power of the scattered light is being measured at some known scattering angle by a detector which may be a photodiode or a photomultiplier tube. The intensity (or power) of the scattered light is being measured as a function of the scattering angle \( \theta \), i.e. the angle of observation of the detector. The measured intensity of the scattered light is divided by the intensity of the incident light which consequently also has to be measured using a reference detector.\(^{50} \)
There are two measurement techniques, namely static light scattering (SLS) and dynamic light scattering (DLS). The techniques will be described in that order because it is necessary to understand SLS in order to understand properly DLS. These two techniques are complementary in the sense that they take advantage of two different and completely independent features of the scattered light: SLS measures the average intensity of the scattered light at many different scattering angles and uses this to derive information about molecular weight, particle size, particle shape and particle interactions. DLS, on the other hand, disregards the intensity of the scattered light but uses the temporal fluctuations in the scattered light to derive spectra of typical fluctuation times which in turn yield information about the diffusion coefficient(s) of the particles and the indirectly about their size. The difference is shown in figure 3.2.\textsuperscript{51} Light scattered from a solution of particles has a mean intensity $\langle I \rangle$ that reflects the molecular weight of the particles while the fluctuations in the intensity have a characteristic fluctuation time $\tau$ that reflects the diffusion coefficient of the particles while the fluctuations in the intensity have a characteristic fluctuation time $\tau$ that reflects the diffusion coefficient of the particles.

Figure 3.1 Sketch of a setup for the measurement of static light scattering, SLS.
3.1.1 Static Light Scattering (SLS)

Static light scattering employs measurement of the intensity of the scattered light at many different angles (typically 10 - 100°). The intensity is usually an average over approximately one second or more. The information about the molecular weight and size of the molecule lies in the intensities themselves at the different scattering angles.

Simple theory for static light scattering (SLS)

When a light scattering experiment is done on a solution (i.e. a suspension of particles), in order to deduce properties of the solution and a measure which is independent of apparatus characteristics but only depends on the properties of the system. The following Rayleigh ratio, \( R_\theta \), for the solution is defined:

\[
R_\theta = \frac{I_s(\theta) \cdot r^2}{I_0 \cdot V_s(\theta)}
\]

Equation 3.1

Figure 3. 2 Scattered light intensity vs the time for the DLS measurement.
where the subscript θ indicates that the Rayleigh ratio is a function of the scattering angle, $I_{s(\theta)}$ is the intensity of the scattered light measured at the angle of observation θ. Figure 3.3, $I_0$ is the intensity of the laser used, $V_{s(\theta)}$ is the scattering volume (i.e. the volume which is illuminated by the laser while at the same time being visible for the detector (see figure 3.3), and $r$ is the distance from the scattering volume to the detector. The constant $K$ is the optical constant and related to the refractive index of the solvent and the dissolved particles through the expression. Where $n_0$ is the refractive index of the solvent, $\lambda_0$ is the wavelength of the laser beam in vacuum and $d\mu/d_C$ is the derivative of the refractive index of the solution with respect to the weight concentration of the dissolved particles. $R(\theta)$ is a function which depends on:

- the molecular weight of the suspended particles (molecules)
- the concentration of the suspended particles (molecules)
- the refractive index of the pure solvent
- the refractive index of the suspended particles (molecules)
- the size of the suspended particles (molecules)
- interaction forces between the suspended particles
3.1.2 Dynamic Light Scattering (DLS)

Simple theory for dynamic light scattering (DLS)

Dynamic light scattering employs measurement of long time series of mean intensity of the scattered light where the averaging is over very short time intervals, typically 100 ns. Averaging over such short time intervals ensures that the magnitude of the intensity fluctuations within the time series become significant. The information about the molecules (diffusion coefficient or size) lies in the typical fluctuation times for the scattered intensity.

The purpose of doing dynamic light scattering experiments is usually to measure the diffusion coefficient of molecules in solution but may also be to measure characteristic relaxation times in e.g. gel systems. We shall here only deal with measurements of diffusion processes. Through the measurement of the diffusion coefficient for particles in suspension it is possible to determine indirectly the size of the particles. The size measure obtained in this way is called the hydrodynamic radius or sometimes the Stokes radius of the particles because the determination is based on the Stokes-Einstein relationship which
relates the diffusion coefficient of suspended spheres with radius \( r \) with their diffusion coefficient \( D \)

\[
D = \frac{k_B T}{6\pi\eta r}
\]

Equation 3.2

where \( T \) is the absolute temperature of the suspension, \( \eta \) is the viscosity of the liquid and \( k_B = 1.38 \times 10^{-23} \text{ J.K}^{-1} \) is Boltzmann’s constant. Strictly speaking equation 3.2 is valid only for non-interacting particles to whose surface the surrounding liquid sticks. If the diffusion coefficient \( D \) of some particles is experimentally determined the diffusion coefficient can be inserted into the Stokes-Einstein equation 3.2 which can then be solved for the radius.

The radius thus obtained the hydrodynamic radius \( r_h \) and is defined as:

\[
r_h = \frac{k_B T}{6\pi\eta D_{exp}}
\]

Equation 3.3

where \( D_{exp} \) is the measured diffusion coefficient of the suspended particles. If the particles are not spheres the hydrodynamic radius is nevertheless a rough measure of the particle size in the same way that the radius of gyration is. The two numbers are usually not exactly equal. If the particles are non-spherical their hydrodynamic radius is often approximately the radius of a sphere with the same volume as the particle. This holds as long as the particles do not have extreme geometry like being very long and thin or being wide and flat.

3.1.3 Information from Extracted the DLS and SLS

According to the measure of DLS and SLS, hydrodynamic radii \( (R_h) \) and radii of gyration \( (R_g) \) of the particles in the solution, more structure information of the particle can be obtained from the ratio of \( R_g/R_h \). When all the mass of the particle is distributed on the
surface, the ratio of $R_g/R_h$ is 1; when ratio of $R_g/R_h = 0.77$, the particle exists with solid spherical structure in solution; when the ratio of $R_g/R_h$ is greater than 1, the structures are expected to be rod-like or anistropic. The following figure gives a summary of the different structures.

![Diagram of structures](image)

$R_g = 0.77 R_h$

$R_g \sim R_h$

$R_g > R_h$

Figure 3.4 The relationship between the morphologies of the aggregates with the ratio of $R_g/R_h$.

3.1.4 Sample Preparation for the Light Scattering Studies

In light scattering sample preparation is crucial, so special precautions need to be taken. The reason is dust. The light scattering power of a species is proportional to $MC$ ($M$ is molecular weight; $C$ is weight concentration). That means that the light scattering power of individual particles is proportional to $M^2$. This means that even the tiniest amounts of dust in a sample can be devastating to measurements. Therefore, the precaution against this is cleaning of buffers, sample cells and filtering of finished samples. Filtering the sample through a 200 nm syringe filter is standard procedure. Then the filtered sample is filtered once more through the same filter. The reason is that standard syringe filters often release small amounts of “dust” from the membrane during the filtering procedure. This dust is the retained by the filter during the second round of filtration.
3.2 Zeta ($\zeta$) Potential Analysis

Zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle, which is caused by the net electrical charge contained within the region bounded by the slipping plane, and also depends on the location of that plane. (see Figure 3.5) It is widely used for quantification of the magnitude of the charge. However, zeta potential is not equal to the Stern potential or electric surface potential in the double layer, because these are defined at different locations. The zeta potential is a key indicator of the stability of colloidal dispersions. The magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent, similarly charged particles in a dispersion. For molecules and particles that are small enough, a high zeta potential will confer stability, i.e., the solution or dispersion will resist aggregation. When the potential is small, attractive forces may exceed this repulsion and the dispersion may break and flocculate. So, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate as outlined in the table 3.1.
Figure 3.5 Diagram showing the ionic concentration and potential difference as a function of distance from the charged surface of a particle suspended in a dispersion medium.

Table 3.1 The regular zeta potential vs the stability behaviors of the colloid

<table>
<thead>
<tr>
<th>Zeta potential [mV]</th>
<th>Stability behavior of the colloid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ~ ±5,</td>
<td>Rapid coagulation or flocculation</td>
</tr>
<tr>
<td>±10 ~ ±30</td>
<td>Incipient instability</td>
</tr>
<tr>
<td>±30 ~ ±40</td>
<td>Moderate stability</td>
</tr>
<tr>
<td>±40 ~ ±60</td>
<td>Good stability</td>
</tr>
<tr>
<td>more than ±61</td>
<td>Excellent stability</td>
</tr>
</tbody>
</table>
All the ζ potential analysis measurements were performed on a Brookhaven Instrument Inc. Zeta PALS Analyzer. The instrument is equipped with a red laser operating at 660 nm wavelength and has an accuracy of (2% for filtrated samples. The sample chamber was kept at 25 ± 0.1°C, and all sample solutions were loaded 30 min prior to measurements in order to achieve thermal equilibrium with the chamber.\textsuperscript{53,54}

3.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail—even as small as a single column of atoms, which is thousands of times smaller than the smallest resolvable object in a light microscope. In all my projects, TEM imaging was performed on a JEOL 1200 EXII transmission electron microscope having an accelerating voltage of 120 kV, and 3 µL of the solutions are deposited onto copper grids. After 3 min, the excess solution was wicked away by a piece of filter paper. The sample was then allowed to dry under ambient conditions. TEM images recorded on a digital CCD camera and processed with the accessory digital imaging system.

3.4 Scanning Electronic Microscopy (SEM)

SEM is another high performance surface microscopy method which allows for high resolution images to be obtained on a wide range of samples. A focused beam of electrons
sweeps across a sample surface and an image is created from the scattered electrons. The electron beam allows for the accurate imaging of features below the resolution limit of visible light. The acquired pictures retain good depth of field, resulting in excellent three dimensional images. All SEM imaging was performed on a JEOL 2000FX scanning electron microscope, and 3 µL of the vesicle solutions are deposited onto aluminum stages. The sample was then allowed to dry under ambient conditions.

3.5 Atomic Force Microscopy (AFM)

Atomic-force microscopy (AFM) or scanning-force microscopy (SFM) is a very high-resolution type of scanning probe microscopy (SPM), with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. With this technique, it is possible to measure a roughness of a sample surface at a high resolution, to distinguish a sample based on its mechanical properties (for example, hardness and roughness). For a typical sample preparation, a few drops of solution were transferred onto glass cover slides, and the solvent was allowed to evaporate. They were then placed in a vacuum oven for several hours to ensure the complete removal of the solvent. AFM was used in the tapping mode to determine the overall thickness of the sample. The tapping mode with a carefully chosen cantilever tip-to-sample force was best for limiting damage to the sample. The scanner was 96 calibrated in both the lateral and vertical directions using the standard grid. The typical measurement conditions were a scan size of 20 µm x 20 µm at a scan rate of 1 Hz with operation and resonance frequencies around 300 kHz. The resolution of the captured image was 512 × 512. Atomic force microscopy (AFM, Dimension V, Veeco Instrument Inc., Santa Barbara, CA) was used to measure the morphologies. The controller is Nanscope V (Veeco Instrument Inc., Santa
Barbara, CA). TM 200 Tapping Mode Probes (Tip Radius < 15 nm, f: 145 – 230 kHz, k: 25 – 95 N/m, SansaProbes, Santa Clara, CA) were used under tapping mode.
CHAPTER IV

SELF-ASSEMBLY OF TRIANGULAR POLYOXOMETALATE-ORGANIC HYBRID MACROIONS IN MIXED SOLVENTS

4.1 Introduction

Inorganic-organic hybrids, constructed by covalently linking independent inorganic and organic components together, are not only able to integrate the properties of inorganic (redox activity, magnetism, catalysis, etc.) and organic (good processibility, compatible with organic media, etc.) components into a single molecule, but also exhibit synergistic effects beyond the individual component, making them new promising materials with a range of modular functions. Polyoxometalates (POMs), a large group of giant metal oxide molecular clusters with rich physical and chemical properties and potential applications as electronic and catalytic materials, are commonly used as inorganic components. Of equal importance are the incorporated organic components, which can be engineered with specific properties. Various POM-containing hybrids have been synthesized in the past few years via different approaches. For instance, inorganic-organic hybrids containing single POM component have been synthesized with one or two organic tails. These hybrids show typical surfactant properties with POMs acting as polar head groups and the organic portions acting as hydrophobic tails. They can form regular vesicles or reverse vesicles depending on the solvent mixture, with the solvophobic interaction being the driving force for the self-assembly process. Meanwhile, a series of “dumb-bell” shaped
POM-organic-POM hybrids also display amphiphilic behaviors, forming single molecule layer vesicular structures due to the two polar head groups and one central organic linker each hybrid possesses.61

4.2 Results and Discussion

Two “triangular” shaped POM hybrids, with three large polar POM head groups and a central relatively hydrophobic organic component, are synthesized. It would be interesting to examine how these hybrids behave in solution. They are still expected to be amphiphilic in nature. However, the hydrophilic portions are more dominant than in conventional amphiphilic compounds, making them similar to giant hydrophilic POM macroions.62 As we demonstrated earlier, various hydrophilic POM macroions carrying moderate charges tend to self-assemble into single-layered, hollow, spherical blackberry-type structures due to counterion-mediated attractions. In this project, the self-assembly behaviours of two “triangular” shaped hybrids containing three identical Wells-Dawson polar head groups (Figure 4.1) in water/acetone mixed solvents are investigated to observe the solution behaviour of these hybrids with such unique architectures.

Figure 4.1 (a) Molecular structures of two “triangular” shaped inorganic-organic hybrids and (b) self-assembly process cartoon. Figure (a) top: hybrid 1 TBA15H3- [{P2V3W15O59(OCH2)3CNHCO}3C3N3] with triazine as the organic linker; (a) bottom: hybrid 2 TBA15H3[{P2V3W15O59(OCH2)3CNHCO}3C6H3] with benzene as the organic linker.
The organic linkers of these two “triangular” shaped hybrid macroions are a triazine ring (hybrid 1) and a benzene ring (hybrid 2). These two hybrid macroions still possess well-defined hydrophilic and hydrophobic domains, but their hydrophilic portions are more dominant than the “dumb-bell” shaped hybrids previously studied. Also, their architectures make their external surfaces mainly hydrophilic, possibly making a solvophobic-interaction driven self-assembly more difficult.

The Laser Light Scattering (LLS) technique is used to sensitively detect any possible formation of large assemblies in solution. Particularly, dynamic light scattering (DLS) measurements with CONTIN analysis provide the hydrodynamic radius \(R_h\) of large assemblies and static light scattering (SLS) determines the scattered intensities \(I\) from solutions and the average radius of gyration \(R_g\) of the assemblies. The scattered intensity \(I\) gives relevant information about assembly status, such as concentration \(I \propto C\) and size \(I \propto R_h^2\).

Both the “triangular” shaped hybrids can be dissolved in acetone at 0.10 mg/mL to form a clear, stable solution. The scattered intensities were both only ~75 kcps (for comparison, benzene has a scattered intensity of 85 kcps), suggesting that both hybrids 1 and 2 remain as individual macroions in solution. Whilst keeping the hybrid concentration at 0.10 mg/mL, but using mixed acetone/water solvent systems, with different solvent compositions, the scattered intensities remained very low (~70 kcps) in the hybrid solutions with the water content < 5 vol% or > 35 vol%, suggesting that the hybrids existed as solvated single macroions under these conditions. In contrast, the scattered intensity of the solution increased to ca. 5,000 kcps without any precipitation for the mixed solvent containing 10 vol% water (Figure 4.2), suggesting the formation of large assemblies.
CONTIN analysis from DLS studies on these solutions indicate the existence of assemblies with average hydrodynamic radius \( R_h \) of 38 ± 5 nm and 69 nm ± 5 nm for hybrids 1 and 2, respectively (Figure 4.3), which are angular independent and with narrow size distributions (See Figure 4.4, 4.5). The average radius of gyration \( R_g \) of these assemblies obtained from the SLS measurements are 40 ± 2 nm and 71 ± 2 nm for hybrids 1 and 2, respectively. The \( R_g \) values are almost identical to the corresponding \( R_h \) values, suggesting hollow, spherical structures for the assemblies (a hollow sphere would typically have an \( R_g/R_h \) ratio of 1). This observation is further confirmed by TEM studies (Figure 4.6). The TEM images show that the shape of the assemblies is spherical, and the structure is hollow due to the obvious contrast between the centre area and the shell area, which is consistent with the DLS results. Furthermore, the TEM studies also confirm that the assembly size of hybrid 1 is smaller than that of hybrid 2, which will be explained in the following section.

![Figure 4.2](image)

Figure 4.2 Change of the scattered intensity from a solution of hybrids 1 and 2 as a function of time in water/acetone mixed solvent containing 90 vol% acetone.
Figure 4.3 CONTIN analysis of the $R_h$ distribution of the assemblies of hybrids 1 and 2 in water/acetone mixed solvent containing 90 vol% acetone.

Figure 4.4 CONTIN analysis showing the change of the $R_h$ distribution of vesicles from hybrid 1 in acetone/water mixed solvent containing 90 vol% acetone at different angle.

Figure 4.5 CONTIN analysis showing the change of the $R_h$ distribution of vesicles from hybrid 2 in acetone/water mixed solvent containing 90 vol% acetone at different angle.
For hybrids 1 and 2, we speculate that they form blackberry-type structures and this is driven by the counterion-mediated attractions, similar to macroanionic POMs in solution, instead of forming vesicles via solvophobic interaction. One obvious piece of supporting evidence for this is the kinetics of self-assembly. The hybrids investigated here take a long time (14 days) to complete their assembly and reach equilibrium (see Figure 4.2), while the “dumb-bell” shaped hybrids reach self-assembly equilibrium within 24 hours under the same conditions, suggesting that there could be a high activation energy that must be overcome during the self-assembly process, similar to the blackberry formation process of the macroanions, but different from the self-assembly of the “dumb-bell” shaped hybrids, driven by solvophobic interaction which reach equilibrium quickly. Furthermore, if the hydrophobic effect is the dominant driving force in this case, the assembly process should be much easier and faster in more polar solvents (higher water content in the acetone/water mixed solvents) than in less polar solvents, because stronger hydrophobic interactions would be expected in the former solution (the hydrophobic ligands become better solvated when more acetone is introduced). Although the hydrophobic interactions are not the major driving force for the self-assembly process, it is noticed that the organic linker still affects the self-assembly process, because hybrid 1 forms smaller assemblies than hybrid 2 under the same conditions. Moreover, the assembly size ($R_h$) stays fairly constant throughout the
whole self-assembly process, as shown in Figure 4.7, indicating that the structures are quite stable. Therefore, the increment of the scattered intensity (Figure 4.2) from solutions over time must be due to the increase in the number of the assemblies rather than an increase in assembly size. This observation is in agreement with our previous studies on the self-assembly of POM macroanions.\textsuperscript{65c}

Figure 4.7 CONTIN analysis showing the change of the Rh distribution of vesicles from hybrid 1 in acetone/water mixed solvent containing 90 vol% acetone at different time.

Figure 4.8 Plot of the average vesicle radius ($R_h$) versus the inversed dielectric constant ($1/\varepsilon$) of the solvent for hybrid 1 in water/acetone mixed solvent. These systems seem to show a roughly linear relationship.
When the self-assembly reached equilibrium, it is found that the assembly size displays a linear relationship with the inverse dielectric constant of the solvent, which implies that size can be determined by controlling charge density of the hybrid macroanion, as shown in Figure 4.8.

Another interesting phenomenon being noticed is that the counterions play an important role in this self-assembly process, analogous to POM macroanions. To further study the effect of the counterions on the self-assembly process, the TBA counterions were replaced by protons using a cation-exchange resin column. For a typical experiment, 5 mg of hybrid 1 or 2 was dissolved in 2 mL of acetonitrile. This solution was then applied to a prepacked, cation-exchange resin column (Amberjet 1200 hydrogen form purchased from Sigma-Aldrich) then rinsed with D.I. water and acetonitrile. An additional 20-50 mL of acetonitrile was used to elute the column, and the yellow fraction was collected. The post elution of the hybrid macroanions sample was further washed with 5 mL of diethyl ether to remove organic impurities. The final solution was transferred into a glass culture plate and kept in the dark for several days for the solvent to fully evaporate. A fine yellow-colored powder was collected and could be easily dissolved in water for further characterizations. It was found that, after replacing the TBA counterions with protons, under the same conditions, the average assembly size becomes larger (Figure 4.8). The underlying mechanism could be attributed to the decrease of charge density of the polar head groups, caused by the specific hydrogen bonding between the proton donors and the abundant acceptors on the POM's surface, including the terminal oxo, hydroxo and bound water ligands. In the case of the POMs and TBAs, there is no equivalent hydrogen bonding. The low charge density reduces the repulsion between the polar heads on the
surface of the assembly. Correspondingly, the curvature of the assemblies decreases, leading to a larger assembly size.

Although the counterion-mediated attractions dominate the self-assembly process, the organic linkers still play a role during the self-assembly. Comparing the two hybrids’ organic linkers, the triazine ring linker is less hydrophobic than the benzene ring. Therefore, the hydrophobic interactions between the TBA tails and benzene rings are stronger than those between the TBA tails and the triazine rings. As a result, the stronger hydrophobic interactions between TBAs and the benzene ring mean the TBAs more effectively shield hybrid 2, resulting in the lower charge density observed. Consequently, hybrid 2 assembles into larger structures, as has been confirmed experimentally. Once more, compared with the individual inorganic macroions, the self-assembly processes of such hybrids not only can be adjusted by counterions, solvent compositions, but also by the organic linkers.

4.3 Conclusions

In summary, the “triangular” shaped POM-organic hybrids can slowly self-assemble into large, hollow, spherical blackberry-type structures in polar solvents (see Figure 4.1(b)). Evidence shows that the driving force of the self-assembly is mainly counterion-mediated attraction, similar to the self-assembly process of hydrophilic macroions, instead of the solvophobic interactions which dominate the self-assembly of dumb-bell shaped hybrids.
CHAPTER V

THE SELF-ASSEMBLY BEHAVIORS OF POLYOXOVANADATE-CONTAINING FLUOROSURFACTANTS: SOLVENT-SWELLING EFFECT OUTWEIGHS REPULSIVE INTERACTION EFFECT

5.1 Introduction

Fluorosurfactants are fluorinated chemical compounds that typically consist of a fluorinated hydrophobic “tail” and a hydrophilic “head”. Fluorine atoms in the structure offer distinct properties from the corresponding hydrogenated counterpart. For instance, fluorosurfactants are not only chemically and thermally more stable, but also more effective at lowering the surface tension of solutions, i.e., they are stronger surfactants. The special properties of these materials have attracted heavy attentions from many research fields. Recently, more sophisticated structures such as tubular nano-tubule microstructures and mixed Langmuir monolayers assembled from fluorinated compounds are the current research interests. Their unique structures show great potentials in many biomedical applications. For example, the fluorinated polymers have been extensively investigated as a possible blood substitutes, due to their superb capability of oxygen transporting.

Polyoxometalates (POMs) is a large class of polyanionic, inorganic transition-metal oxide nanoclusters with a broad range of potential applications in catalysis, medicine, and material science. These hydrophilic compounds have well-defined size, shape, charge
and other structural features and they also exhibit the capability of reversible and stepwise multi-electron transfer or storage without significant structural change. Recently these inorganic nanoclusters have been successfully covalently grafted with organic components through various synthetic methods, forming novel amphiphiles of various structures. For example, inorganic–organic hybrids containing single POM component have been synthesized with one or two organic tails. These hybrids show typical surfactant properties with POMs acting as polar head groups and the hydrocarbon organic components acting as hydrophobic tails. They form regular vesicles or reverse vesicles in different solvents with the solvophobic interaction being the driving force for the self-assembly process. Meanwhile, a series of “dumb-bell” shaped POM–organic–POM hybrids also display amphiphilic behaviors and form single molecule layer vesicular structures in solution. When the molecular architecture changes to the “triangular” shape, with three large polar POM head clusters and a central relatively hydrophobic organic linker, slow self-assembly into large, hollow, spherical “blackberry” structures in polar solvents occurs. The driving force of the self-assembly is mainly due to the counterion-mediated attraction, similar to the self-assembly process of hydrophilic macroions, which is distinct from the solvophobic interactions dominating the self-assembly of dumb-bell shaped hybrids.

Currently, the self-assembly behaviors and vesicle structures of organic fluorosurfactants and POMs-containing hydrocarbon surfactants have been extensively studied. To date, to our best knowledge, the POM-containing fluorosurfactants by covalently linking unique hydrophobic fluorinated “tails” with a hydrophilic POM “head” cluster into one molecule unit have not been reported. Therefore their self-assembly
behaviors associated with the unique components in solutions remain unexplored. Hence, the self-assembly behaviors of such novel POM-containing fluorosurfactants in solution may contribute to the better understanding of their physicochemical properties and further help the applications of such type compounds. Here, in this project, we report two typical POM-containing fluorosurfactants covalently linked POV clusters with two fluorocarbon chains of different chain lengths and their self-assembly behaviors in solution.

5.2 Experimental Section

In the following several paragraphs, the materials, instruments and characterizations will be described.

5.2.1 Materials, instruments and characterizations

Two POV-containing fluorosurfactants are constructed by incorporating two fluorocarbon tails onto one Lindqvist-type polyoxovanadate $[V_{6}O_{13} \{(OCH_{2})_{3}CNH_{2}\}]^{2-}$, $[(n-C_{4}H_{9})_{4}N]_{2}[V_{6}O_{13} \{(OCH_{2})_{3}CNH(COO)CH_{2}C_{6}H_{4}CH_{2}CH_{2}(CF_{2})_{5}CF_{3}\}]_{2}^{2-}$ (TBA$_{2}$·6F-V$_{6}$) and $[(n-C_{4}H_{9})_{4}N]_{2}[V_{6}O_{13} \{(OCH_{2})_{3}CNH(COO)CH_{2}C_{6}H_{4}CH_{2}CH_{2}(CF_{2})_{7}CF_{3}\}]_{2}^{2-}$ (TBA$_{2}$·8F-V$_{6}$), respectively, as shown in Figure 5.1. The detailed synthesis and characterization are described in following section.

![Molecular structures](image)

Figure 5.1 Molecular structures of the POV-containing fluorosurfactant with hexavanadate as the huge polar head and two fluorinated tails as nonpolar tails, $[(n-C_{4}H_{9})_{4}N]_{2}[V_{6}O_{13} \{(OCH_{2})_{3}CNH(COO)CH_{2}C_{6}H_{4}CH_{2}CH_{2}(CF_{2})_{5}CF_{3}\}]_{2}^{2-}$ (TBA$_{2}$·6F-V$_{6}$) and $[(n-C_{4}H_{9})_{4}N]_{2}[V_{6}O_{13} \{(OCH_{2})_{3}CNH(COO)CH_{2}C_{6}H_{4}CH_{2}CH_{2}(CF_{2})_{7}CF_{3}\}]_{2}^{2-}$ (TBA$_{2}$·8F-V$_{6}$).
All the chemical reagents used here are purchased from commercial vendors in their highest purity. Hexavanadate triester, \([(n-C_4H_9)_4N]_2[V_6O_{13}\{\text{OCH}_2\text{CNH}_2\}_2](V_6)\) was synthesized according to the literature method.\(^{75}\) Two \(N\)-Hydroxysuccinimide (NHS)-activated fluorocarbon-chain carboxybenzyl compounds, \(F_6\text{-Cbz-NHS}\) and \(F_8\text{-Cbz-NHS}\) were synthesized according to literature methods.\(^{59a}\)

Nuclear magnetic resonance spectrum (\(^1\)H, and \(^{13}\)C) was recorded on a Varian INOVA 400 or 600 MHz instrument and referenced to the deuterated solvent used in the experiment. Chemical shifts (\(\delta\)) are expressed in parts per million (\(\delta\) scale, ppm). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet and/or multiple resonances, br = broad), integration, and assignment. Yields refer to spectroscopically (\(^1\)H NMR spectroscopy) homogeneous materials if applicable. \(^{19}\)F NMR spectra were recorded on a Varian INOVA 400 MHz instrument and referenced externally by the sample replacement method to neat \(\text{CF}_3\text{COOH}\) and chemical shifts were reported relative to \(\text{CF}_3\text{COOH}\). \(^{51}\)V NMR spectra were recorded on a Varian INOVA 600 MHz instrument and referenced externally by the sample replacement method to neat \(\text{VOCl}_3\), and chemical shifts were reported relative to \(\text{VOCl}_3\). Fourier transform infrared spectra (FTIR) were recorded as KBr pellets on a Nicolet 510 FTIR. UV-Vis spectra were recorded on a Varian Cary 100 Bio spectrophotometer. Elemental analyses for C, H, F, N, and V were performed by Galbraith Laboratories, Knoxville, TN.
5.2.2 Synthesis and characterization of hybrid clusters

Figure 5.2 The synthesis method of hybrids TBA$_2$·6F-V$_6$ or TBA$_2$·8F-V$_6$.

An anhydrous CH$_3$CN (1 mL) solution of V$_6$ (100mg, 0.081mmol) and 4-DMAP (2 mg, 0.016mmol) were added to an anhydrous DMF (2 mL) solution of F$_6$-Cbz-NHS (96.2mg, 0.162mmol) or F$_8$-Cbz-NHS (112.6mg, 0.162mmol) (See the above ). The resulting orange solution was stirred under argon gas at room temperature. The reaction was monitored using $^1$H NMR. When the reaction was completed, the solution was added to THF (30 mL) and an orange precipitate was collected by removal of the supernatant by centrifugation. The precipitate was re-dissolved in DMF and re-precipitate with THF or diethyl ether. The process of dissolution and precipitation was repeated for 3 times to remove side products and impurities. Finally, the product TBA$_2$·6F-V$_6$ or TBA$_2$·8F-V$_6$ was dried under vacuum overnight before further characterizations.

TBA$_2$·6F-V$_6$, Yield 169 mg (~ 95%).

$^1$H NMR (600 MHz, DMSO-d$_6$): $\delta$ = 7.32-7.26 (m, 8H; -ArH-), 7.20 (s, 2H; -NH-), 5.05 (s, 12H; -C(CH$_2$O)$_3$-), 4.93 (s, 4H; -Ar(CH$_2$O)-), 3.18-3.14 (t, 16H; (CH$_3$CH$_2$CH$_2$CH$_2$)$_4$N$^+$), 2.88-2.84 (t, 4H; -ArCH$_2$CH$_2$-), 2.57-2.53 (t, 4H; -ArCH$_2$CH$_2$-), 1.56-1.52 (quin, 16H; (CH$_3$CH$_2$CH$_2$CH$_2$)$_4$N$^+$), 1.35-1.26 (sext, 16H; (CH$_3$H$_2$CH$_2$CH$_2$)$_4$N$^+$), 0.95-0.91 ppm (t, 24H; (CH$_3$CH$_2$CH$_2$CH$_2$)$_4$N$^+$);
$^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 162.2, 138.5, 135.1, 128.3, 127.9, 82.4, 64.9, 57.5, 50.9, 35.7, 30.7, 25.3, 23.0, 19.2, 15.3, 15.1, 13.4$ ppm;

$^{19}$F NMR (600 MHz, DMSO-$d_6$): $\delta = -80.7$ (t, 3F; CF$_3$-), -113.8 (m, 2F; CF$_3$CF$_2$-), -122.2 (m, 6F; CF$_3$CF$_2$CF$_2$-), -123.1 (m, 2F; CF$_3$CF$_2$CF$_2$ CF$_2$-), -123.3 (m, 2F; CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$ CF$_2$-);

$^{51}$V NMR (600 MHz, DMSO-$d_6$): $\delta = 136.7$ ppm;

UV-Vis (M$^{-1}$ cm$^{-1}$ in DMSO): $\varepsilon_407 = 1.59 \times 10^5$;

FTIR (KBr): $\nu = 3426$ (br), 3021 (m), 2958 (m), 2860 (m), 1662 (s), 1556 (s), 1475 (m), 1376 (m), 1262 (s), 1181 (m), 1040 (m), 964 (s), 856 (m), 814 (s), 797 (w), 717 (m), 586 (s) cm$^{-1}$;

Elemental analysis calcd. (%) for C$_{72}$H$_{106}$N$_4$F$_{26}$O$_{23}$V$_6$: C, 39.39; H, 4.87; F, 2.50; N, 2.55; V, 13.92; found: C 38.69; H 4.68; F 20.15; N 2.88, V 13.0.

TBA$_2$·8F-V$_6$, Yield 190 mg (98%)

$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta = 7.32-7.26$ (m, 8H; -ArH-), 7.20 (s, 2H; -NH-), 5.04 (s, 12H; -C(CH$_2$O)$_3$-), 4.93 (s, 4H; -Ar(CH$_2$O)-), 3.18-3.14 (t, 16H; (CH$_3$CH$_2$CH$_2$CH$_2$)$_4$N$^+$), 2.88-2.84 (t, 4H; -ArCH$_2$CH$_2$-), 2.56-2.52 (t, 4H; -ArCH$_2$CH$_2$-), 1.56-1.52 (quin, 16H; (CH$_3$CH$_2$CH$_2$CH$_2$)$_4$N$^+$), 1.35-1.26 (sext, 16H; (CH$_3$CH$_2$CH$_2$CH$_2$)$_4$N$^+$) 0.95-0.91 ppm (t, 24H; (CH$_3$CH$_2$CH$_2$CH$_2$)$_4$N$^+$);

$^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 162.3, 138.5, 128.4, 128.0, 115.6, 82.4, 79.6, 64.9, 57.5, 50.9, 46.6, 35.7, 30.7, 23.0, 19.2, 15.1, 13.4$ ppm;

$^{19}$F NMR (600 MHz, DMSO-$d_6$): $\delta = -80.6$ (t, 3F; CF$_3$-), -113.8 (m, 2F; CF$_3$CF$_2$-), -121.9 (m, 6F; CF$_3$CF$_2$CF$_2$CF$_2$F$_2$-), -122.8 (m, 2F; CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$ CF$_2$-), -123.2 (m, 2F; CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$ CF$_2$-), -126.1 (m, 2F; CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$ CF$_2$CF$_2$F$_2$-),
$^{51}$V NMR (600 MHz, DMSO-$d_6$): $\delta = 137.4$ ppm;

UV-Vis (M$^{-1}$ cm$^{-1}$ in DMSO): $\varepsilon_{407} = 1.13 \times 10^3$.

FTIR (KBr): $\nu = 3420$ (br), 3022 (m), 2962 (m), 2864 (m), 1656 (s), 1552(s), 1466(m), 1372(m), 1265(s), 1184 (m), 1044(m), 962(s), 858(m), 816(s), 799(w), 719(m), 583(s) cm$^{-1}$.

Elemental analysis calcd. (%) for C$_{76}$H$_{106}$N$_4$F$_{34}$O$_{23}$V$_6$: C, 38.11; H, 4.46; F, 26.97; N, 2.34; V, 12.76; found: C 37.65; H 4.27; F 24.38; N 2.45, V 11.7.

Preparation of surfactant solution for the self-assembly studies.

The powder of each surfactant was first dissolved in acetonitrile (MeCN) at room temperature, and then deionized water was added dropwise with gentle stirring until the desired solvent ratio was achieved. The solutions were stored at room temperature for use.

5.3 Results and Discussion

Static light scattering (SLS) measurements showed a very low scattered intensity at $\sim 70$ kcps for 0.1 mg/mL of TBA$_2$·6F-V$_6$ in MeCN (the scattered intensity of pure solvent is $\sim 65$ kcps), indicating that the hybrid surfactant molecules remained as individual molecules in pure organic MeCN solution. However, when water was introduced to the MeCN solvent up to water of 65 ~ 95% in volume, the scattered intensity started to increase significantly over time (Figure 5.3A) and large assemblies were observed (Figures 5.3B and C) as revealed by dynamic light scattering (DLS) measurements, showing a peak with very narrow size distribution and an average hydrodynamic radius ($R_h = 43 \pm 2$ nm) under the condition with water content 95vol%. Furthermore, the $R_h$ value is not angular dependence, implying that the assemblies were spherical (Figure 5.3b). From SLS measurements, the average radius of gyration ($R_g$) of the assemblies measured at different
angles was at *ca.* 42 ± 2 nm. The relationship of $R_g = R_h$ for spherical structures indicates that the assemblies are probably hollow spherical vesicles. The TEM image (Figure 5.4A) confirms the vesicular structures by clearly showing a contrast between their walls and centers. SEM image (Figure 5.4b) shows some defects on the vesicle surface, reflecting their hollow nature, which could be generated when putting the samples under vacuum conditions. The formation of vesicular structures was further supported through AFM results when vesicle solutions were coated and dried on a flat surface (see Figures 5.4c and d). The diameter of vesicles measured by the AFM was *ca.* 80 nm, comparable to that of vesicles measured by the DLS (86 ± 2 nm), while the smaller height was of 24 nm reflecting the collapse of vesicle membranes. Each membrane’s thickness (12nm) approximates to the sum of two POMs’ diameter (0.7 nm) and one tail zig-zag length (8.5nm). Based on the above experimental results (laser light scattering and electronic microscopy results) and molecular structure, we deduced that assemblies possess hollow and double layer vesicle structures (see the model in figure 5.2).

The time-resolved scattered intensity of the hybrids in solution was recorded by SLS technique. Interestingly, it was found that the equilibrium took three weeks to reach (Figure 5.3a), but the vesicle size did not change during the process (Figure 5.3c). This observation implies that the scattered intensity increment should be attributed to the increase of vesicle number instead of vesicle size. The vesicle formation was through a closed association mechanism and did not experience any intermediate state (Figure 5.4) and needed high activation energy. The self-assembly process of the regular fluorosurfactant are supposed to complete quickly due to the strongly hydrophobic fluorocarbon chains. However, because of the giant nanosize of the POM polar head and the rigidness of the fluorinated
tails in the two POM-containing fluorosurfactants, the fluorinated tails need to overcome the high energy to bend and form the vesicles. (Figure 5.4)

Figure 5. 3 (a) The change of the scattered light intensity over time in water/MeCN mixed solvent with 5 vol% MeCN content for surfactant TBA$_2$-6F-V$_6$; (b) CONTIN analysis of the $R_h$ distribution of the vesicles of TBA$_2$-6F-V$_6$ in water/MeCN mixed solvent containing 5 vol% MeCN at different angles; (c) CONTIN analysis of the $R_h$ distribution of the vesicles of TBA$_2$-6F-V$_6$ in water/MeCN mixed solvent containing 5 vol% MeCN at different time.
Figure 5. 4 (a) TEM image of vesicular structures of surfactant TBA$_2$·6F-V$_6$ in water/MeCN mixed solvent containing 5 vol% MeCN; (b) SEM image of vesicular structures of TBA$_2$·6F-V$_6$ in water/MeCN mixed solvent containing 5 vol% MeCN; (c) and (d) AFM images of vesicular structures of TBA$_2$·6F-V$_6$ in water/MeCN mixed solvent containing 5 vol% MeCN.

Figure 5. 5 Cartoon of hollow and bilayer vesicle formation occurring in the presence of POM-containing fluorosurfactant and the TBA countercation in MeCN/water mixture.
More interestingly, the vesicle size can be tuned by adjusting the solvent polarity. Solutions of 0.1 mg mL\(^{-1}\) TBA\(_2\)-6F-V\(_6\) in MeCN/water mixed solvents containing 95, 90, 80, 75 and 70 vol\% of water were prepared, respectively. The vesicle sizes measured by the DLS showed a linear relationship with the inverse of the dielectric constant of the solvent. TBA\(_2\)-8F-V\(_6\) shows similar dependence on the solvent polarity which implies both hybrids have similar self-assembly mechanism (Figure 5.6a).

![Figure 5.6](image)

Figure 5.6 (a) Plot of the average vesicle radius (in \(R_h\)) versus the inversed dielectric constant (1/\(\varepsilon\)) of the solvent for TBA\(_2\)-6F-V\(_6\) and TBA\(_2\)-8F-V\(_6\) in water/MeCN mixed solvent; (b) Zeta potential (mv) versus the inversed dielectric constant (1/\(\varepsilon\)) of the solvent for TBA\(_2\)-6F-V\(_6\) in water/MeCN mixed solvent.

There are several interesting observations from Figure 5.6a. Firstly, in the most polar solvents, the two surfactants show almost identical sizes with TBA\(_2\)-8F-V\(_6\) being slightly larger. This is reasonable because for both, the fluorinated-chains pack very tightly to each other in the bilayer due to the solvent nature. Secondly, vesicle size increases with decreasing solvent polarity. This indicates a charge-regulated assembly process. Zeta potential analysis shows higher charge in less polar solvents (Figure 5.6b). Therefore, this trend should be explained as that the solvent coming into the bilayer when the composition of organic solvent increases. This increases the volume of the hydrophobic domain and
therefore larger sizes. The packing parameter has been changed. Finally, the vesicle size of \( \text{TB} \text{A}_2\cdot 8\text{F-} \text{V}_6 \) was always bigger than that of \( \text{TB} \text{A}_2\cdot 6\text{F-} \text{V}_6 \), due to the longer fluorinated tails. These findings are fundamentally important and instructive for design new surfactant materials.

5.4 Conclusions

To understand the self-assembly behaviors of the POM-containing fluorosurfactants in solutions, two unique polyoxometalate-containing fluorosurfactants with hydrophobic fluorinated “tails” and big hydrophilic POM “head” cluster in one molecule unit were synthesized for the first time. The self-assembly of such novel surfactants forming spherical, bilayer and hollow vesicles in solutions and their self-assembly behaviors are thoroughly investigated by using multiple characterizing methods. The solvent-dependent swelling effect is the primary factor in directing the change of vesicle size, while the repulsion among the polar heads plays some role. The fundamental understanding of the self-assembly behaviors of such novel inorganic POM-fluorosurfactants in solution would provide the new knowledge for the development of new materials for potential applications.
CHAPTER VI

THE SELF-ASSEMBLY BEHAVIORS OF GIANTAMPHIPHILIC MOLECULES
(nDPOSS-PS₉₆, n=1,2,3,4) IN SOLUTION

6.1 Introduction

Traditional amphiphiles including small surfactants and linear block copolymers are able to self-assemble into varieties of hierarchical superstructures in selective solvents due to their chemically distinct hydrophobic and hydrophilic components. The self-assembly behaviors of these two traditional amphiphiles have been well studied in literature due to their extensive applications. For small surfactants, it is easy to self-assemble into micelles, cylindrical micelles, vesicles, and reverse micelles, depending on the molecular packing parameter values of the molecules, and the self-assembly processes can be completed quickly due to the fast mobility of the molecules in solution; on the other hand, the linear amphiphilic block copolymers can also self-assemble into varieties of superstructures, but it is hard to determine the morphologies of the superstructures in solution due to the flexible chains, and during the self-assembly processes, the kinetic control are often involved because of high molecule weights of the block copolymers.

With the advancement of technology, traditional amphiphiles could not meet the higher requirements of the materials scientists. Recently, one unique type of giant amphiphilic molecules are designed and successfully synthesized. Such giant amphiphilic
molecules, consisting of nanosized particles as polar heads and polymer as nonpolar tails, not only bridge the gap between the two traditional amphiphiles (small surfactants and amphiphilic block copolymers) at an intermediate length scale of ~10 nm, but also possess advantages of both individual traditional amphiphiles. Compared with the traditional small surfactants, giant amphiphilic molecules are much more versatile to provide a broad platform for structural engineering, because the nanoscale particle polar heads have more surface functional sites. Meanwhile, compared with the amphiphilic block copolymers, the nanosized polar heads not only have well-defined 3D molecular structures, shapes and explicit chemical compositions, but also are relatively independent on solvents (the overall shape and symmetry of nanoscale particles are well defined and can be maintained during the change of the solvent nature or chemical modification). Obviously, nanoscale particles have consistent shapes and the exact number, identity, and positions of the surface functional groups on nanoscale particles can often be determined precisely and varied systematically. It can be concluded that such giant amphiphiles not only possess the amphiphilic properties, but also bring new unique properties and overcome the weaknesses of the traditional small surfactants and block copolymers. Similarly, to build advanced materials with such giant amphiphiles as building blocks through the bottom-up self-assembly method, firstly, the solution behaviors of such giant amphiphilic molecules should also be thoroughly explored, like small surfactants. Although in early experimental studies, it had been pointed out that the giant amphiphiles are similar to small surfactants in solution, based on the phenomenon that the polymer tails in micellar core are highly stretched, exhibiting fast relaxation and self-assembly dynamics. However, there is still lack of solid evidences to support the deduction that the giant amphiphilic molecules are
similar small surfactants. Furthermore, some researchers challenge the concept of the thermodynamic equilibrium morphology of the giant amphiphilic molecules in solution with the belief that the final superstructures are irreversible colloid structures. In this study, the solution behaviors of a series of giant amphiphilic molecules \((n \text{ DPOSS-PS}_{96}, n=1,2,3,4)\) consisting of different number of polyhedral oligomeric silsesquioxane clusters functionalized by dihydroxy groups hydrophilic cluster (DPOSS) and same volume of hydrophobic tail polystyrene (PS) are studied.

6.2 Experimental Section

In this section, the synthesis method of the giant amphiphilic molecules \(n \text{ DPOSS-PS}_{96}\) \((n=1,2,3,4)\) will be described, and the characterization techniques will also presented, and the method of the solutions preparing will also described in details.

6.2.1 Synthesis of a Series of Giant Amphiphilic Molecules \(n\text{DPOSS-PS}_{96}\) \((n=1,2,3,4)\).

A series of giant amphiphilic molecules \((n\text{DPOSS-PS}_{96}, n=1,2,3,4)\) are synthesized according to literature.\(^{80, 82}\) Their molecular structures and cartoons are given in the following figure 6.1.

![Molecular structures and cartoons of a series of giant amphiphilic molecules](image)

Figure 6. 1 The molecular structures and cartoons of a series of giant amphiphilic molecules \((n\text{DPOSS-PS}_{96}, n=1,2,3,4)\) consisting of different number of DPOSS hydrophilic cluster and same number of hydrophobic PS tail.
6.2.2 Laser Light Scattering

Static light scattering (SLS) and dynamic light scattering (DLS) measurements were performed by using a Brookhaven instrument spectrometer that was equipped with laser operating at 532 nm. The sample solutions were filtered with 0.2 µm filter membranes into dust-free light-scattering cells. The sample chamber was thermostatted and could be controlled to within 0.1°C. For DLS measurements, the intensity-intensity time correlation function was measured by means of a BI-9000 AT multichannel digital correlator. The normalized electric field time correlation function was then analyzed by the CONTIN method, which yielded information on the distribution of the characteristic line width that can be used to determine the particles apparent diffusion coefficient D and then the average hydrodynamic radius ($R_h$) through the Stokes-Einstein equation.

\[ R_h = \frac{k_BT}{6\pi \eta_0 D} \]  

Equation 6.1

where $k_b$ is the Boltzmann constant, $\eta_0$ is the viscosity of the solvent, and T is the temperature of the solution. The basis of the SLS is the Rayleigh-Gans-Debye equation, which is used to determine the radius of gyration ($R_g$). SLS experiments were performed at scattering angles of 30 -100° at 2° intervals.

6.2.3 Transmission Electron Microscopy.

Transmission electron microscopy (TEM) was carried out on a Phillips EM410 microscopy operating at an acceleration voltage of 120 kv. Copper grids were precoated with a thin film of formvar and then coated with carbon. 0.01mL of the diluted solution was deposited on the resulting grids. After drying in air overnight, the samples were used for TEM studies.
6.2.4 Preparation of the Giant Amphiphilic Molecules Solution for the Self-assembly Studies

Due to large fraction of hydrophobic portion in the whole amphiphilic molecule, such giant amphiphiles could not, like traditional small surfactants, self-assemble into large supramolecular structures in polar solvent by directly dissolving. To prepare stable solutions of the supramolecular structures, such giant amphiphilic molecules were firstly dissolved in a common solvent dimethylformamide (DMF) for both hydrophobic components PS and hydrophilic components DPOSS. Subsequently, water was slowly added by a pump at 100 µL/hour with strong stirring such that the quality of the mixed solvent gradually decreases for the PS tail. When the supramolecular structures were formed from a homogeneous solution by water addition, a micro-phase separation process was involved. Scattered intensity from the SLS is used to explore the phase separation behaviors of the giant amphiphiles as a function of added water content (Figure 6.2 a). It was found that the giant amphiphiles in DMF undergo microphase separation when the added water content reached critical water content (CWC) value. The critical water content (CWC) is defined as the amount of added water at which the supramolecular structures start to form, and is determined from the sudden change of the scattered intensity in the course of water addition. It shows that the supramolecular structures start to form at CWC 9.73 vol%. Before reaching CWC, the change of the scattered intensity is small (from 41.5 kcps to 68 kcps) due to the tiny change of physical properties of the mixed solvent (like refractive index and viscosity). However, the scattered intensity suddenly jumps from 68 kcps to 1000 kcps at CWC, because the large nanoparticles are formed. The scattered intensity continues to increase until to reach plateau 16790 kcps at water content of 21.5
vol%, because the number and size of assemblies increase \((I \propto CR^2)\). During the process of adding water, the aggregation number \(N_{agg}\) increases to avoid the contact surface between the hydrophobic part and the solvent due to the polarity of the solvent increase when the \(R_h\) increases with the increase of the water content (Figures 6.2 b and c).

6.3 Results and Discussion
Thermodynamics of the Self-Assembly process and the morphologies of the assemblies will be discussed in the following two sections.

6.3.1 The Study of Thermodynamics of the Self-Assembly

Furthermore, in order to prove conclusively that the supramolecular structures are thermodynamically stable, one reversible experiment of the assembly size is designed. It is found that the self-assembly processes are reversible with the change of the mixed solvent polarity. For instance, during the process of water addition, the supramolecular structure sizes are 56 nm and 69 nm, in the mixed solvent DMF/water with water content 15 vol% and 20 vol%, respectively. If the mixed solvent composition is adjusted in the opposite direction, i.e. add the DMF organic solvent to the mixed solvent with water content from 20 vol% to 15 vol%, the size of the supramolecular structure correspondingly decreases from 69 nm to 56 nm. This result further proves that the supramolecular structures are not frozen during the above two opposite processes. Furthermore, the assembly solution containing 20 vol% water was kept being monitored at room temperature for three weeks. The supramolecular structures size did not change with time (Figure 6.2d), even after being kept at 50 degree (Figure 6.2e), which further proves that the supramolecular structures are thermodynamically stable. To further prove the nature of the supramolecular structures, the assembly solutions are prepared by two different approaches: direct dissolution method
(DD) and water addition method (WD). For the DD method, the giant amphiphilic molecules are directly dissolved in the mixed solvent with desired composition and the solution was sonicated for two hours and then left for three weeks. For the WD method, the giant amphiphilic molecules are firstly dissolved in DMF and then water is slowly added until the desired water content. From the CONTIN analysis, it is found that the supramolecular structures sizes prepared with the above two methods are very close, and the distribution of the Rh method is broader than that by WD method (Figure 6.2 f). The reason could be that for the DD method, the time is not enough long to reach the equilibrium. This is another confirmation that the assemblies are in thermodynamic equilibrium.

![Figure 6.2](image-url)

Figure 6.2 (a) The change of the scattered light intensity with water content for giant amphiphile 2DPOSS-PS96; (b) Rh change with the added water content for giant amphiphile 2DPOSS-PS96; (c) CONTIN analysis of the superstructure of the 2DPOSS-PS96 in water/DMF mixed solvent with different water contents; (d) CONTIN analysis of superstructure of the 2DPOSS-PS96 in water/DMF mixed solvent with water content 20 vol% at different time; (e) CONTIN analysis of superstructure of the 2DPOSS-PS96 in water/DMF mixed solvent with water content 20 vol% at different temperatures; (f) CONTIN analysis of superstructure of the 2DPOSS-PS96 in water/DMF mixed solvent with water content 20 vol% by different preparing methods.
6.3.2 Study of the Morphologies of the Assemblies

In this section, the solution behaviors of a series of topological amphiphiles (nDPOSS-PS\textsubscript{96}, n=1,2,3,4) that have identical hydrophobic volume V\textsubscript{PS} but different numbers of hydrophilic cluster DPOSS, are compared with each other. An exceptional sensitivity of the resulting superstructures to molecular topology was observed, as shown by the TEM images in figure 6.3. The morphologies change from cylinder micelles, vesicles to reverse micelles with the decrease of the number of the polar head groups. This phenomenon can be explained in terms of molecular packing parameter. The concept of molecular packing parameter (P), as a very important term in surfactant science, is widely invoked in the literature to explain, rationalize and even predict molecular self-assembly in small surfactant solutions. The molecular packing parameter is defined as

\[ P = \frac{v}{l \times a_0} \]  

Equation 6.2

where v is the surfactant tail volume, l is the tail length, and a\textsubscript{0} is the equilibrium area per molecule at the aggregate surface. A particular value of the molecular packing parameter can be translated via simple geometrical relations into specific shape of the equilibrium superstructure (see table 6.1), which is the predictive application of the concept of molecular packing parameter, as discussed in the literature. The formation of various micelle structures is thus characterized by the value of P. If P < 1/3, spherical micelles are formed; if 1/3 < P < 1/2, cylindrical micelles are favored; if ½ < P < 1, bilayer vesicles are produced; if P approaches 1, bilayer planers are expected; while if P > 1, reversed micelle structures are constructed. According to previous work, the packing parameter values of each giant surfactant are given in table 2. The detailed calculation could refered the
literature. The packing parameter values can give a reasonable explanation for the
different morphologies.

The giant amphiphilic molecule 4DPOSS-PS$_{96}$, which has bigger hydrophilic volume,
leading to significant steric interaction, has the P value of 0.37, greater than 1/3, smaller
than 1/2, which is expected to result in cylinder micelle morphology. The expected
morphology is confirmed by the TEM image (Figure 6.3a). Meanwhile, DLS results show
the $R_h$ is 32 nm (table 6.2). When the number of the DPOSS cluster decreases, the steric
interaction also becomes less significant, the P value increase. Therefore, the P values of
the 3DPOSS-PS$_{96}$ and 2DPOSS-PS$_{96}$ are 0.49 and 0.74, respectively. According to the
relationship between the morphologies of the superstructures and the specific value of the
molecular packing parameter, the expected morphologies are cylinder micelles and vesicles,
respectively, as shown by the TEM images (Figure 6.3 b, c). The DLS results show that
the superstructures are 45 nm and 65 nm, respectively. The giant amphiphile DPOSS-PS$_{96}$,
has the packing parameter value of 1.37, greater than 1, which means that this amphiphile
should self-assemble into reverse micelles. However, TEM image and DLS results give
aggregates (Figure 6.3 d and table 6.2), significantly bigger than the reverse micelles. The
only explanation should be that reverse micelle cannot stably stay in the mixed solvent
(consisting of water 20 vol% and DMF 80 vol%) with strong polar property, which causes
the reverse micelles to further aggregate.

Table 6. 1 The molecular packing parameter values of the traditional small surfactants
correspond to the morphologies of the superstructures.

<table>
<thead>
<tr>
<th>P =v/(a$_0$ *l)</th>
<th>$P \leq 1/3$</th>
<th>$1/3 &lt;P&lt;1/2$</th>
<th>$1/2 &lt;P&lt;1$</th>
<th>$P&gt;1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>morphology</td>
<td>spherical micelle</td>
<td>cylinder</td>
<td>bilayer</td>
<td>reverse micelle</td>
</tr>
</tbody>
</table>

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Table 6. The self-assembly behaviors from different DPOSS-PS$_{96}$ amphiphile in DMF/water.

<table>
<thead>
<tr>
<th></th>
<th>$P = \frac{V}{(\alpha^*l)}$</th>
<th>$R_h$</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>4DPOSS-PS$_{96}$</td>
<td>0.37</td>
<td>32 nm</td>
<td>rod-like micelle</td>
</tr>
<tr>
<td>3DPOSS-PS$_{96}$</td>
<td>0.49</td>
<td>45 nm</td>
<td>vesicle</td>
</tr>
<tr>
<td>2DPOSS-PS$_{96}$</td>
<td>0.74</td>
<td>65 nm</td>
<td>vesicle</td>
</tr>
<tr>
<td>DPOSS-PS$_{96}$</td>
<td>1.32</td>
<td>180 nm</td>
<td>reverse micelle, aggregate</td>
</tr>
</tbody>
</table>

Figure 6.3 TEM images of the giant amphiphiles nDPOSS-PS$_{96}$, (n = 1,2,3,4) in mixed solvent with water content 20 vol%.

Figure 6.4 CONTIN analysis of the superstructures of a giant amphiphiles nDPOSS-PS$_{96}$, (n = 1,2,3,4) in mixed solvent with water content 20 vol%.
6.4 Conclusion

This class of giant amphiphiles are precisely-defined amphiphilic macromolecules that not only capture the essential structural features of the traditional small surfactants, at larger sizes, but also have similar solution behaviors with the small surfactants. In polar solvent, these giant amphiphiles are indeed found to readily undergo microphase separation and self-assemble into various ordered morphologies. Furthermore, an exceptional sensitivity of the resulting structures to the molecular topology was observed. The particular values of the molecular packing parameter can be translated via simple geometrical relations into specific shape of the equilibrium aggregate. This project has greatly improved our understanding of the thermodynamics and kinetics of the self-assembly processes of the giant amphiphiles and opened enormous opportunities in modern nanotechnologies.
CHAPTER VII

The SELF-ASSEMBLY STUDY OF THE POM-CONTAINING HYBRIDS WITH TWO PEPTIDE TAILS IN SOLUTION

7.1 Introduction

Hybrid molecules are promising materials to develop micro-devices for various applications ranging from catalysts, photovoltaic cell, to molecular magnetism. Among these molecules, POM-based hybrids are one of the most attractive materials due to their desired electronic and optical properties. POMs, a large group of metal oxide clusters, are ideal building blocks to develop novel hybrid materials. Over the past two decades, the syntheses of POMs-based hybrids have received continuous attention. Incorporating organic molecules into inorganic POMs can improve the compatibility due to the combination with hydrophilic and hydrophobic domains, thus extending their applications. For example, the Lindqvist-type POMs functionalized with pyrene groups showed fluorescence-enhanced properties during the self-assembled process, which might be potential smart molecules for fluorescent probes. Another example is highly stable catalyst based on POM and metal-organic framework (MOF) with high surface area as a heterogeneous acid catalyst. These hybrids reshape our fundamental views of materials.

Meanwhile, more scientists start to focus on the supramolecular structures assembled by POM-based hybrids. As we know, the properties of the supramolecular structures are
not only dependent on the chemical composition of hybrids but also controlled by the arrangement of the individual molecule. The driving forces of the self-assembly process provide a pathway to construct and control these supramolecular structures. For the self-assembly of the POM macroanions in solution, several driving forces including counterion-mediated interactions, H-bonding, Van de Waals interactions, hydrophobic interactions have been discussed. Owing to the charges of pure inorganic POMs, the counterion-mediated attraction is the major driving force for the self-assembly process of the POMs, leading to single-layer, hollow and spherical “blackberry” structures. Since the POM-based hybrids contain organic groups, other non-covalent interactions should be considered during the self-assembly. Previous study showed that vesicle structures were formed by POM-based hybrids with two alkyl chains in acetonitrile/water mixture solutions, mainly resulting from the strong hydrophobicity of alkyl tails with counterion-mediated interactions. An interesting following question is what will happen if the hydrophobicity of tails is reduced, or fully hydrophilic tails are grafted onto POMs domains. In this project, the self-assembly behaviors of POM-based hybrids with two peptide tails will be studied in solution. As peptides have polar or charged functional groups, different contributions to the self-assembly process are expected. To explore the self-assembly mechanism, the solution behaviors of a series POM-peptide hybrids are compared with each other. The self-assembly processes are monitored and characterized by Laser light scattering (LLS), Transmission electron microscopy (TEM), 2D NMR technique and ion-mobility mass spectrometry (IMS-MS).
7.2 Experimental Section

In this section, POM-peptide hybrid solution will be prepared and ESI-IMS-MS, SLS, TEM and NMR will also be used to monitor and characterize the self-assembly process.

7.2.1 Ion Mobility Mass Spectrometry (IM-MS)

ESI-IMS-MS experiments were carried out with Waters Synapt G1 HDMS quadrupole/time-of-flight (Q/TOF) mass spectrometer (Waters, Milford, MA), equipped with a traveling wave ion mobility device. Samples with concentration of 5 µg/mL were injected to the instrument with a flow rate of 20 µL/min. Instrument parameters were adjusted as follows: ESI capillary voltage, 3.16 kV; sample cone voltage, 35 V; extraction cone voltage, 3.2 V; desolvation gas flow, 500 L/h (N₂); trap collision energy (CE), 6.0 eV; transfer CE, 4.0 eV; trap gas flow, 1.5 mL/min (Ar); IM gas flow, 22.7 mL/min (N₂); source temperature, 50 °C; desolvation temperature, 150 °C; IM traveling wave velocity, 200 m/s; and IM traveling wave height, 10.0 V. All of the mass spectra were obtained in negative mode. Therefore, the observed ions were formed by either loss of a counterion, [M - TBA]⁻, loss of a proton possibly from the carboxylic acid ends, [M - H]⁻, or even both, [M - TBA - H]²⁻. Ions with different charges were observed depending on the number of TBA or H losses.

7.2.2 Laser Light Scattering

Dynamic light scattering (DLS) and static light scattering (SLS) data were measured on a Brookhaven Instruments Inc. light scattering spectrometer, equipped with a diode-pumped solid-state (DPSS) laser operating at 532 nm and a BI-9000AT multichannel digital correlator. The SLS was performed over a broad range of scattering angles from 30° to 90°, with a 2° interval. The radius of gyration \( R_g \) was calculated using a partial Zimm
plot derived from the Rayleigh-Gans-Debye equation. The partial Zimm plot stems from the following approximate formula: \( \frac{1}{I} = C(1 + R_g \cdot q^2) \). The \( R_g \) was determined from the slope and intercept of a plot of \( \frac{1}{I} \) vs \( q^2 \). For DLS measurements, the intensity-intensity time correlation functions were analyzed by the constrained regularized (CONTIN) method. The average apparent translational diffusion coefficient, \( D_{\text{app}} \), was determined from the normalized distribution function of the characteristic line width, \( \Gamma(G) \). The hydrodynamic radius \( R_h \) was converted from \( D \) through the Stokes-Einstein equation: \( R_h = kT/6\pi\eta D \), where \( k \) is the Boltzmann constant and \( \eta \) is the viscosity of the solvent at temperature \( T \).

7.2.3 Transmission Electron Microscopy (TEM)

The TEM images were taken on a JEOL JEM-1230 electron microscope operated at 120 kV. Samples for the TEM analysis were prepared by dropping a small volume of the solution onto a carbon film on a copper grid and drying for several days.

7.2.4 Nuclear Magnetic Resonance Spectroscopy (NMR)

All 1D \( ^1H \) NMR measurements in the liquid state were measured on a Varian NMRS 500 spectrometer equipped with a 5 mm dual broadband probe. 2D nuclear Overhauser enhancement spectroscopy (2D NOESY) experiments were performed on Varian INOVA 750 with 256 \( t_1 \) increments and 16 scans. The relaxation delay varied from 1 to 2 s, and the mixing time changed from 0.2 to 0.6 s. Base line correction and noise reduction were performed when appropriate. 2D Diffusion Ordered Spectroscopy (2D DOSY) experiments were performed on Bruker 500 MHz spectrometer with the magnetic field gradient \( g \) varying from 0 to 32 G/cm in 16–32 steps. All spectra were taken at room temperature. The raw data was fit by CONTIN methods.
7.3 Results and Discussion

The self-assembly of the POM-peptide hybrids in solutions will be described and mechanism will be discussed.

7.3.1 Hybrids Structures

A series of POM-peptide hybrids were synthesized (See figure 7.1). Two identical peptide chains were symmetrically grafted on Anderson, with TBA as the counterions. The six peptide chains with different length were chosen. All six hybrids had two carboxylic acid groups as end functional groups. The synthesis route has been published in the previous paper.\textsuperscript{89}

![Figure 7.1 Molecular structures of six POMs-peptide hybrids.](image)

7.3.2 The Self-Assembly of POM-Peptide Hybrids in Acetonitrile/water Mixed Solvents

These POM-peptide hybrids were quite soluble in polar organic solvent such as acetonitrile (MeCN) and dimethylformamide (DMF) but less soluble in water due to the
TBA counterions. To prepare the solutions, the hybrids were first dissolved in MeCN, then water was slowly added with stirring to keep the solutions homogeneous. Supramolecular structures were observed in the MeCN/water mixed solvents with MeCN volume content from 10% to 80%. From the results shown in figure 7.2, there exist lag phase (low scattering intensity) around 5-10 days in the self-assembly process. All scattered intensity increases sharply at different critical points and continues to increase until the plateau state, indicating the formation of large structures. The similar increase trends of the scattered light from the six hybrids show that all six hybrids follow similar solution behaviors regardless of their chain length.

Figure 7.2 (a) The scattered intensity of the six hybrids at different time in mixed solvent with water vol 50%. (b) TEM images of the supramolecular structures from TBA-Phe with concentration 0.2mg/mL in mixed solvent with water vol 50%. (c) CONTIN analysis of the hybrid TBA-Phe solutions 0.2mg/mL at different angles in mixed solvent with water vol 50%, $R_{h,0} = 69.5$ nm.

7.3.4 The Mechanism of Self-Assembly Processes

For POM-based hybrids such as Anderson POMs with two long alkyl chains, the self-assembly process is drive by hydrophobic interaction, forming vesicle in polar mixed solvent. The peptide tails especially Ala and Gly are more hydrophilic than alkyl chains, so they maybe change the self-assembly mechanism of these POM-peptide hybrids. 2D
NOESY NMR technique was applied to study the interaction between TBA counterions and POM-peptide hybrid clusters. The nuclear Overhauser effect (NOE),\(^9\) which relies on spatial distance between two protons, could give an overview about how close two protons are.\(^9\) There are two possible interactions between TBA with POM-peptide hybrid clusters, either bound to Anderson POMs or close to negatively charged peptide tails. The NOESY spectrum of the self-assembly of the TBA·Ala is given in Figure 7.3. The negative NOE cross peaks (rectangle) indicate strong binding between TBA and clusters. However, no obvious cross peaks were observed between the peptide tails and TBA, which suggests far distance (>5 Angstrom). In order to achieve strong binding, TBA counterions are likely to be associated with POMs.

Figure 7.3 (a) 2D NOESY spectrum of TBA·Ala in D\(_2\)O/Acetonitrile-d\(_3\) mixed solvent. Signal A comes from TBA counterions and signal B comes from the peptide tails. The negative NOE peaks are highlighted with solid rectangular. (b) \(R_H\) of TBA-Phe supramolecular structures at different temperatures. (c) \(R_H\) of TBA-Phe supramolecular structures at different concentration (d) Illustration of single layer blackberry-like formation process.
Moreover, the $R_h$ value has an unexpected dependence on temperature and concentration, and the disassembly process can be further controlled by increasing the concentration or decreasing the temperature. This smart, multi-stimuli responsive self-assembly reveals the essentiality of charged chains, which can be correlated to the deprotonation degree of carboxylic acid groups. Compared POM-peptide hybrids with the Anderson POM-alky chains hybrid and Lindqvist POM-pyrene hybrids, the self-assembly of POM-peptide hybrids is different because the charged tails are much more hydrophilic. In previous studies, supramolecular structures were only observed due to solvophobic interaction. However, POM-peptide hybrids are different since the peptide tails and POMs are both soluble in acetonitrile/water mixed solvent.

The IM-MS technique can track the charge states of the hybrids at the molecular level. The mass spectrum of the hybrid TBA·Phe shows a molecular ion peak at m/z 2134 (Figure 7.4). As we early mentioned that blackberry formation involves the oligomer stage. During the ionization, the formation of different multiply charged ions of oligomers result in overlapping of isotope patterns of the monomer and those oligomers at the same m/z value (m/z 2134). Here, the IM-MS technique proved to be very useful for the separation of ions based on their size and charge state. The monomer and oligomers were successfully separated along the drift time scale through this technique. Three major species were observed at m/z 2134. They were the monomer with one negative charge due to one TBA loss, the dimer with two negative charges due to two TBA losses, and the trimer with three negative charges due to three TBA and H losses, viz. $[\text{M-TBA}]^-$, $[2\text{M-2TBA}]^{2-}$, and $[3\text{M-3TBA}]^{3-}$, respectively. The presence of dimer and trimer species proves that the self-assembly of these POM-peptide hybrids follows the blackberry formation process.
7.3.4 Exploring Size-Rule

The self-assembly of POMs which is dominant by counterion-mediator attraction, the blackberry size can be tuned via adjusting solvent polarity.\cite{20} Given concentration (0.2mg/mL) solutions were prepared in MeCN/water mixture solutions, and $R_h$ was measured when the scattering intensity reaches plateau stage. Unexpectedly, instead of showing a linear relationship between blackberry size and solvent polarity, the size-rule of these POM-peptide hybrids seems to be more complex, as shown in figure 5. This indicates that multi-type driving forces may play role during the self-assembly. In order to understand how different driving forces affect the size-rule, the potential driving forces,
counterion-mediated attraction, hydrogen bonding, hydrophobic interaction, were explored respectively.

Figure 7.5 (a) $R_h$ of the supramolecular structures of the six hybrids in the acetonitrile/water mixed solvent. (b) 2D DOSY spectrum of the hybrid TBA-Phe in acetonitrile-d3. (c) 2D DOSY spectrum of the hybrid TBA-Phe in D$_2$O/Acetonitrile-d3 mixed solvent.

For the charged hybrids, the counterion-mediated attractions play an important role in the self-assembly process. The negative charge contribution is from the deprotonation of carboxylic acid groups and the disassociation of TBAs. The temperature and concentration are two important factors to the self-assembly due to the role of carboxylic acid groups. The increase of the solvent polarity can induce the carboxyl group to deprotonate. On the other hand, diffusion-ordered spectroscopy (DOSY) NMR could be applied to study the relationship between disassociation of the counterions TBA and solvent polarity. In pure acetonitrile, the diffusion of TBAs is slightly faster than the hybrid clusters, which means that TBAs are partial released from cluster. However, when more water is added to acetonitrile, the TBAs diffuse obviously quicker than the hybrid
clusters, which mean that the TBAs are disassociated from the hybrid clusters at high water content.

Because the deprotonation of carboxylic acid groups and the TBA disassociation are both favored at high water content, there is a linear relationship between the overall charge and the solvent polarity. The hydrophobic interaction can be easily ruled out by observing the scattered intensity of TBA-Phe, TBA-PhePhe and TBA-PhePhePhe (see Figure 7.2). The reason is that if the hydrophobic interaction is the dominant driving force, the scattered intensity of the hybrid TBA-PhePhePhe should be strongest compared to TBA-Phe and TBA-PhePhe, due to the strongest hydrophobic interactions between tails. The hydrogen bonding, a well-known force in peptide science, may contribute to the self-assembly. The temperature will affect the self-assembly if the hydrogen bonding dominate during the self-assembly due to the sensitivity of the hydrogen bonding to temperature. It is worth noting that the electrostatic interaction should not be fully ignored because the temperature can also affect the deprotonation.

In order to further understand the hydrogen bonding effect, the hybrid clusters were prepared in H2O and D2O with identical concentration. Due to the strong repulsion force in pure water, no large supramolecular structures were observed. To decrease the repulsion between the charged ions, additional sodium chloride was added to trigger the self-assembly. From the results (see Figure 7.6), the Rh difference becomes more obvious with the adding salt, which imply that the hydrogen bonding is not dominant, because the sodium ion can screen the charge more effectively, while the difference of hydrogen bonding remain almost same. In polar mixed solvent, the weak hydrogen bonding and strong electrostatic interaction simultaneously affect the size of the supramolecular
structures. It is concluded that at high water content, the electrostatic interaction is dominant, which leads to charge-regulated mechanism (linear increase on size), while at low water content, the electrostatic interaction decreases dramatically, the dominant hydrogen bonding induces the size decreasing.

Figure 7.6 (a) Hydrodynamic radius of TBA∙Ala depending on sodium concentration in H₂O and D₂O solutions. (b) DLS results of 1mg/mL Na∙PhePhePhe in H₂O solution. (c) TEM images from 1mg/mL Na∙PhePhePhe.

7.3.6 Effect of TBA Counter-Ions

It is well known that counterions play an important role during the charge-regulated self-assembly. Considering that the TBAs are more complex than sodium ions, the TBAs were replaced by sodium ion through sodium ion-exchange resin. The hybrid clusters with sodium ion, named Na∙PhePhePhe, can be easily dissolved in pure water. Interestingly, unlike the TBA∙PhePhePhe, which takes weeks to self-assemble, the Na∙PhePhePhe will self-assemble immediately after adding water. One explanation is that the hybrids with sodium ion are more amphiphilic than hybrids with TBA as counterions, although the PhePhePhe peptide tails remain relatively hydrophobic. The sodium ion changes the amphiphilic properties of hybrids, which kinetically affects the self-assembly processes. It is suggested that the supramolecular structures of Na∙PhePhePhe could be vesicle because
the shape amphiphilic properties of Na·PhePhePhe in water, where the tails prefer to bend themselves rather than staying outside.

7.4 Conclusions

In this project, the self-assembly behaviors of six POM-peptide hybrids have been studied. Regardless of the peptide chain length, these hybrids exhibit similar solution behaviors, due to the same molecular architecture with end-functional carboxylic groups. Instead of forming double-layer vesicle structures, they followed the single-layer blackberry formation, resulting from the charged properties of peptide chains. The temperature and concentration could control self-assembled process via controlling the deprotonation degree. The relationship between the blackberry sizes and the solvent polarity is more complicated than simple charged-regulated process, because the electrostatic interaction and hydrogen bonding are involved simultaneously.
CHAPTER IX

SUMMARY

The self-assembly behaviors of macroions (including polyoxometalates, nanocages, and quantum dots) and amphiphilies (including traditional small surfactants, amphiphilic block co-polymers, and giant surfactants) in solutions are studied. We focus on the mechanism of the self-assembly process, the morphology control of the superstructures through the internal and external conditions, such as the composition of the giant amphiphilies, molecular architectures, solvent nature, temperature, concentration, and the added salts. Based on knowledge of the physical chemistry, colloid and polymer science, the self-assembly behaviors of the macroions and amphiphiles are explored in terms of thermodynamics and kinetics.

“Triangular” shaped POM hybrids, which consist three large polar POM head groups and a central relatively hydrophobic organic component within one molecule unit, are still expected to be amphiphilic in nature. However, they are found that they can slowly self-assemble into large, hollow, spherical “blackberry” structures in polar solvents. The driving force of the self-assembly is mainly counterion-mediated attraction, similar to the self-assembly process of hydrophilic macroions, which is distinct from the solvophobic interactions dominating the self-assembly of “dumb-bell” shaped hybrids. The reason is that the hydrophilic portions are more dominant than in conventional amphiphilic compounds, making them similar to giant hydrophilic POM macroions.
Two novel POM-containing fluorosurfactants \([((n-C_4H_9)_4N)_2[V_6O_{13-}\{(OCH)_3CNH(COO)CH_2C_6H_4CH_2CH_2(CF_2)_5CF_3\}_2] \text{ (TBA}_2\cdot 6F-V_6) \) and \([(n-C_4H_9)_4N)_2[V_6O_{13-}\{(OCH)_3CNH(COO)CH_2C_6H_4CH_2CH_2(CF_2)_5CF_3\}_2] \text{ (TBA}_2\cdot 8F-V_6) \) are designed and successfully synthesized. They can self-assemble into hollow, double-layer vesicle structures. It is found that the vesicle sizes demonstrate dynamic change over different solvent composition: the vesicle sizes increase with the increase of the organic solvent content. This trend is opposite to regular surfactants’ behaviors in solution. The main reason could be the solvent-swelling of the fluoro-chains. The repulsion among the polar heads plays negligible roles during the self-assembly process. The number of charges on the POVs changes over the solvent polarity as well, but its effect on the self-assembly is negligible.

A series of giant amphiphilic macromolecules \((n\text{DPOSS-PS}_{96}, n=1,2,3,4)\), consisting of nanosize polyhedral oligomeric silsesquioxane clusters functionalized by dihydroxy groups (DPOSS) as hydrophilic component and polystrene (PS) as hydrophobic component, were studied in solution. In polar solvent, these giant amphiphiles are found to readily undergo microphase separation and self-assemble into various ordered morphologies, like micelles, cylindrical micelles, vesicles, and reverse micelles. Furthermore, the sensitivity of the resulting superstructures to molecular topology is observed. The particular values of the molecular packing parameter can be translated via simple geometrical relations into specific shape of the equilibrium superstructures.

UV-vis, FTIR, NMR, Mass spectrometer and GPC et.al. techniques are used to characterize the macroions and polymer materials. Laser Light Scattering (LLS), Zeta
Potential, AFM, SEM, TEM are used to characterize the morphologies of the assembly nanoparticles.

Such research work can help understand biological systems, drug delivery and designing advanced materials, and will provide many prospects for interesting, cutting edge study.
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