SELF-ASSEMBLY OF CARBOXYLIC ACID-FUNCTIONALIZED HYDROPHILIC FULLERENE MACROANIONS IN DILUTE SOLUTION

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SELF-ASSEMBLY OF CARBOXYLIC ACID-FUNCTIONALIZED HYDROPHILIC
FULLERENE MACROANIONS IN DILUTE SOLUTION

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Thesis

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ABSTRACT

By functionalizing the fullerenes with hydrophilic carboxylic acids, the fullerenes can be transformed into macroanions that are geometrically symmetrical, highly hydrophilic and negatively charged.

The solution behavior of the 12 carboxylic acid group-capped fullerene macroions ($\text{AC}_{60}$) was characterized by using laser light scattering (LLS), transmission electron microscopy (TEM) and atomic force microscopy (AFM). The $\text{AC}_{60}$ shows unique solution behavior by self-assembling into single-layer, hollow, spherical, “blackberry” structures in solution via counterion-mediated attraction. Furthermore, the assembly size can be tuned by changing the polarity of the solvents. $^{1,2}$
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CHAPTER I

INTRODUCTION

1.1 Introduction of Functionalized Fullerene

Buckminsterfullerene (C\textsubscript{60}) is a symmetrically truncated icosahedron which contains 60 carbon atoms with 12 pentagons and 20 hexagons.\textsuperscript{3-5} Due to its unique structure, excellent electronic properties and appreciable applications, \textsuperscript{3-7} C\textsubscript{60} molecule has attracted extensive attentions since it was first discovered in 1985. However, C\textsubscript{60} molecule has poor solubility in solution and will easily precipitate after aggregation, which strongly hampers its practical applications.\textsuperscript{8-10} Functionalizing the fullerene through chemical and supermolecular methods can highly improve the solubility of C\textsubscript{60} molecule, \textsuperscript{9,10} while retain the main features of C\textsubscript{60}, such as precise three dimensional architecture, electroactivity, photoactivity, high hydrophobicity, and superconductivity.\textsuperscript{11-15} Consequently, functionalized fullerenes are very popular in different fields, especially in the biotechnology and drug discovery, such as biosensors, targeted gene and drug delivery, photodynamic therapy, cellular imaging, and diagnostics.\textsuperscript{16-23}

1.2 Self-Assembly of Conventional Functionalized Fullerene in Solution

The self-assembly of fullerene derivatives has been investigated by many research groups.\textsuperscript{24-26} In particular, as a class of most intensively studied fullerene derivatives,
amphiphilic functionalized fullerenes were found to self-assemble into different morphologies in solution. Three typical examples for the self-assembly of the amphiphilic functionalized fullerenes are briefly introduced below.

Langmuir-Blodgett Film: Uniform Langmuir-Blodgett film was formed from amphiphilic fullerene carboxylic acid at the air-water interface and could be deposited on substrates. Because of the amphiphilicity of the molecule, the hydrophilic carboxylic group prefers to standing towards the water side while hydrophobic C_{60} moiety prefers to facing towards the air, which resulting the formation of Langmuir-Blodgett film. In addition, the film is hydrogen bonded.\textsuperscript{27,28}

Nanorods: Fullerene amino salt was found to self-assemble into nanorods in water, probably because of the strong π-π attractions and the hydrophobic-hydrophilic interactions.\textsuperscript{29}

Figure 1 Models of (1) Langmuir-Blodgett film. Reprinted with permission from ref. 28. Copyright 1995 American Chemical Society. (2) Nanorods. Reprinted with permission from ref. 29. Copyright 2002 National Academy of Sciences, USA. (3) The bilayer vesicle formed from functionalized fullerenes. Reprinted with permission from AAAS from ref. 30. Copyright 2001, American Association for the Advancement of Science.
Spherical Bilayer Vesicles: The penta-substituted fullerene has two moieties, the hydrophobic hydrocarbon ball and the hydrophilic ion, so overall it is amphiphilic and is soluble in aqueous solutions. The potassium salt of pentaphenyl fullerene (Ph$_5$C$_{60}$K) acts as surfactants in solution and are able to self-assemble into spherical bilayer vesicles.

1.3 The Motivation for Study the Hydrophilic, Charged Fullerene

As it is discussed in the previous section, the non-covalent interactions are vital in the self-assembly of functionalized fullerenes. The hydrophobic interaction, hydrogen bonding and aromatic stacking are the most common driving forces for the assembly of fullerene derivatives. However, besides those, the electrostatic interaction is another important non-covalent interaction and has not been fully explored in the study of assembling fullerenes. On the other hand, most of existing results are based on the amphiphilic fullerenes, but the solution behavior of fully hydrophilic fullerene has not been well studied yet. Therefore, it is attractive to investigate the self-assembly of hydrophilic, charged fullerenes in solution, which is more convenient for processing in solution and may pave a way for relevant applications. In addition, the study of these hydrophilic, charged fullerene in this thesis expends our knowledge of small macroions to the sizes around 1.5 nm.

1.4 Solution Behavior of Macroions

Debye-Hückel theory is widely applied to describe the dilute simple ionic solutions, which assumes that the ions can be treated as point charges. On the other hand, for the colloidal suspensions, Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory was
proposed to explain the stability of colloids. The DLVO theory actually describes the balance between the electrostatic repulsion force and van der Waals attraction force. However, the size and charge density of macroions are at somewhere between the small simple ions and large colloids. In the other word, the macroions no longer can be treated as point charges, so they cannot be described by Debye-Hückel theory. In addition, they are still soluble and stable in solution, so they cannot be described by DLVO theory either. Interestingly, various macroions, such as polyoxometalates, metal–organic cationic cages, and polyhedral oligomeric silsesquioxane, tend to self-assemble into unique single-layer, hollow, spherical structures in dilute solutions.

One landmark of the self-assembly behavior of macroions was published in 2003 by Tianbo, L et al. The wheel-shaped \( \text{Mo}_{154} \) was typically studied in this paper. Based on the discoveries from laser light scattering (LLS) and electron microscopy, the schematic model was built up as a hollow, spherical, single-layer “vesicle” and the macroions are not touching each other. Since the single-layered structure looks similar to the blackberry, this structure is also called “blackberry type structure” by many researchers.

Figure 2 Schematic plot showing the supramolecular blackberry structure formed by macroions in aqueous solution. Reprinted with permission from ref 1. Copyright 2003 Nature Publishing Group.
1.5 Counterion-Mediated Attraction

The counterion-mediated attraction is considered as the major driving force for the self-assembly of macroions into blackberry structures. Due to the size disparity between the small counterions and large macroions, some small counterions will not exist as free ions in solution but closely associate with large macroions. As a result, the charges on the macroions surface are partly neutralized by the associated counterions, which means the effective charge density is relative lower than the theoretical value.

More importantly, the counterions can further form ion-pairs with macroions under strong electrostatic attraction, as a result the two like-charge macroions tend to be glued together by the counterions in the middle.

The counterion-mediated attractions are balanced mainly by the electrostatic repulsions between the two like-charge macroions. When the solvent polarity decreases, the hydrophilic counterions will less “like” the solvent but closer associate with the macroions. Consequently, the charge density on the macroion’s surface is lower, which leads to the repulsions between two like-charge macroions decrease and the counterion-mediated attractions increase. Above theory is supported by experimental results, such as small-angle X-ray scattering (SAXS) studies, conductivity measurements, laser light scattering measurements and so force.
Figure 3 Illustration of counterion-association and “blackberry” formation in acetone/water mixed solutions of POM. Reprinted with permission from ref 40. Copyright 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
1.6 Kinetics of Blackberry Formation

It has been reported that the energy barrier between the single ions and the assemblies is very high,\textsuperscript{43} hence the reaction rate for the transition of single ions into unimers or oligomers should be very slow at beginning.\textsuperscript{44} On the other hand, SLS and DLS studies revealed that there was only one dominant size during the self-assembly process, so the transition from unimers or oligomers into blackberries should be very fast that smaller assemblies do not have time to form.\textsuperscript{44} The proposed route for the formation of blackberry is illustrated below.

![Illustration of the possible mechanism of the formation of “blackberry”](image)

Figure 4 Illustration of the possible mechanism of the formation of “blackberry”

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CHAPTER II

EXPERIMENTAL SECTION

2.1 Sample Preparation

The carboxylic acid–functionalized fullerene, C_{60} (C(COOCOOH)_2)_6 (AC_{60}), was synthesized by Prof. Stephen Z. D. Cheng’s group at the University of Akron. Twelve 4-oxopentanoic acid groups are homogenously functionalized on the fullerene periphery by six active sites.

![Chemical structure of AC_{60}](image)

Figure 5 Chemical structure of AC_{60}. Reprinted with permission from ref 2. Copyright 2015 American Chemical Society.

The sample cells (vials and tubes) were previously cleaned with condensing acetone vapor to remove dust and the caps were previously washed by liquid acetone. A series of ca. 0.5 mg/mL AC_{60} solutions in required solvents (THF, methanol, DMSO, DMF, acetonitrile, acetone, ethanol, isopropanol, n-butanol, water, HFIP) were prepared in the 15 mL corning centrifuge tubes at room temperature. For toluene/acetonitrile mixture, 0.5 mg/mL AC_{60} was first dissolved in 1.5 mL acetonitrile and then different amount of toluene
(200µL-2000µL) was slowly added using a 1000µL fixed-volume pipette with gentle stirring. Each solution was sonicated for 20 minutes to realize complete dissolution. Then all the resulting solution were filtered into dust-free cells through 0.45µm sterile filter membranes for light scattering studies.

2.2 UV-Vis Spectroscopy (UV-Vis)

HEWLWTT PACKARD G1103A UV-Vis spectrometer was employed to determine the accurate concentrations of AC$_{60}$ solutions. THF solution of AC$_{60}$ with accurate concentration as 1.0 mg/mL was prepared and was subjected to UV-Vis measurement to record the UV absorption spectrum. Then the solution was diluted two-fold and was characterized by UV-Vis accordingly. The dilution and UV-Vis measurements were sequentially carried out for 20 times. The concentration and the UV absorption of each diluted solution at the wavelength of 425 nm were collected respectively. Eventually, the calibration curve ($y=1.9536x+0.035$) (Figure 6) for the solution concentrations was determined through linear fitting.

![Figure 6 UV-Vis Calibration Curve](image)
The concentrations of three solutions of AC₆₀ in THF that would be used in laser light scattering study were calculated as 0.93, 0.65, and 0.20 mg/mL, respectively, from their corresponding UV-Vis absorption.

The UV-Vis measurements were further used in determining the concentrations of assemblies for Zimm plot analysis. When the self-assembly process reached the equilibrium state, the three solutions were filtered by 0.1μm sterile filter membranes to remove the assemblies right after the SLS measurements for generating the Zimm plot, and were subjected to UV-Vis to determine the concentration of solution without assemblies. The assembly concentrations were calculated by subtracting the concentrations of solutions after filtration from the concentrations of solutions before filtration, respectively. Finally, the concentrations of the assemblies in three solutions were determined as 0.088, 0.075, and 0.024 mg/mL, respectively.

2.3 Static Light Scattering (SLS).

The laser light scattering (LLS) experiments including static light scattering (SLS) and dynamic light scattering (DLS) were carried out on a commercial Brookhaven Instrument LLS spectrometer which equipped with a diode pumped solid-state (DPSS) laser operating at 637 nm or 532 nm, and a BI-9000AT multi-channel digital correlator. The SLS experiments recorded the time-averaged total intensity at scattering angles θ between 20° and 120°, at 2° intervals. For a series of solutions (THF) with different concentrations, further information on the weight average molecular weight of assemblies
M_w) and second virial coefficient (A_2) was generated from Zimm Plot, as well as the radius of gyration (R_g). 45

\[
\frac{Hc}{R_\theta} = \left(\frac{1}{M} + 2A_2c\right)(1 + \frac{16\pi^2Rg^2}{3\lambda^2}\sin^2\frac{\theta}{2})
\]

In the above equation, H is the optical parameter, R_θ is the Rayleigh ratio, c is the solution concentration, and dn/dc is the change in refractive index of the solution with change in concentration. The data points from 40° to 20° was removed from the plot, because the scattered intensity is too low.

2.4 Dynamic Light Scattering (DLS).

DLS actually measured the intensity-intensity time correlation function which was converted into electric field time correlation functions later. Then normalized electric field time correlation functions were analyzed by the constrained regularized (CONTIN) method in order to calculate the distribution of the characteristic line width, G (Γ). 46 The particle’s apparent diffusion coefficient D_app could be obtained from \( \Gamma = Dq^2 \) where q is equal to \( 4\pi n \sin(\theta/2)/\lambda \) (n is the refractive index of sample solution, \( \theta \) is the scattering angle, \( \lambda \) is the laser wavelength), and the average hydrodynamic radius (R_h) is related to D through the Stokes-Einstein equation 47:

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

In above equation, \( k_B \) is the Boltzmann constant and \( \eta \) the viscosity of the solvent at temperature T.

Consequently, the average hydrodynamic radius (R_h) of large assemblies and particle size distribution in solution could be solved by plotting \( \Gamma G (\Gamma) \) versus R_h. The DLS
measurements were performed at 90, 75, 60, and 45 scattering angles. If angular dependence was existed among $R_{h,\text{app}}$ values at different scattering angles, an extrapolation to zero scattering angle was required to obtain $R_{h,0}$.

2.5 Transmission Electron Microscope (TEM)

Bright filed images of transmission electron microscope (TEM) were performed on a JEOL-1230 microscope with an accelerating voltage of 120 kV. Samples were prepared by titrating 20 µL of the sample solutions onto carbon coated copper grids and the excess solution was wicked away by a piece of filter paper. The samples were then put under ambient conditions for several days until they were dry. TEM images were obtained on a digital CCD camera and processed with the accessory digital imaging system.

2.6 Atomic Force Microscope (AFM)

AFM studies were done with the assistant of Yan Sun and Prof. Alamgir Karim at the University of Akron, using a Dimension Icon AFM (Bruker AXS). Samples were prepared by depositing 30 µL of AC$_{60}$ assembly solution in THF onto the silicon wafer and drying under ambient conditions. The images were obtained at the scanning rate of 0.5 Hz in the tapping mode over $1.2 \times 1.2 \, \mu \text{m}^2$. 
CHAPTER III
RESULTS AND DISCUSSION

3.1 Self-Assembly Behavior of AC\textsubscript{60} into “blackberry” structures

The size of AC\textsubscript{60} is ca. 1.5nm based on DFT optimization and the dynamic analysis of the soft chain.	extsuperscript{2} With the twelve highly hydrophilic carboxylic acid groups on periphery, AC\textsubscript{60} is soluble in water with pH > 11.2 and in a wide range of polar organic solvents. The particle size in the AC\textsubscript{60} aqueous solution is determined as ca. 1.3 nm from Dynamic light scattering (DLS) measurements, which is consistent with the structural analysis results and indicates the AC\textsubscript{60} molecules exist as discrete anions in aqueous solution.

Concentrations of the THF solutions were all calibrated by UV-Vis measurements in this thesis. In a typical experiment, the AC\textsubscript{60} was dissolved in THF at the concentration ca. 0.65 mg/mL. The scattered intensity of the freshly prepared solution is very low, at 8.5kcps (scattered intensity for benzene is ca. 69 kcps), indicating that there was no large assembly presenting in such solution at very beginning and AC\textsubscript{60} macroaions homogeneously distributed as discrete anions in solution. The scattered intensity of the solution was monitored by static light scattering (SLS) every an hour in the first day and then every one or two days later. The scattered intensity continuously increased with time, suggesting the formation of larger structures in the solution (Figure 7). The overall intensity
growth shows a sigmoid-shape kinetic curve at room temperature, that demonstrates a lag phase of four days due to the large energy barrier and keeps increasing until reaches equilibrium state after one month.\textsuperscript{43} Additionally, the average radius (R\textsubscript{h}) of the larger structures was calculated by CONTIN analysis of dynamic light scattering (DLS) data at 90° scattering angle, which is 95±5nm. The R\textsubscript{h} remains almost unchanged over time, which is consistent with our previous work, as introduced in CHAPTER I, about the kinetics of the formation of blackberries, that the process of the unimers or oligomers assembling into large blackberries is so fast that there are no “small” blackberries forming and the molecules kept assembling into larger number of assembled structures with certain assembly size.\textsuperscript{1,42,44}

Figure 7 Scattered intensity in THF solution of 0.65 mg/mL AC\textsubscript{60} at 90° scattering angle. Reprinted with permission from ref 2. Copyright 2015 American Chemical Society.
Figure 8 CONTIN analysis of DLS data shows average hydrodynamic radius (R_h) remains unchanged with time in THF solution of 0.65 mg/mL AC_60 at 90° scattering angle. Reprinted with permission from ref 2. Copyright 2015 American Chemical Society.

As it is shown in Figure 9, the average R_h values at different scattering angles are not angular dependent, which supports a spherical morphology.

On the other hand, The R_h values of other two AC_60 solutions in THF with concentration 0.20 and 0.93 mg/mL, respectively, were also obtained from DLS measurements, that are 91 ± 5 and 85 ± 5 nm, respectively. The sizes of AC_60 assemblies in the three THF solutions show no obvious concentration dependence, so Zimm plot analysis of SLS data can be applied to indicate the average radius of gyration (R_g) of the assemblies in three AC_60 solutions, that is 90±5 nm. The R_g/R_h ratio approaching to 1 stands for a typical hollow sphere model as all the mass should be distributed on the surface,
whereas for solid spheres, $R_g/R_h$ should be close to 0.77. This hollow spherical structure was further confirmed by bright-field TEM observations. (Figure 10).

Figure 9 CONTIN analysis of DLS data shows average hydrodynamic radius ($R_h$) in THF solutions of AC$_{60}$ is not angular dependent. Reprinted with permission from ref 2. Copyright 2015 American Chemical Society.

Figure 10 TEM image for THF solution of AC60, exhibiting the hollow spherical structure of assemblies with back ring circles at the outsides and more transparent part at insides.
Further Zimm plot analysis of these three THF solutions of AC\textsubscript{60} indicates the molecular weight of the assemblies is ca. 1.44 $\times$ 10\textsuperscript{5} kDa. Since both the molecular weight of single molecules and the molecular weight of assemblies are known, the aggregation number for each assembly is calculated as around 76000. Assuming all the AC\textsubscript{60} are distributed on the surface of a hollow sphere with a radius of 95 nm by close packing, the intramolecular distance is ca. 1.4 nm, which is almost equal to the size of single AC\textsubscript{60} molecule. Therefore, single-layered molecular packing model was proposed for the AC\textsubscript{60} assemblies.

Besides, since the back ring circle at the outsides of assemblies is distinguishable in the TEM images of AC\textsubscript{60} solution in THF, the thickness of the black wall was measured to be ca. 2 nm for estimation of the assembly layer thickness. The wall thickness is close to the size of single AC\textsubscript{60} molecule (ca. 1.5 nm), providing another evidence for the single-layer structure.

To further confirm the blackberry-type structures, atomic force microscopy (AFM) was applied to measure the layer thicknesses of the collapsed assemblies resulted from slow evaporation of solvent. The average thickness of collapsed assemblies was characterized to be 4±0.5 nm based on ten independent measurements, which agrees well with the theoretical double layer thicknesses of AC\textsubscript{60} molecules in “blackberries” (ca. 3 nm).
Figure 11 (Left) Zimm plot analysis to measure the average radius of gyration (\(R_g\)) of THF solution of AC\(_{60}\). Reprinted with permission from ref 2. Copyright 2015 American Chemical Society. (Right) Typical model of the hollow spherical structure.

Figure 12 (Left) Typical AFM height profile of two collapsed assemblies of AC\(_{60}\) (Right) Model of collapsed single-layer, hollow, spherical assembly. Reprinted with permission from ref 2. Copyright 2015 American Chemical Society.
3.2 Driving Force for the Formation of “Blackberry” Structures

The formation of hollow spherical structures was also observed in acetonitrile, acetone, ethanol, isopropanol, and butanol. The solution behaviors in these solvents all possess following features: scattered intensities increasing with time (Figure 17), stable size during the self-assembly process (Figure 18), and spherical structures appearing in TEM (Figure 19).

However, no assembly was found in methanol, DMSO, DMF and water (at pH>11.2), which all have even higher polarities.

It is more noteworthy that, from acetonitrile to butanol, the assembly size increases with decreasing the value of polarity index, a good indication of solvent polarity.48,49 (Figure 14)

![Graph showing scattered intensity in different solvents](image)

Figure 13 Scattered intensity in DMF, DMSO, H2O and Methanol solutions of 0.5 mg/mL AC60 at 90° scattering angle. Reprinted with permission from ref 2. Copyright 2015 American Chemical Society.
Figure 14 (Left) CONTIN analysis of DLS data of ca. 0.5 mg/mL AC$_{60}$ solutions in acetonitrile, acetone, ethanol, isopropanol and butanol (Right) The plot of $R_h$ versus polarity index of different polar solvents. Reprinted with permission from ref 2. Copyright 2015 American Chemical Society.

Since the fullerene is fully covered by hydrophilic carboxylic acid groups, the hydrophobic interactions and $\pi-\pi$ stacking interactions of the fullerene do not likely contribute to the formation of large structure. In addition, there is no self-assembly in solvents with high polarity, further ruling out the hydrophobic interaction as major driving force, since the hydrophobic interaction-driven self-assembly process should be favored in solution with higher polarity.

On the other hand, because the existence of abundant alcohol molecules could terminate the AC$_{60}$ to AC$_{60}$ intermolecular hydrogen bonding, the self-assembly of AC$_{60}$ in ethanol, isopropanol and butanol rules out the hydrogen bonding as the major driving force. Moreover, the HFIP is known as a common hydrogen bonding cutting agent,$^{50}$ but
the formation of hollow spherical structure is observed in light scattering and TEM, providing another strong evidence to rule out the hydrogen bonding as major driving force.

Figure 15 (Left) CONTIN analysis of DLS data of the HFIP solution of 0.5 mg/mL AC$_{60}$ at scattering angle as 90°. (Right) TEM image for the HFIP solution of 0.5 mg/mL AC$_{60}$. Reprinted with permission from ref 2. Copyright 2015 American Chemical Society.

In addition to the hydrophobic interaction, the aromatic stacking and the hydrogen bonding, counterion-mediated attraction is another important non-covalent driving force and is expected to be the major driving force in this work. As previously introduced in Chapter I, due to the disparities on ionic size and charge density between the small hydrogen cations and large AC$_{60}$ macroanions, the cations can closely associate and further form strong ion pairs with macroanions under the electrostatic interaction. This leads to two main effects: first, the effective charge density is relatively lowered by counterion-association; second, the two like-charge macrions are attracted together by the small counterions between them through ion-pairing. In addition, the counterion-mediated attraction is balanced by the electrostatic repulsion of the macroions.$^{37}$
Since the carboxylic acid groups will partially dissociate into hydrogen cations and carboxylate anions in polar solvents, the effective charge density of the AC$_{60}$ can be easily tuned by changing the solvent polarity. With higher solvent polarity, the counterion-association is less significant, therefore effective charge density on the AC$_{60}$ surface becomes higher, and the stronger electrostatic repulsions between two negatively charged AC$_{60}$ arise. In total, the attraction force among the macroanions deceases, so less AC$_{60}$ can be held together and the preferred curvature is increased with formation of smaller assemblies. Meanwhile, for methanol, DMSO, DMF and water (at pH > 11.2), their polarities are too high that the repulsion forces among the like-charge are too dominant. Accordingly, the counterion-mediated attraction cannot overcome the repulsive force to bring the AC$_{60}$ together. The formation of “blackberry” structures with tunable size is nicely explained by counterions-mediated attraction as major driving force.

This explanation is also supported by the growth curve of assembly size R$_h$ over toluene content in the acetonitrile solutions of AC$_{60}$. The mixed solvent polarity is lowered by adding more toluene into acetonitrile, hence the corresponding assembly sizes increase as a result of stronger counterion-mediated attractions and weaker electrostatic repulsions.
Figure 16 Plot of the hydrodynamic radius ($R_h$) versus the toluene content (vol%). The $R_h$ values of first two points (41±5nm and 42±5nm, respectively) are lower than the one of pure acetonitrile solution, respectively, but they are still in the error rang.
CHAPTER IV
CONCLUSIONS

In summary, we have reported that the carboxylic-acid functionalized hydrophilic fullerene macroions (AC_{60}) self-assemble into single-layered, hollow, spherical structures in solvents with appropriate polarity and the assembly size can be tuned by adjusting the solvent polarity. Counterion-mediated interaction between macroions is confirmed to be the major driving force for the self-assembly process. Our studies open up a new way to fabricate highly ordered and size tunable assembly structures from fullerene derivatives for advanced materials and devices.
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APPENDIX

All the scattered intensity was measured by LLS quipped with green laser (532nm) (scattered intensity of benzene is ca. 69 kcps). All the other data were measured by LLS quipped with red laser (637nm).

Figure 17 Scattered intensity of ca. 0.5 mg/mL AC_{60} in (a) acetonitrile; (b) acetone; (c) ethanol; (d) isopropanol; and (e) butanol (f) HFIP. Reprinted with permission from ref 2. Copyright 2015 American Chemical Society.
Figure 18 Average hydrodynamic radius ($R_h$) remains unchanged with time in ca. 0.5 mg/mL AC₆₀ in (a) acetonitrile; (b) acetone; (c) ethanol
Figure 19 THF imagines of ca. 0.5 mg/mL AC$_{60}$ in (a) acetonitrile; (b) acetone;(c) ethanol; (d) isopropanol; and (e) butanol. Reprinted with permission from ref 2.

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