SOLUTION BEHAVIOR OF DUMBBELL-SHAPED FULLERENE MACROIONS

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Ruixin Li

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SOLUTION BEHAVIOR OF DUMBBELL-SHAPED FULLERENE MACROIONS

Ruixin Li

Thesis

Approved:	Accepted:
Advisor Dr. Tianbo Liu	Department Chair Dr. Mark D. Soucek
Committee Member Dr. Nita Sahai	Dean of the College of Engineering and Polymer Science Dr. Craig Menzemer
	Dean of the Graduate School Dr. Suzanne Bausch
	Date

ABSTRACT

Dumbbell- and bola-shaped surfactants are commonly expected to self-assemble into vesicles with condensed hydrophobic domains due to the dominant hydrophobic interaction. Meanwhile, macroions are expected to self-assemble into porous blackberry structure due to counterion-mediated interaction. Which structure will be formed by dumbbell-shaped macroions and what is the main driving force? It is reasonable to assume that the study on dumbbell-shaped macroions can help people have further understanding of vesicles, blackberry structure, and counterion-mediated interaction. Moreover, the unique permeability of blackberry structure may provide some reference significance in biology research on ion transport.

In this work, a series of dumbbell-shaped fullerene macroions (AC_{60}-C_6H_4-AC_{60}, AC_{60}-PEG_n-AC_{60}, n denotes the number of repeat units) are applied as a model system to studied the features of assemblies formed by dumbbell-shaped macroions. We examined the assemblies of these macroions and found that they assemble into hollow, spherical structures and the main driving force is counterion-mediated interaction. Besides, the length and hydrophobicity of organic linker were found as significant factors that can affect the size of assemblies.

ACKNOWLEDGEMENT

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CHAPTER I

INTRODUCTION

1.1. Introduction of fullerene macroions

1.1.1. Overview of macroions

It is challenging to understand electrolyte solutions due to the coexistence of many different intermolecular and intramolecular interactions (such as electrostatic interactions, van der Waals forces and hydrogen bonds).[1] Based on ion sizes, electrolyte solutions can be classified to simple ionic solutions and colloidal solution, in which solutes are simple ions (< 1nm) and charged colloidal particles (10nm~100nm) respectively. Simple ionic solution is well described by Debye-Hückel theory[2] and its extended form, while Derjaguin-Landau-Verwey-Overbeek theory (DLVO theory)[3] attributes to the stability of charged colloids to the competition between attractive van der Waals forces and repulsive electrostatic interactions in solutions. Whereas, when it comes to how macroions (1nm~10nm) behave in solutions, Debye-Hückel theory and DLVO theory cannot be applied due to the large size of macroions and their stability. These large ions cannot be regarded as point charges, and they do not precipitate and form homogenous solutions which are thermodynamically stable. These features lead to unique solution behaviors of macroions, which are different from the solution behavior of simple ions and colloids, inspiring various studies on them. Macroions are common, including polyhedral oligomeric silsesquioxanes (POSS),[4] polyoxometalates (POMs),[5] fullerene derivates,[6] metal-organic cages (MOC),[7] uranyl peroxide,[8] etc.

1.1.2. Overview of surfactants

Surfactant is a surface agent, capable of reducing the surface tension of a liquid, which has chemically distinct parts, hydrophobic and hydrophilic parts, connected by chemical bonds. Most amphiphilic organic molecules are surfactants, such as sodium stearate (soaps), alkylbenzene sulfonates, fatty alcohol ethoxylates, and alkylphenol ethoxylates, which are all produced in industrial scales for everyday uses.[9] Amphiphilic block polymers can also be classified as a kind of surfactants, which have hydrophilic and hydrophobic regions. With the development of organic synthesis, a new class of surfactant called giant surfactant has been developed based on molecular nanoparticles (MNPs).[10] Typical MNPs include but are not limited to [60]fullerenes (C_{60}),[11] polyhedral oligomeric silsesquioxanes (POSS),[12] polyoxometalates (POMs),[13] and folded globular proteins.[14] The MNPs possess unique features such as persistent shape and volume, precisely defined chemical structures and surface functionalities.[10] These features allow chemists design and synthesis the surfactant with unique topology and functional groups. Based on their topological differences, giant surfactants show different solution behaviors (such as different self-assembling structure) which has drawn great attention due to their promising applications. Figure 1-1 illustrates structural differences among small-molecule surfactant, giant surfactant, and amphiphilic linear diblock polymer.[10]

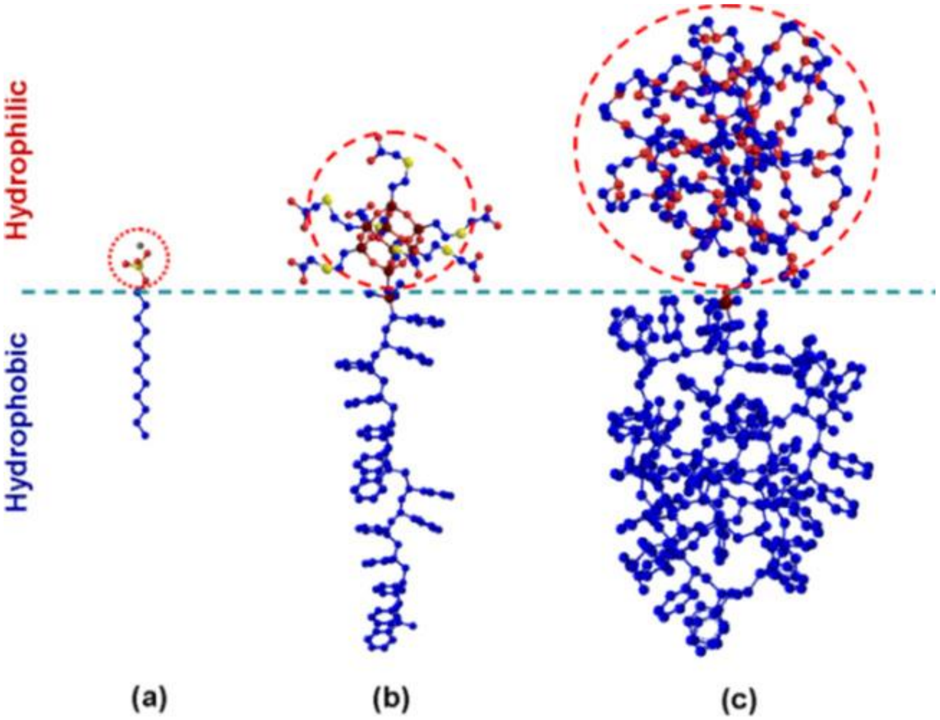

Figure 1-1. Structural comparison between (a) a typical small-molecule surfactant (such as sodium dodecyl sulfate); (b) a giant surfactant, (such as seven carboxylic acid groups functionalized POSS with a polystyrene tail); and (c) a typical amphiphilic block copolymer (such as polystyrene-*block*-poly (ethylene oxide)).

Dumbbell-shaped amphiphiles, formed by two “head groups” connected by a short solvophobic linker, are a new type of giant surfactant. Typically, the linker consists of an organic segment, while the “head groups” composed by functionalized MNPs.[15] When a long, hydrophobic chain serves as the linker, the amphiphiles are called bola amphiphiles (Figure 1-2). Compared to simple giant surfactant with only one head and one tail, dumbbell-shaped surfactants and bola amphiphiles show unique solution behaviors. The two polar head groups can be designed as identical or different, charged or uncharged, introducing more variety in their self-assembly features. Symmetric dumbbell- and bola-shaped amphiphiles generally assemble into hollow spherical supramolecular structures through hydrophobic interaction, which are commonly expected to be amphiphilic vesicles.[16,17] However, another possibility exists that the assembled structures formed by the charged amphiphilic dumbbells might not be vesicles but blackberry-type structures.[15]

Figure 1-2. Cartoons of dumbbell-shaped amphiphiles (left) and bola-shaped amphiphiles (right).

1.2. The facts influencing the self-assembly behavior of macroions

1.2.1. The driving force of self-assembly structure in solution – distinguish between blackberry structures and vesicles

Vesicles, commonly formed by amphiphilic lipids, are hollow, spherical, shell-like supramolecular assemblies consisting of a condensed hydrophobic domain stabilized by hydrophilic layers on both sides. There are various kinds of amphiphiles satisfying the packing parameter in polar solvents, including conventional small-molecule surfactants, giant surfactants, block polymer, as well as supramolecular amphiphiles.[18] The main driving force behind the formation of vesicles is hydrophobic interaction.

Many macroions can self-assemble into single-layered, hollow, spherical blackberry structures, which are similar to vesicles. Compared to surfactants, macroions are fully hydrophilic, meaning that the driving force for the self-assembly cannot be hydrophobic interaction. Taking research on $\{Fe_{30}Mo_{72}\}$ ($Mo^{VI}_{72}Fe^{III}_{30}O_{252}L_{102}\cdot$ca. $\cdot 180H_2O$ with $L=H_2O/CH_3COO^-/Mo_2O_{8/9}^{n-}$) as an example to figure out the main driving force of the blackberry formation.[16] The dynamic light scattering (DLS) results show radii of assemblies formed by $\{Fe_{30}Mo_{72}\}$ basically not change with $\{Fe_{30}Mo_{72}\}$ concentration increase, and the critical association concentration (CAC) is independent to temperature, indicating that the driving force is physical interaction instead of chemical-bonding. Considering the absence of assemblies of $\{Fe_{30}Mo_{72}\}$ in lower polar solvents, the van-der-Waals force can be ruled out. Another possible attraction comes from the hydrogen bonds formed between macroions in blackberries via water molecules. However, no blackberry formation occurs when the charge density of macroions is low, the effect of hydrogen bonds cannot be dominant on blackberry formation. The study discloses that the charges on macroions' surface have a dual effect: they contribute to both repulsion in short-range, and attraction in long-range, via small counterions. Based on its long-range attraction and the precipitation of small counterions, this force is called counterion-mediated interaction.

The counterion-mediated interaction can be supported by Sogami-Ise theory.[19] The electrostatic Helmholtz free energy ΔF is not equal to the electrostatic Gibbs free energy ΔG for simple ionic solutions, and the difference, ΔG-ΔF, becomes larger with increasing charge number (for example, highly charged macroions), while ΔG-ΔF=0 was postulated in DLVO theory. Sogami showed the mean-field approach based on Gibbs energy indicated both attraction and repulsion existed between charge like particles and the attractive force between particles with like charges increases through the intermediary of counterions between particles. Therefore, at a certain situation, sufficient counterions can be disposed between the particles to mediate a strong attraction over the repulsion. Based on this theory, the formation of blackberry structure can be explained. At the beginning, the size-disparity between macroions and small counterions leads to moderate counterion association around macroions. Finally, the counterion-mediated interaction brings macroions together to form single-layered 2D nanosheets, which could further bend and enclose to form hollow, spherical, single-layered blackberry structures (Figure 1-3).[20]

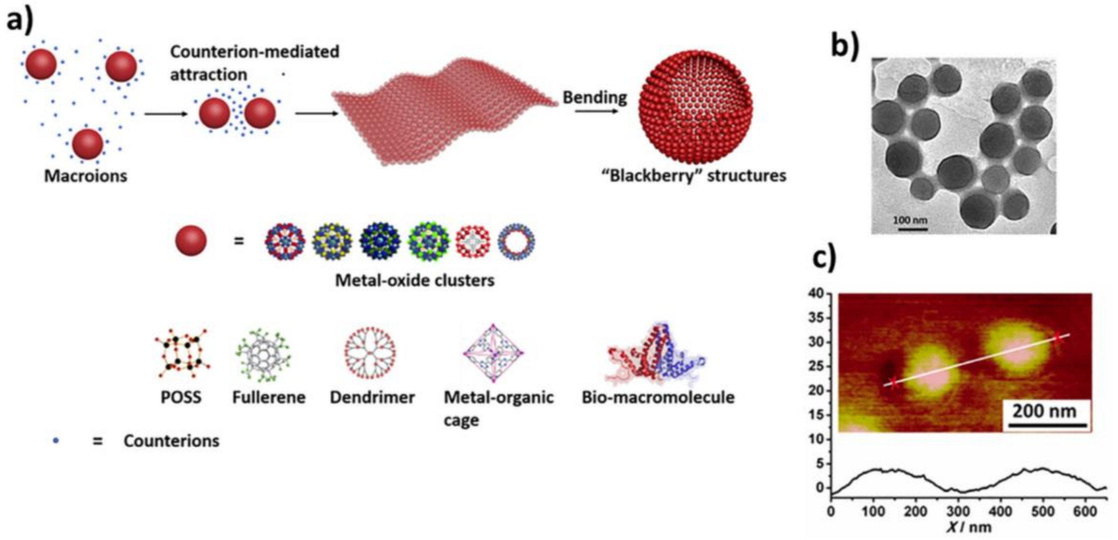

Figure 1-3. (a) Self-assembly of macroions into blackberry structures (top), and cartoons of different macroions and hybrids with capability to self-assemble into blackberry structures(bottom). (b) TEM images and (c) AFM imaging of blackberry structures.

Since counterion-mediated interaction is the domain on blackberry formation, the factors, which can affect the counterion-mediated interaction, will lead to different self-assembly behavior, including size and morphology of assemblies, etc. For example, the size of blackberry formed by $\{Fe_{30}Mo_{72}\}$ can be affected by chloride salt concentration.[21] Cation exchange process, most importantly including the exchange of different monovalent metal cations, can be achieved around $\{Fe_{30}Mo_{72}\}$, leading to change of counterion-mediated attraction. A critical salt concentration exists for the blackberry formation of $\{Mo_{72}Fe_{30}\}$ macroions, where up to that point there is no significant change in blackberry size. Cations with more charges and less hydration degree can bind stronger to $\{Fe_{30}Mo_{72}\}$ assemblies, resulting smaller critical salt concentration.

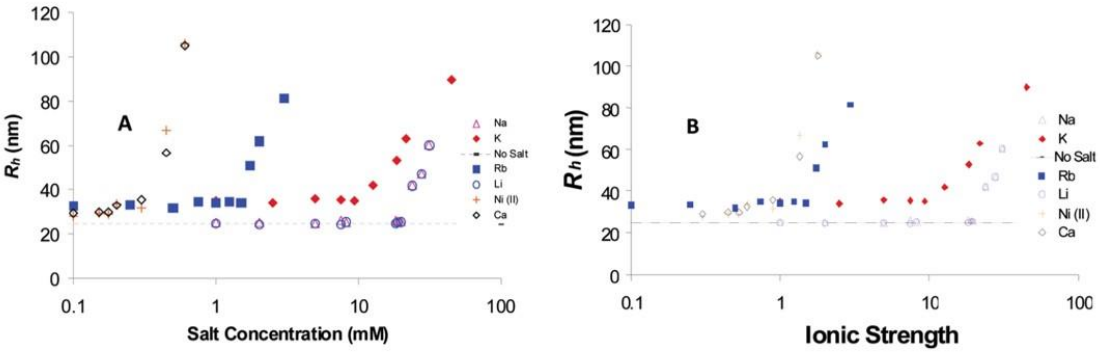

Figure 1-4. Blackberry size (R_h) changing with chloride salt concentration (a) and Ionic strength (b). There is a CSC (critical salt concentration), above CSC the blackberry size increases with salt concentration increase.

Both of vesicles and blackberry are hollow, spherical, supramolecular structures, whereas the main driving force is totally different. The similar morphology means that it is very difficult to distinguish them via laser light scattering (LLS) and microscopic measurement. However, the difference between vesicles and blackberry structures still exists: vesicles consist of bilayer molecules, with condensed hydrophobic domain surrounded by two hydrophilic domains, while the shell of blackberry structures is composed by only one layer fully hydrophilic macroions. Due to the electrostatic repulsion between macroions, there is a large distance between macroions in blackberry structure (DLS and TEM measurements indicate the interionic distance of blackberry structure formed by

{Fe30Mo72} is around 1nm),[16] meaning blackberry structure may have permeability to small counterions.

The charged dumbbell-shaped molecule can self-assemble and form both of vesicles and blackberry structures, depending on its molecular properties. The component and structure of charged dumbbell-shaped molecule determine whether hydrophobic interaction or counterion-mediated interaction will take the main part in self-assembling, leading to different structures. Pradeep et al. reported self-assembly of some symmetric, charged, dumbbell-shaped inorganic−organic hybrid amphiphiles into hollow, spherical, vesicle-like structures (Figure 1-5, a−c). Hydrophobic interaction was considered as main driving force with the help of their organic counterions, tetrabutylammonium (TBA+), which contribute their hydrophobic long tails to fill up the hydrophobic region inside the vesicle surface since short organic linkers between two inorganic "bells" may not be enough. Figure 1-5d illustrates structural difference between vesicles and blackberry structures formed by dumbbell-shaped molecule.[15] A closed, hollow spherical structure is formed through hydrophobic interaction, while another porous, hollow spherical structure is formed through counterion-mediated interaction.

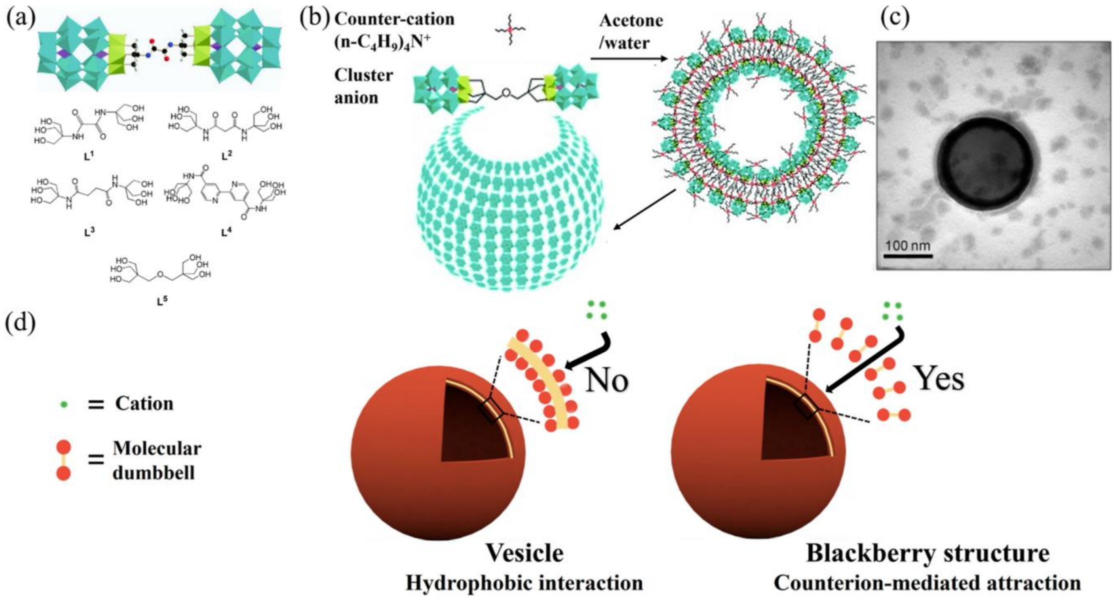

Figure 1-5. Self-assembly of dumbbell-shaped amphiphiles in solution. (a) Scheme of the molecular structure of the dumbbell-shaped anion with different tethers. (b) Scheme of the vesicle-like structure formed by the dumbbell-shaped anions shown in (a) and TBA+ countercations. (c) TEM image of the assembly shown in (b). (d) The structural difference between vesicles and blackberry structure formed by dumbbell-shaped molecules.

1.2.2. The permeability of self-assembly structure in solution

Both of vesicles and blackberry are hollow, spherical, supramolecular structures, whereas the main driving force is totally different. The similar morphology means that it is very difficult to distinguish them via laser light scattering (LLS) and microscopic measurement. However, the difference between vesicles and blackberry structures still exists: vesicles consist of bilayer molecules, with condensed hydrophobic domain surrounded by two hydrophilic domains, while the shell of blackberry structures is composed by only one layer fully hydrophilic macroions, indicating the permeability difference can be a special property to distinguish them. The condensed hydrophobic domain in vesicles is permeable to some small non-polar molecules but it is impermeable to ions. For example, O_2 and CO_2 can pass through the cell membrane directly, while Na^+ and K^+ can only be transported by membrane transport proteins. For blackberry structures, due to the electrostatic repulsion between macroions, there is a large distance between macroions (DLS and TEM measurements indicate the interionic distance of blackberry structure formed by $\{Fe_{30}Mo_{72}\}$ is around 1nm),[16] meaning blackberry structure may have permeability to small counterions. Liu et al. proved the permeability of $\{Fe_{30}Mo_{72}\}$ blackberry structure to small cations.[22] Small ions are added into the solution fluorophore-containing $\{Mo_{72}Fe_{30}\}$ blackberries and the quantum yield of the solution is observed. If the small ion could gradually diffuse through the shell of blackberry assemblies, quantum yield of the solution will change. Due to the electrostatic repulsion, the negative charged surface of $\{Mo_{72}Fe_{30}\}$ blackberries (single $\{Mo_{72}Fe_{30}\}$ cluster is negative charged) show the permeability to cations and the impermeability to anions.

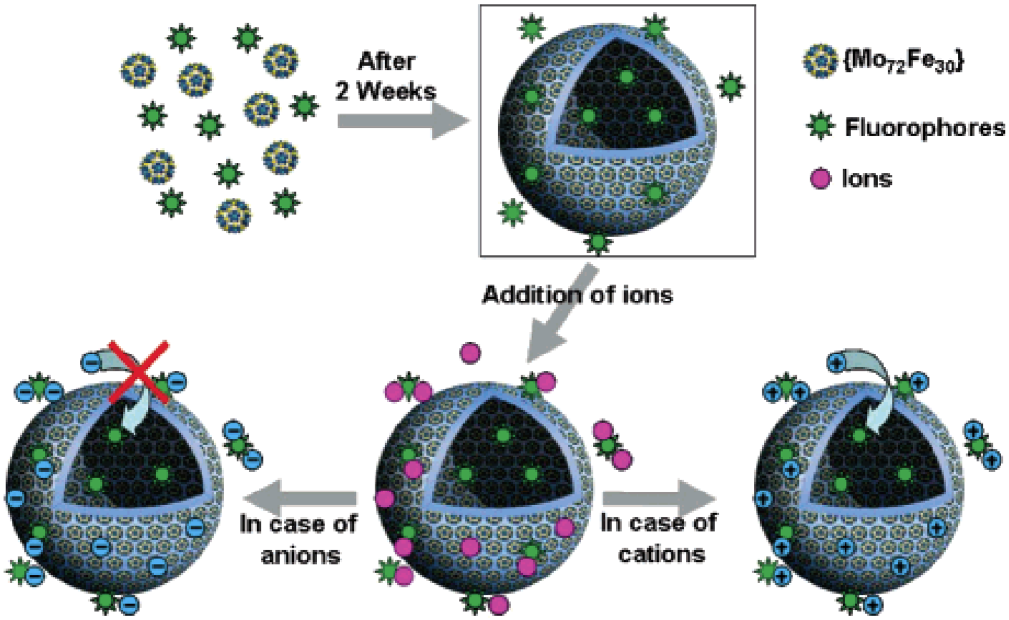

Figure 1-6. Schematic representation showing the formation of fluorophore-containing {$Mo_{72}Fe_{30}$} blackberries and their permeability to small ions.

1.3. Introduction to the solution behavior of fullerene macroions

1.3.1. Introduction to fullerene and fullerene derivates

A fullerene, an allotrope of carbon, is composed of carbon connected by single and double bonds so as to form a closed or partially closed mesh, with fused rings of five to seven atoms. C_{60} is a member of fullerene family, with unique molecular structure, excellent electronic properties, appreciable medical application, continuously drawing attention in different fields since its discovery.[23] Moreover, the unique rigid spherical structure of C_{60} molecule and the double bonds with high reactivity in the ring structure make it possible to synthesize C_{60} derivatives with different topologies and functional groups by chemical reaction as materials for self-assembly research. Therefore, various C_{60} derivates were accurately designed and synthesized, as a critical method to understand the role of different non-covalent forces in self-assembling, including hydrophobic interaction,[24] π-π stacking,[25] hydrogen bonding,[26] etc.

1.3.2. Deprotonation of AC60

AC_{60} is fullerene molecule functionalized with 12 carboxylic groups, which lead to better solubility in water. Figure 1-7 illustrate the molecular structure of AC_{60}.[23]

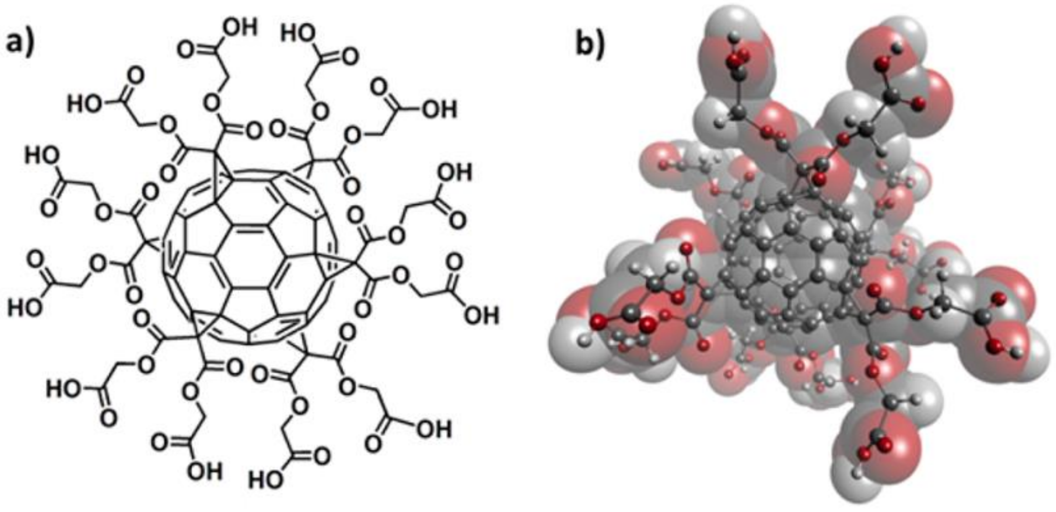

Figure 1-7. Chemical structure (a) and ball−stick model (b) of the AC_{60} molecule.

1.3.3. Deprotonation of AC_{60}

It is believed that the carboxylic acid groups are able to partially deprotonated. Therefore, the AC_{60} molecules are charged in polar solvents, which can be regarded as typical microanions. According to the definition of polarity index (PI), a measure of the ability of the solvent to interact with various test solutes, indicating solvent polarity, PI can be used to estimate the interaction between the solvent molecules and the solute of carboxylic acid-capped fullerenes and the interaction will directly lead to the deprotonation of the carboxylic acid groups. Yin et al. estimated the amount of charge AC_{60} carries relies on the degree of deprotonation (α) of the capped carboxylic acid groups based on FT-IR results.[23] According to the calculation, the AC_{60} possesses a much higher α value in DMF (ca. 62%) and methanol (ca. 47%) than that in THF (ca. 19%), meaning that the degree of deprotonation of carboxylic acid groups will increase in solvent with larger polarity.

1.3.4. Introduction to the self-assembly driving force of AC_{60}

Yin et al. reported the self-assembling of AC_{60}.[23] In polar solvents, AC_{60} can form hollow spherical assemblies. Zimm plot fitting of the SLS measurements of the assemblies (Figure 1-8a) in THF solution indicates the radius of gyration (R_g) of assemblies is close to the hydrodynamic radius (R_h), as evidence for the hollow spherical structure. The TEM result also proves these features (Figure 1-8b). The driving force of the assembles is counterion-mediated interaction, as the carboxylic acid groups shelled AC_{60} are highly charged in solvents with high polarities, which could surpass the charge density limit in forming blackberry structures.

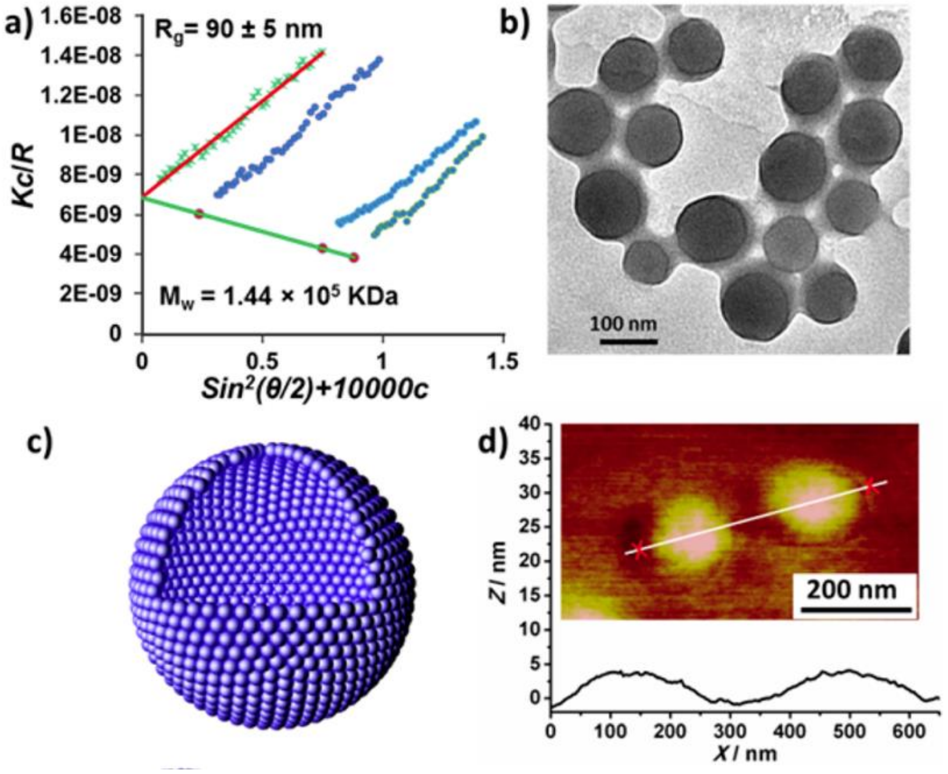

Figure 1-8. (a) Zimm plot of three AC_{60}/THF solutions with different concentrations (b) TEM images of the assemblies from the AC_{60}/THF solution (c) Schematic illustration of single layer hollow spherical structure formed by AC_{60} in THF (each blue sphere represents one AC_{60} molecule). (d) AFM height profile of collapsed assemblies after solvent evaporation. Inset is typical AFM image of two individual assemblies.

1.4. Study motivation

Dumbbell- and bola-shaped surfactants are commonly expected to self-assemble into vesicles with condensed hydrophobic domains due to the dominant hydrophobic interaction.[16,17] Meanwhile, macroions are expected to self-assemble into porous blackberry structure. In our previous publication, the main driving force of self-assembling of dumbbell-shaped POM hybrids are seen as hydrophobic interaction, because of the short, hydrophobic and organic linker between two charged POMs.[15] In this case, the counterion mediated interaction was ignored and the hydrophobic and organic linker might be too short to form condensed hydrophobic region in vesicles. It will be interesting to check if the dumbbell-shaped macroions with hydrophilic linkers can self-assemble to form similar structure. If so, counterion-mediated interaction is the main driving force instead of hydrophobic interaction and the hollow spherical assemblies are blackberry structures instead of vesicles, since there is no hydrophobic part in these dumbbell-shaped macroions. It is reasonable to assume that the study on dumbbell-shaped macroions can help people have further understanding of vesicles, blackberry structure, and counterion-mediated interaction.

In this work, a series of dumbbell-shaped fullerene macroions (Figure 1-9) are synthesized. These molecules are applied as a model system to studied the features of assemblies formed by dumbbell-shaped macroions, including the structure and factors that may affect self-assembling.

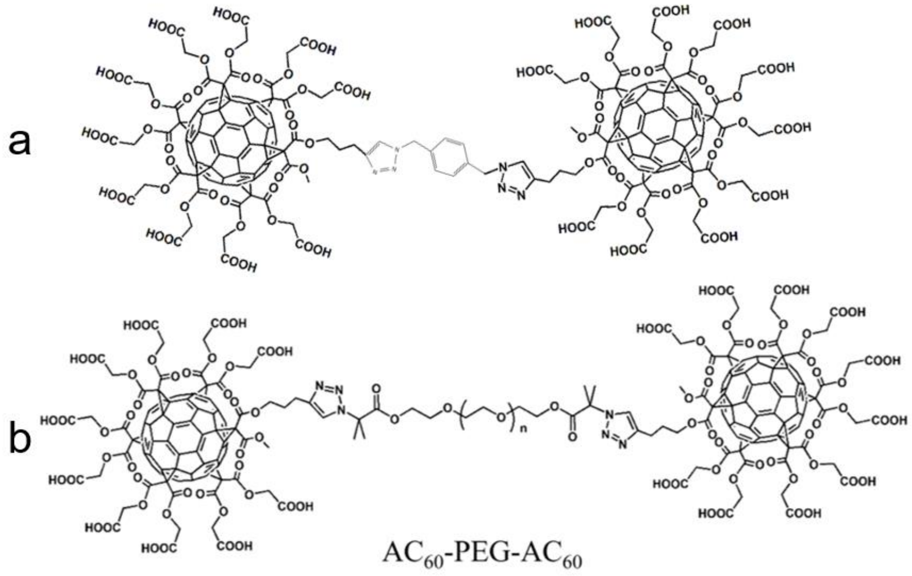

Figure 1-9. Molecular structures of dumbbell-shaped fullerene molecules. (a) AC_{60}-C_6H_4-AC_{60}. (b) AC_{60}-PEG_n-AC_{60}, n denotes the number of repeat units.

CHAPTER II

EXPERIMENT

2.1 Sample Preparation

A series of 2.00 mL fullerene macroions aqueous solutions with concentrations of 0.25mg/mL, 0.30mg/mL, 0.50mg/mL were prepared by dissolving dumbbell-shaped fullerene sample (AC_{60}-C_6H_4-AC_{60}, AC_{60}-PEG_3-AC_{60}, AC_{60}-PEG_9-AC_{60}, AC_{60}-PEG_{77}-AC_{60}) in NaOH solution. NaOH solution with pH values of 11.2, 11.4 was prepared by adding solid NaOH into deionized water.

2.2 pH meter

The SevenExcellence^{TM} bench meter was applied for measuring pH values. All the experiments related to pH values without any special annotation, including solutions preparation and pH measurements, were conducted at room temperature around 20°C. The pH meter was calibrated by three buffer solutions with the pH values of 4.00, 7.00, 10.01 respectively before each measurement.

2.3 Laser Light Scattering

Both of dynamic light scattering (DLS) and static light scattering (SLS) measurements were conducted by Brookhaven Instrument Inc. A solid-state laser with the wavelength of 633nm (red laser) was used in DLS and SLS experiments. The scattering intensity of samples were measured at 90°. The sample vials were cleaned with distilled acetone and sample solutions were filtered by the hydrophilic filter with the pore diameter of 1.00 μm. To figure out the temperature dependence of self-assembling, sample solutions were put in water bath at fixed temperature about 1 hour, and the temperature of sample cell was also controlled by a heating system to keep the same.

From DLS measurement, analyzed by the CONTIN method,[27] the average hydrodynamic radius (R_h) of the particles in solution can be determined, while average radius of gyration (R_g) of particles can be determined by Rayleigh-Gans-Debye equation,[28] the basis of the SLS data analysis.

CHAPTER III

RESULTS AND DISCUSSION

3.1 Solubility and Stability of Dumbbell-shaped Fullerene Molecules in Aqueous Solution

All of the dumbbell-shaped fullerene molecules has limited solubility in water at room temperature (20ºC) and the solubility of them can be significantly affected by pH of the solution. The deprotonation of these dumbbell-shaped molecules in aqueous solutions has been studied in our previous publication (Table 3-1).[15] This result shows a significant change of charges on dumbbell-shaped molecules with pH change, indicating the hydrophobicity of dumbbell-shaped molecules decreases with increase pH. OH^- anions can neutralize the carboxyl groups in fullerene molecules, leading them become more hydrophilic and have larger solubility in aqueous solution. When the pH gets higher than 5.5, all the fullerene macroions carry the maximum charge. Even though these molecules can dissolve in basic solution (like NaOH aqueous solution) more easily, more than 30 minutes of ultrasonication is necessary to get clear sample solutions with concentration of 0.5mg/mL. These solutions are thermodynamically stable since no precipitant or phase separation was observed in several months.

Table 3-1. The solubility of AC_{60}-PEG_{68}- AC_{60}

pH of aqueous solution without AC_{60}-PEG_{68}- AC_{60}	Solubility of AC_{60}-PEG_{68}-AC_{60}	pH of solution containing AC_{60}- PEG_{68}-AC_{60}	Number of negative charges per AC_{60}-PEG_{68}-AC_{60} from calculation
13.2	Fully dissolve	13.1	20
12.1	Fully dissolve	11.9	20
11.3	Partially dissolve	5.5	20
10.2	Partially dissolve	3.5	>7
8.2	Partially dissolve	4.1	>1

3.2 Self-assembly of Dumbbell-shaped Fullerene Molecules in Aqueous Solution: Basic Facts and Temperature Dependence

In DLS experiments, fast increase of light intensity was observed at the beginning, indicating large aggregates formed in solutions. After that increase, the light intensity of the solution kept stable. The size (R_h) distribution figure of particles in solution can be generated by analyzing the DLS result with CONTIN method. Take the R_h distribution of particles in AC_{60}-PEG_9-AC_{60} solution at room temperature as an example, as shown in Figure 3-1.

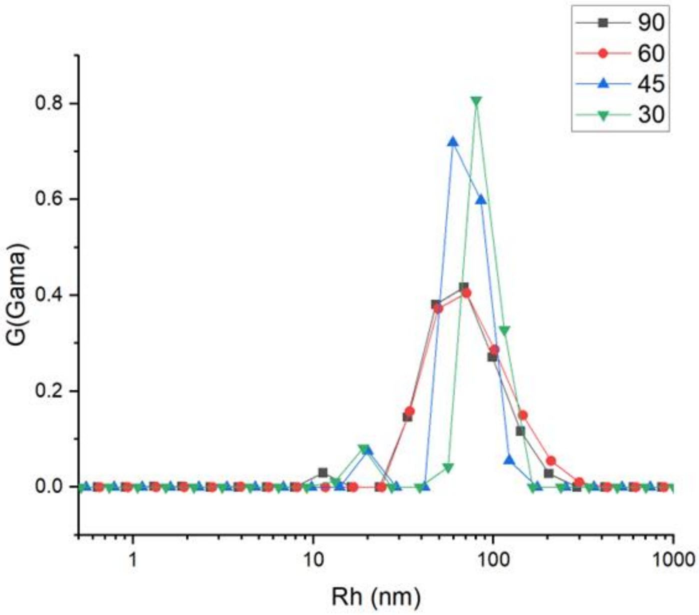

Figure 3-1. The R_h distribution of particles in AC_{60}-PEG_9-AC_{60} solution at room temperature at different angles.

DLS result shows assemblies of AC_{60}-PEG_9-AC_{60}, and the $R_{h,0}$ (the hydrodynamic radius of particles at 0 degree) of AC_{60}-PEG_9-AC_{60} can be calculated as 83 nm. The R_h distributions of other fullerene macroion solutions are similar while the only difference is the peek position, meaning that all of these different macroions can self-assemble, whatever the organic linker in dumbbell-shaped macroions is hydrophobic or hydrophilic. Table 3-2 shows the $R_{h,0}$ of assembles of the series of dumbbell-shaped macroions. Due to the absence of hydrophobic parts in AC_{60}-PEG_n-AC_{60} molecules, hydrophobic interaction is not the main driving force of the self-assembling. Considering the deprotonation of AC_{60}, charges on each buckyballs can induce the counterion-mediated interaction, which drag these macroions together with associated small counterions, and then eventually formed larger structures, the blackberry structures.

Table 3-2. The $R_{h,0}$ of different assemblies at room temperature

	AC_{60}-C_6H_4-AC_{60}	AC_{60}-PEG_3-AC_{60}	AC_{60}-PEG_9-AC_{60}	AC_{60}-PEG_{77}-AC_{60}
$R_{h,0}$ (nm)	60	80	83	109

The radii of gyration (R_g) of these assemblies of different fullerene macroions can be measured by SLS experiments. The R_g of AC_{60}-PEG_9-AC_{60} is 77nm and the ratio R_g/R_h ~1 for spherical objects for a typical hollow spherical model. Similar hollow spherical supramolecule structure are also observed in the other fullerene macroion solutions.

Interestingly, we find that the size of assemblies formed by different fullerene macroions show different temperature dependence. For assemblies of AC_{60}-PEG_9-AC_{60} and assemblies of AC_{60}-PEG_{77}-AC_{60}, their R_h decrease with temperature increase, while no obvious temperature response to the assemblies of AC_{60}-PEG_3-AC_{60} (Table 3-3, Table 3-4, Table 3-5).

Table 3-3. The R_h of AC_{60}-PEG_9-AC_{60} assemblies at different temperature

	$R_{h,\ 90°}$ (nm)	$R_{h,\ 75°}$ (nm)	$Rh_{,\ 45°}$ (nm)	$Rh_{,\ 30°}$ (nm)	$Rh_{,\ 0°}$ (nm)
RT	61	66	76	80	83
33 ℃	61	67	69	76	76
43 ℃	60	65	70	72	74

Table 3-4. The R_h of AC_{60}-PEG_{77}-AC_{60} assemblies at different temperature

	$R_{h,\ 90°}$ (nm)	$R_{h,\ 75°}$ (nm)	$R_{h,\ 60°}$ (nm)	$R_{h,\ 0°}$ (nm)
RT	84	88	95	109
36℃	87	90	91	97
45℃	75	83	85	100

Table 3-5. The R_h of AC_{60}-PEG_3-AC_{60} assemblies at different temperature

	$R_{h,\ 90°}$ (nm)	Rh, $_{75°}$ (nm)
RT	71	73
40℃	74	72

One assumption to explain the size decrease with temperature increase is that the pH of the solution change. The size of blackberry structure can be regulated by pH and this rule also works for assemblies of dumbbell-shaped fullerene macroions in our previous publication.[15] At higher solution pH, fullerene macroions carry larger charge, leading to stronger like-charge repulsion between each other and decrease of assembly size. pH meter was used to find the pH change of sample solutions at higher temperature and the data is shown in Table 3-4. It is obvious that the change of solution pH is very limited with increase temperature, indicating the change is too small to induce such significant size decrease. As a result, solution pH is not the main reason.

Table 3-6. The pH of fullerene macroion solutions

	pH at 20℃	pH at 40℃
AC_{60}-PEG_3-AC_{60}	4.68	4.65
AC_{60}-PEG_9-AC_{60}	6.81	7.04
AC_{60}-PEG_{77}-AC_{60}	6.36	6.40

Another assumption is that the PEG chain length changes with increase temperature. The organic linker in dumbbell-shaped fullerene macroions, PEG, is hydrophilic polymer. However, its hydrophobicity will increase with temperature increase, and water will be no more good solvent for PEG. As a result, PEG chain in water will shrink when the temperature of solution increases. There are two models to illustrate the structure of dumbbell-shaped fullerene macroions (Figure 3-2). Model A is a vesicle-like structure and organic linkers are surrounded by two layers of functionalized bulky balls, while organic linkers are dangling on the surface of the single-layered structure in model B.

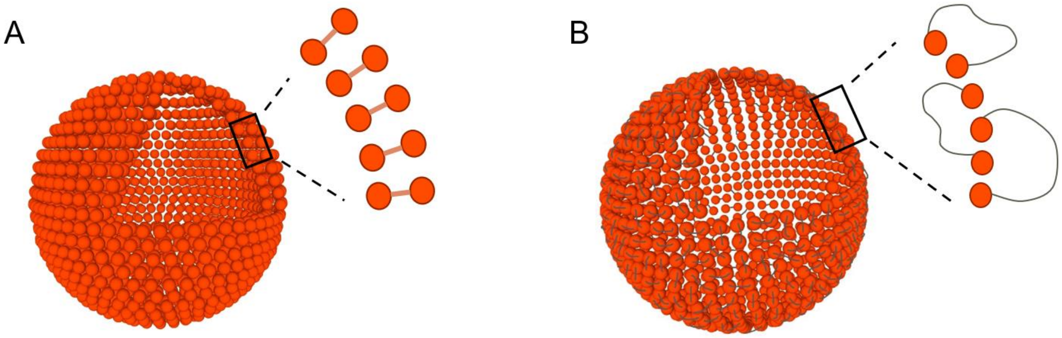

Figure 3-2. Two models of assemblies of dumbbell-shaped fullerene macroions.

For dumbbell-shaped fullerene macroions with longer PEG chain (AC_{60}-PEG_9-$AC_{60}$and AC_{60}-PEG_{77}-AC_{60}), the structure of assemblies may be like the model B. When keep sample solutions at higher temperature, the dangling PEG chains shrink and drag macroions more closely, leading to size decrease of these assemblies. For dumbbell-shaped fullerene macroions with longer PEG chain (AC_{60}-PEG_3-AC_{60}), the structure of assemblies is like model A and the PEG chain is too short to induce any size change.

CHAPTER IV

CONCLUTION

In summary, due to the deprotonation of carboxylic groups on the bulky ball, dumbbell-shaped fullerene molecules can dissolve in basic aqueous solutions and become macroions. The macroions with different organic linkers, hydrophobic linker (AC_{60}-C_6H_4-AC_{60}) and hydrophilic linker (AC_{60}-PEG_n-AC_{60}), can assemble to form hollow, spherical structure, which proves that counterion-mediated interaction is the main driving force, instead of hydrophobic interaction. The length and hydrophobicity of organic linker are proved as significant factors which may affect the assembly structure of dumbbell-shaped macroions. For dumbbell-shaped fullerene macroions with short linker, they can arrange side-by-side to form vesicle-like structure. For dumbbell-shaped fullerene macroions with longer organic linker, they may form blackberry structure with dangling organic chain on the surface.

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