MOLECULAR JANUS PARTICLES BASED ON FUNCTIONALIZED [60]FULLERENES: PRECISE SYNTHESIS AND SELF-ASSEMBLY BEHAVIORS IN SOLUTION

A Thesis
Presented to
The Graduate Faculty of The University of Akron

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

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May, 2016
MOLECULAR JANUS PARTICLES BASED ON
FUNCTIONALIZED [60]FULLERENES: PRECISE SYNTHESIS
AND SELF-ASSEMBLY BEHAVIORS IN SOLUTION

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ABSTRACT

Since the concept of “Janus particles” was introduced by de Gennes, a great deal of attention has been arisen due to their asymmetric structures, special properties and diversified self-assembly behaviors. In this work, a new Janus particle with precisely defined structures composed of a positively (NC$_{60}$) and negatively charged fullerene (AC$_{60}$) was synthesized based on “click” chemistry. Starting from commercialized fullerenes (C$_{60}$), a functionalized C$_{60}$ installing one, two or four alkyne groups and ten protected amino groups (BNC$_{60}$-alkyne/2alkynes/4alkynes) as well as a functionalized C$_{60}$ bearing one azide group and ten protected carboxylic acid groups (TC$_{60}$-N$_3$) were synthesized under the Bingel-Hirsch cyclopropanation reaction. The copper-catalyzed alkyne-azide Huisgen [3+2] cyclo-addition reaction was employed to chemically connect the alkyne and azide group, affording the BNC$_{60}$-TC$_{60}$, BNC$_{60}$-2TC$_{60}$ and BNC$_{60}$-4TC$_{60}$ with protection groups. The deprotection of the protected groups was readily achieved by treating with trifluoroacetic acid to give final target products (NC$_{60}$-AC$_{60}$, NC$_{60}$-2AC$_{60}$ and NC$_{60}$-4AC$_{60}$). The precisely well defined structures of important intermediates and final products were well characterized by Nuclear Magnetic Resonance (NMR) Spectroscopy and Matrix-assisted laser desorption/ionization-time-of-flight (MALDITOF) mass spectra. The further self-assembly behaviors were studied in solution and investigated under Transmission electron microscopy (TEM).
ACKNOWLEDGEMENTS

I really feel grateful to Dr. Stephen Z.D. Cheng, during the whole process of my master academic period. First of all, I would thank him for taking me in his research group. Under his guidance, I became mature in a big group and learned a lot in this group. Second, I really appreciate his kind help for both academic life and daily life. The two years’ life would not be so meaningful without his favor. Whenever I encountered problems or had confusion, he was always the one who I turned to and there is no doubt that he helped get out of the bad condition every time. When I was also benefited from him is his attitude towards science. It is not how much you work but how much you think will decide what kind of person you will be. He always taught me how to think instead of showing me the right way based on his knowledge and experience. During the experiment, he often talked with me about my recent results and some great ideas occurred during these talks. His broad knowledge in polymer physics field often impressed me. It has been a period of amazing experience to work with him.

Besides, I have to thank my committee member Dr. Miyoshi for his advice and his help for my research career in Akron. Being my thesis reader and thesis defense committee, Dr. Miyoshi always made me feel his passion for science. We had conversations time to time and he offered great advice to my project and that was indeed helpful.

I would also like to thank Mr. Zhiwei Lin, a Ph.D. candidate in my group. He was the one who gave me so many synthesis skills and the ability to operate those physics
characterization instruments. To design the molecules and the synthetic routes, we had a lot of discussions and his idea were always novel and promising. He was very patient when I first started doing something. Without his detailed instructions and guidance, my master thesis would not complete.

The help from other group member cannot be ignored. I should thank all the group members and it is really my honor to work in this group.

Last but not the least, I am very thankful to my parents and all my friends. You are the source of my motivation. Thank you for your powerful support and generous favors.
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**CHAPTER**

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1.1 [60] Fullerene

Fullerene, as one of the allotrope of carbon, has gained so much attention in the past few decades due to special properties and potential application value in many kinds of areas.

1.1.1 Development History and Basic Background

Matter based on carbon element was not paid too much attention to until the discovery of carbon allotropes including diamond, graphite and fullerene. Unlike diamond and graphite, fullerene is sphere-like molecule and can be dissolved in multiple organic solvents. Due to these two unique properties, fullerene is attached much more importance to by synthesis chemists.[1]

Back to 1966, D.E.H Jones came up with the idea about creating a hollow carbon cage, so called giant fullerenes nowadays, but unfortunately the academic community downplayed his idea.[2] In 1970, Osawa, the first scientist, proposed the $C_{60}$ as a spherical $I_h$-symmetric molecule, which was just like the shape and structure of a football.[3][4] After that, a lot of research was done to find out this new material $C_{60}$. There was no breakthrough until 1985 in Rice University in Houston, Kroto and Smalley wanted to
study refractory clusters by using mass spectroscopy. They focused pulsed laser on solid graphite because their primal aim was to stimulate carbon nucleates. Accidentally, under this condition, the 720 mass peak standing for $C_{60}$ appeared in the mass spectra, as well as the 840 mass peak standing for $C_{70}$.\[^{[5]}\]

It is very interesting that fullerene is made of a combination of pentagons and hexagons. So far, the $I_{h}$-symmetrical Buckminsterfullerene $C_{60}$ is the most stable and abundant fullerene with a relatively small size. Since Kroto and Smalley discovered $C_{60}$, plenty of efforts have been made to find out the best way to prepare $C_{60}$. At present, arc process, thermal evaporation, combustion and chemical vapor deposition are the most common methods to prepare $C_{60}$.\[^{[6][7]}\]

1.1.2 Fullerene Chemistry

Fullerene chemistry is a part of organic chemistry which is hammered away at studying the properties of fullerene and reactions relevant to fullerene.\[^{[8][9][10]}\] Fullerene is a very novel material so fullerene chemistry is very popular and worth investigating. There are
two kinds of forms to functionalize fullerene. One is to make substituent outside the carbon cage while the other is to trap molecules inside the carbon cage. They are called exohedral and endohedral fullerenes respectively. There are 12 pentagons and 20 hexagons in a $C_{60}$ but interestingly in this structure no pentagons contact with each other. Due to the existence of nucleophiles, fullerenes can be electrophiles nucleophilic additions. Also it can react in electrophilic additions. Due to the unique properties of fullerene, it can undergo a variety of reactions. Under certain conditions, fullerene can proceed to nucleophilic addition reactions$^{[11]}$, pericyclic reactions$^{[12]}$, hydroxylation$^{[13]}$, electrophilic addition$^{[14]}$ and so on. Based on various reactions that can occur on fullerene, the surface of fullerene can be functionalized.

1.2 Bingel-Hirsch Reaction

The most successful and widely-used reaction to functionalize the surface of $C_{60}$ is known as the Bingel-Hirsch reaction.

1.2.1 Basic Background and Mechanism

As is mentioned, fullerene is suitable for various reactions and it can be functionalized internally and externally. Among large quantities of exohedral fullerene reactions, the cycloaddition reaction which substituent were able to be added to [6,6] double bonds, first discovered by Bingel$^{[15]}$ in 1993 further modified by Hirsch$^{[16]}$, is the most important and widely used reaction. The so called Bingel-Hirsch reaction can be done with the presence of bromo derivative of diethyl malonate and a base like 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)$^{[15]}$. The significance of Bingel-Hirsch reaction is
that it enables to extent the property of fullerene by functionalizing it further to widen the its application in different areas. Another advantage of Bingel-Hirsch reaction is that the main product obtained via this reaction can be easily separated by silica chromatography.\cite{1}

The process of Bingel-Hirsch reaction obeys an intramolecular nucleophilic substitution mechanism (SN$_{1}$).\cite{1} As shown in Figure 1.2\cite{1}, it is a typical Bingel reaction process.

![Figure 1.2 Process of Bingel cyclopropanation\cite{1}](image)

Cyclopropanation of C$_{60}$ can undergo in solvent toluene with NaH as auxiliary base in room temperature. A base is used to abstract the proton on the malonate leading to a generation of carbanion or enolate which can react with the electron deficient fullerene double bond. Reversely, a carbanion can be created and it will displace bromine in a nucleophilic aliphatic substitution.\cite{1}

1.2.2 Application to Fullerene Surface

Fullerene itself has no surface activity but its surface can be modified mainly by nucleophilic addition, cycloaddition, and radical addition.\cite{1} As discussed previously, the cycloaddition reaction is the most important approach to exohedral functionalization.\cite{15}

There are six positions where cycloaddition can be done in fullerene. Among monoadducts to hexakisadducts that have been synthesized, hexakisadducts are more
interesting due to their special structure, especially when $T_h$-symmetrical octahedral pattern was formed.

Figure 1.3 a) VB-structure of $C_{60}$ which includes double bond; b) and c) hexakisadduct of $C_{60}$ structure viewed from different directions and their octahedral addition pattern; d) relationships of the double bonds in $C_{60}$ based on their positions\textsuperscript{[17]}

To functionalize fullerene, Bingel-Hirsch reaction is commonly utilized. Hirsch synthesized $T_h$-$C_{66}$(COOEt)$_{12}$ successfully by using diethyl bromomalonate and NaH as a base step by step.\textsuperscript{[17]} Below is Figure 1.4 to show the $T_h$-$C_{66}$(COOEt)$_{12}$ and its step-by-step synthesis.
The success example of synthesizing hexakisadduct of C$_{60}$ is meaningful because based on fullerene malonates C$_{66}$(COOEt)$_{12}$, we can modify fullerene surface the way we want by changing the –OEt group for Bingel-Hirsch reaction or some other reactions that can occur on side chain, the –COOEt functional group. A very typical example is the hydrophilic C$_{66}$(COOH)$_{12}$ obtained by the hydrolysis of Th-C$_{66}$(COOEt)$_{12}$.[18] The hydrophobic fullerene can be hydrophilic as a result of modifying the surface by Bingel-Hirsch reaction.

1.3 Huisgen 1,3-dipolar Cycloaddition “Click” Reaction

The Huisgen 1,3-dipolar Cycloaddition “Click” Reaction, shortly called “Click” reaction has been used in many areas with its high efficiency and no by-products.
1.3.1 Basic Background and Mechanism

The concept of “click chemistry” was first introduced by Dr. Sharpless in 1998 but the reaction was discovered in 1960s.\cite{19} The so called “click reaction” is the cycloaddition of azides and alkynes to form a five-membered heterocyle. It is a fusion process that can connect two reactants with each other.\cite{20} The problem for this reaction is that even if cycloaddition between azides and alkynes is under a relatively high temperature, the triazoles forming cycloaddition always results by-products which could be a mixture of both 1,4 and 1,5 regioisomers.\cite{21}

![Figure 1.5 Formation of by-products in “click” reaction\cite{21}](image)

To avoid the formation of 1,4 and 1,5 regioisomers, Sharpless et al., in 2002, found that copper(I) serving as a catalyst for the reaction could regiospecifically unite azides and alkynes to give only 1,4—disubstituted 1,2,3-triazoles with few or even no by-products. To improve the reaction more, they also found that the Copper catalyst could become better if it was reduced by Cu(II) salts like CuSO$_4$$\cdot$5H$_2$O rather than using Cu(I) directly, which would be more expensive but less pure.\cite{21} For the reductant, two ideal candidates are ascorbic acid and sodium ascorbate because they are helpful to the preparation of a broad spectrum of 1,4-triazole products in high yields and purity at 0.25-2 mol% catalyst loading. In case the formation of undesired by-products in Cu(I) system, oxygen must be excluded from the system during the whole process of this reaction.
The mechanism for the catalytic cycle for the “click reaction” was also proposed by Sharpless after he did a lot of investigation. Figure 1.6 is below showing the whole process and can be used to explain the mechanism.\[21\]

The first step is that Copper (I) species generated with the terminal alkynes. Then the terminal hydrogen becomes the most acidic part. With the existence of a base, it can be deprotonated to offer a Cu acetylide intermediate. The ligand in the system is not very stable and weakly coordinating. The azide can displace one ligand to generate a copper-azide-acetylide complex.

1.3.2 Applications

The Cu-catalyzed azide/alkyne cycloaddition (CuAAC) reaction has been broadly utilized in different areas such as soft matter design\[22\], organic synthesis and dendrimers fabrication.\[23\]
A new way to synthesis copolymer has been put forward due to the application of CuAAC. Polymers containing end functional groups like azide or alkyne can be combined together under certain condition. Among copolymers, benefited from the special physical properties, block copolymers are very important in the industry of material and engineering. Unlike using various living polymerization, now we can synthesize block polymer by connecting two polymers with end-functional group together by the high efficient “click reaction” which results in less by-products and low polydispersity. Figure 1.7 is a typical example showing PS-PEO diblock polymer synthesized by CuAAC.

Another very successful application of CuAAC is to make dendrimers for which a lot of efforts were made to investigate in the past decade. In 2004, Wu et al. published a paper in which a whole process using CuAAC to synthesize convergent dendrimer. An AB$_2$ dendron with two end-alkyne groups and one chloride group was used. After the first step
“click reaction”, by reacting with NaN₃, the chloride could be substituted to an azide group. Then the second step “click reaction” could be done with the presence of a convergent compound containing several end-alkyne groups.

As a consequence of the successful CuAAC, numerous molecules become capable of carrying fragments which further can influence and change their properties to make them valuable to be used in the area of catalyst or biomedicine. [25]

1.4 Self-assembly

More and more studies have been focused on self-assembly and more and more interesting morphologies have been discovered recently.

1.4.1 Basic Background

Self-assembly, independent on molecule sizes and species, is a spontaneous process during which molecules form ordered and high-uniformity structure, separating or gathering. The most important factor whether self-assembly occur or not is the condition for molecule and this means self-assembly is not limited to molecule scale. [26] Self-assembly can also occur at macroscopic scale because some building blocks have been observed that they can externally propelled or self-propelled under proper condition. [27][28] Therefore, self-assembly plays a vital part in chemistry and material science.

So far, all the self-assembly investigations are based on molecule process. Five significant characteristics are used to determine whether the self-assembly process succeeds or not. They are components, interactions, reversibility, environment and mass transport and agitation respectively.
A self-assembling system is composed of molecules that can be same or can be different. What drives self-assembly occur is the interactions including attractive and repulsive interactions between molecules. The result of self-assembly is to transfer less ordered structure into more ordered structure. Environment matters most and typically, self-assembly favors solution state or interface state. In solution, the required motion to bring the molecules into contact is provided by thermal motion.\textsuperscript{[26]}

![Diagram](image)

Figure 1.8 (A) A net attraction and an equilibrium separation drives aggregation (B)

Components blue interacts with each other irreversibly and forms disordered green glasses (C) Components that can adjust their positions, can form ordered pink crystals (D)

An examples of self-assembly in biology\textsuperscript{[26]}

1.5 Janus Particles

Janus particles with different unique properties have been designed and synthesized, for their interesting self-assembly behaviors.
1.5.1 Basic Background

Named after the god Janus, “Janus grains” was first mentioned by De Gennes in his Nobel lecture in 1992. What makes it special is that it has two sides of which one is polar and the other is apolar. Therefore it is potential to be used as a surfactant.[29] The first “Janus grains” was created by embedding half of a spherical particles in a plastic and making the rest on an accessible side.[30] The Janus principle is that two different elements combine together in one same molecule structure and further they can lead to spontaneously assemble into some novel superstructures.[31]

![Figure 1.9 Janus particles that one side is polar and the other side is apolar can assemble when dissolved in water to form superstructures.][31]

To form Janus particles is relatively easy to realize. Colloids particles, one kind of larger particle in size but still under a few micrometers, can be used to form Janus particles. Another advantage of colloids particles over other kind of particles is that their sizes are almost in order. Others are possibly usable for Janus particles are tiny spheres, rods, cubes and ellipsoids. Imagine if one particle is facing to a wall and getting sprayed by some chemicals, this would result in a two-side particle that half side with chemicals covered and the other without any changes. One way to prepare Janus particles is using
liquid-liquid interfaces of emulsions by which particles can be modified chemically and selectively from each liquid.\textsuperscript{[31]} Since the concept of Janus particles was introduced, chemists have found out a lot of techniques to produce Janus particles. The investigation is still undergoing to invent new approach.

Applicably synthesized Janus particles have anisotropic chemical properties. First successful example that Janus particles were applied to was from catalytic reactions in which gas acted as a jet. Interestingly the gas was created by the other side of a particle.\textsuperscript{[31]} In consideration of the excellent physical and chemical properties of Janus particles, clever scientists are trying to figure out more applications based on Janus particles.

1.5.2 Previous Work in Our Group

The most fundamental principle of the Janus particles synthesis is to break the molecule symmetry structure to get different elements in one unit structure which gives Janus particles a great ability to self-assemble under certain conditions.\textsuperscript{[32]} As discussed above, colloids particles are the best candidate to prepare Janus particles. Actually, inorganic Janus particles are easily to achieve as well. Till now plenty of well-developed methods have been utilized to synthesize Janus particles based on colloids and inorganic nanoparticles such as partial contact with reactive media,\textsuperscript{[33]} directed fluxes and fields,\textsuperscript{[34]} spontaneous assembly,\textsuperscript{[35]} and so on. Although these methods are extremely sophisticated, synthesis of Janus particles with well-defined size and homogeneity is still challenging. Our group has been devoted to working on the well-defined and precisely-synthesized
Janus particles based on polyhedral oligomeric silsesquioxanes (POSS) and fullerene. These Janus particles show great capability of self-assembling.

In 2011, Yiwen Li published a paper about nonspherical Janus particles based on POSS including the synthesis route with the application of “click reaction” and their phase behaviors characterized by using differential scanning calorimetry (DSC), small angle X-ray diffraction (SAXD), wide angle X-ray diffraction (WAXD) and TEM. POSS was differently functionliized by thiol-ene reaction such as isobutyl groups functionalized POSS (BPOSS), carboxylic groups functionalized POSS (APOSS) and other types. Thiol-ene reaction also can offer a clickable POSS. To break the symmetry, click reaction is used to link different POSS together. Their self-assembly behaviors were investigated under bulk state. Fortunately they could form hierarchically regular supramolecules. For instance, BPOSS-APOSS Janus particle can shape bilayered structure with head-to-head and tail-to-tail structure which would further cause the formation of a three-dimensional orthorhombic lattice.[36]

Recently, Hao Liu also published a paper describing the synthesis and self-assembling of molecular Janus particles. In this paper, molecular nanoparticles including POSS, fullerene (C$_{60}$) and lindqvisttype polyoxometalate (POM) were the basis of Janus particles. Four kinds of molecules were designed and precisely synthesized, BPOSS-APOSS, BPOSS-POM, BPOSS-carboxyl functionalized C$_{60}$(AC$_{60}$) and DiBPOSS-AC$_{60}$. “Click reaction” was the main reaction for the whole synthetic route and the products were characterized by TEM, SAXD and AFM to study their self-assembly behaviors. The results indicated that under certain conditions, these molecular Janus particles could self-assemble and then form two-dimensional natocrystal structures made of double layers.
2.1 Molecule Design

Janus particles, due to their distinguishing structures, can self-assemble under some given conditions. So far, large amounts of Janus particles have been synthesized and their self-assembly behaviors have been studied by the advanced techniques. But among those Janus particles, a majority of them are amphiphilic which means they are both hydrophilic and hydrophobic. That’s where the discrimination exists. As has discussed above, Hao has reported the synthesis of a series of Janus particles based on POSS, POM and C$_{60}$ and their self-assembly behaviors. It is easy to find out that all the Janus particles described in that paper were amphiphiles. Taking BPOSS-AC$_{60}$ as an instance, BPOSS is isobutyl groups functionalized POSS which hates water and AC$_{60}$ is carboxyl groups functionalized C$_{60}$ which likes water. When they are dissolved in water or polar solvents, self-assembly can happen immediately. Observed by TEM, two-dimensional natocrystal structures can be formed once they self-assemble.$^{[37]}$
Then we wonder if we can design a kind of Janus particle which is no longer amphiphiles but still with different properties. Carboxyl and amino are both hydrophilic but when in water, they can form negative charges and positive charges respectively. This phenomenon might cause self-assembly. The well-developed Bingel-Hirsch reaction and “Click reaction” make our synthesis work realistic. Bingel-Hirsch reaction can provide “clickable” monoadducts $C_{60}$ and functionalized hexakisadduct $C_{60}$. Four main kinds of $C_{60}$ were synthesized, protected amino groups functionalized $C_{60}$ with alkyne group (BNC$_{60}$-alkyne, BNC$_{60}$-2alkynes and BNC$_{60}$-a4lkynes) and protected carboxyl groups functionalized $C_{60}$ with an azide group (TC$_{60}$-N$_3$).
Once we get the functionalized C$_{60}$, Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of azide and alkyne can be done. After two kinds of C$_{60}$ are linked, a deprotection reaction should be carried out to obtain target product: C$_{60}$ carrying amino groups (NC$_{60}$) and carboxylic acid groups (AC$_{60}$).

After the product BNC$_{60}$-TC$_{60}$ was achieved, a deprotection reaction was performed in dichloromethane (DCM) by trifluoroacetic acid. Target product of C$_{60}$ containing 10 amino groups and 10 carboxylic acid groups, positively charged and negatively charged respectively, were obtained. The Janus particle hydrophilic NC$_{60}$-AC$_{60}$ with different kind of charges were studied in different solvents like water or tetrahydrofuran (THF) due to their self-assembly behaviors. Figure 2.4 shows the process of the protection reaction and the structure of the final product NC$_{60}$-AC$_{60}$.
Further linkers with two alkyne groups or four alkyne groups were designed to synthesize Janus particles with different numbers of charges (NC\textsubscript{60}-2AC\textsubscript{60} and NC\textsubscript{60}-4AC\textsubscript{60}). Same methods were used such as Bingel-Hirsch cyclopropanation reaction to functionalize the C\textsubscript{60} and “click” reaction to connect C\textsubscript{60}s together. Their self-assembly behaviors were studied as well.

![Deprotection reaction of BNC\textsubscript{60}-TC\textsubscript{60}](image)

Figure 2.4 Deprotection reaction of BNC\textsubscript{60}-TC\textsubscript{60}

2.2 Chemicals and Instruments

Chemicals that were used during the synthesis work: 3-Azido-1-propanol (Aldrich 97%), methyl malonyl chloride (Aldrich 97%), pyridine (Sigma-Aldrich 99.8%), 4-Pentyn-1-ol
(Aldrich 97%), tert-butyl bromoacetate (Aldrich 98%), malonic acid (Sigma-Aldrich 99%), triethylamine (Sigma-Aldrich 99%), 3-(Boc-amino)-1-propanol (Aldrich 97%), [60]Fullerene (C60, MTR ltd., 99.5%), iodine (Aldrich 99.8%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich 99%), CuBr (Aldrich 98%), N,N',N',N'',N''-pentamethyldiethylenetriamine (PMDETA, Aldrich 99%), and CDCl3 (Aldrich 99.8 at %D), malonyl chloride (Aldrich 97%), hexane (Sigma-Aldrich 95%), ethyl acetate (Sigma-Aldrich 99.8%), toluene (Aldrich 99.5%), dichloromethane (Sigma-Aldrich 99.5%), methonal (Sigma-Aldrich 99.5%), tetrahydrofuran (Sigma-Aldrich 99.5%), 1,2-dichlorobenzene (ODCB, Aldrich 99%), tetrabutylammonium fluoride solution (TBAF, Sigma-Aldrich 1M in THF), acetic acid (Sigma-Aldrich 0.1M), 5-trimethylsilyl-4-pentyn-1-ol (Sigma-Aldrich 95%), Sodium sulfate (Sigma-Aldrich 99%), methyl 3,5-dihydroxybenzoate (Sigma-Aldrich 97%), propargyl bromide solution (Sigma-Aldrich 80 wt. % in toluene), potassium carbonate (Sigma-Aldrich 99.9%), acetone (Sigma-Aldrich 99.9%), 18-Crown-6 (Sigma-Aldrich 99%), lithium aluminum hydride (Sigma-Aldrich 95%), triethylamine (TEA, Sigma-Aldrich 99.9%) and 4-(Dimethylamino)pyridine (DMAP, Sigma-Aldrich 99%).

To characterize the product, 1H and 13C NMR spectra were acquired using a Varian Mercury 300 NMR Spectrometer. Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectra measurements were carried out on a BrukerUltraflex III TOF/TOF mass spectrometer. Further self-assembly behavior study was based on transmission electron microscope (TEM). The TEM images were recorded in a JEOL-1230 microscope with an accelerating voltage of 120 kV. One drop of the micelle
solutions was deposited onto carbon coated copper grids. The solvent was placed under normal condition overnight to let the solvent evaporate.

2.3 Synthesis Procedures

Two main kinds of functionalized C$_{60}$ were synthesized, carboxyl groups functionalized and amino groups functionalized. The “clickable” and functionalized C$_{60}$ can be obtained by Bingel-Hirsch reaction. For the BNC$_{60}$ carrying different number of alkyne groups, different linkers were used. Therefore, six kinds of malonates need to be prepared for the whole synthetic route. After the clickable C$_{60}$s were obtained, click reaction was used to connect two C$_{60}$s. Then final products were gained after deprotection reaction.

2.3.1 Synthesis of Various Malonates

Six kinds of malonates were designed and synthesized in this study for functionalizing C$_{60}$.

2.3.1.1 Malonate with One Azide Group (M1)

3-Azido-1-propanol (0.89 g, 8.8 mmol) and pyridine (0.69 g, 8.8 mmol) was dissolved in CH$_2$Cl$_2$ (70 mL) in an ice bath. Methyl malonyl chloride (0.77 g, 8.8 mmol) was added into the system dropwise. The reaction was stirred overnight. Then the mixture was filtered to remove salt and washed by water. Anhydrous Na$_2$SO$_4$ was added to absorb water overnight. CH$_2$Cl$_2$ was removed by rotary evaporator. To get target product, silica gel chromatography was done by using solvent hexane and ethyl acetate and their volume ratio is four to one.
2.3.1.2 Malonate with One Alkyne Group (M2)

4-Pentyn-1-ol (0.75 g, 8.9 mmol) and pyridine (0.70 g, 8.9 mmol) was dissolved in CH$_2$Cl$_2$ (70 mL) in an ice bath. Methyl malonyl chloride (0.78 g, 8.9 mmol) was added into the system dropwise in one hour. The reaction was stirred overnight. Then the mixture was filtered to remove salt and washed by water. Anhydrous Na$_2$SO$_4$ was added to absorb water overnight. CH$_2$Cl$_2$ was removed by rotary evaporator. To get target product, silica gel chromatography was done hexane and ethyl acetate and their volume ratio is four to one.

2.3.1.3 Malonate with Protected Carboxylic acid Groups (M3)

Tert-butyl bromoacetate (11.4 g, 58 mmol) and malonic acid (2.967 g, 29 mmol) were dissolved in ethyl acetate (120 mL) in a round bottom flask. After that, triethylamine (5.77 g, 58 mmol) was dropwise added into the system in 30 minutes. The reaction took three days. To get product, the solution was first filtered to get rid of the salt and then rotary evaporator was used to make solvent out of the system. Dissolve the raw product into CH$_2$Cl$_2$ (150 mL) and extract into water for three times. The CH$_2$Cl$_2$ solution then was collected and anhydrous Na$_2$SO$_4$ was added to absorb water overnight. The solvent was removed again by rotary evaporator. The residue was refined by Silica gel chromatography in solvent hexane/ethyl acetate with a volume ratio of 8:1.

2.3.1.4 Malonate with Protected Amino Groups (M4)

3-(Boc-amino)-1-propanol (10 g, 56 mmol) and pyridine (4.6 g, 56 mmol) were dissolved in CH$_2$Cl$_2$ (150 mL) in a round bottom flask in an ice bath. Malonyl chloride (4 g, 28
mmol) was dropwise added into the system in one hour. The reaction was carried out in an ice bath overnight. Extract the reaction solution by water (200 mL) for three times then collect the organic phase in a round bottom flask. Anhydrous Na$_2$SO$_4$ was added to absorb water overnight. After that, by using solvent ethyl acetate and hexane (1:1) through silica gel chromatography final product was obtained.

2.3.1.5 Malonate with Two Tetramethylsilane Groups (M5)
5-trimethylsilyl-4-pentyn-1-ol (2.1 mL, 11.7 mmol) and pyridine (0.97 mL, 12.0 mmol) were prepared and then dissolved in CH$_2$Cl$_2$ (80 ml). An ice bath was used to maintain the temperature of the system about 0 degree C. Malonyl chloride (0.55 mL, 5.7 mmol) was then added into the mixture drop by drop. The ice bath was then removed 2 hours later. The reaction was stirred under room temperature overnight. To purify the product, the mixture was first filtered, then washed by water with brine three times. Sodium sulfate was used to dry the mixture. The final product was obtained by silica gel chromatography by hexanes and ethyl acetate with a volume ratio of 6:1.

2.3.1.6 Malonate with Four Alkyne Groups (M6)
Methyl 3,5-dihydroxybenzoate (6.4 g, 38.1 mmol), propargyl bromide solution (12.5 g 83.8 mmol), potassium carbonate (5.8 g, 42 mmol) and 18-crown-6 (38 mg 0.14mmol) were dissolved in acetone (150 ml) under the protection of nitrogen. Oil bath was used to heat the reaction. The reaction was refluxed overnight. After the solvent was removed,
methanol was used as the solvent in the recrystallization at 50 degree C to obtain the final product methyl 3,5-bis(prop-2-yn-1-yloxy)benzoate.

Methyl 3,5-bis(prop-2-yn-1-yloxy)benzoate (3.0 g, 12.3 mmol) was dissolved in THF (15 ml) in an ice bath condition. Lithium aluminum hydride (15.2 ml, 15.4 mmol) was added into system dropwise. After 2 hours, the ice bath could be removed and the reaction was stirred under room temperature overnight. The product 3,5-bis(prop-2-yn-1-yloxy)phenol was extracted by CH₂Cl₂ and water was used to wash the product and take the exceed lithium aluminum hydride out of the system.

3,5-bis(prop-2-yn-1-yloxy)phenol (2.34 g, 5.4 mmol), TEA (1.31 g, 5.3 mmol) and DMAP (40 mg, 0.33 mmol) were dissolved in CH₂Cl₂ (100 ml) in an ice bath. Malonyl chloride (0.91 g, 5.4 mmol) was added into the system dropwise after which the ice bath was removed. The reaction was stirred under room temperature overnight. Water was used to wash the raw product with CH₂Cl₂ for three times. Then methanol was used for recrystallization at 50 degree C to get the target product.

2.3.2 Synthesis of TC₆₀-azide

C₆₀ (500 mg, 0.69 mmol) was dissolved in toluene (500 mL) into a round bottom flask. The solution was stirred under a dark condition with nitrogen for 3 hours to make C₆₀ completely dissolved and no oxygen in the system. M1 (140 mg, 0.69 mmol) and I₂ (177 mg, 0.69 mmol) were added into the system one by one. Another half an hour’s stirring and degassing, DBU (212 mg, 1.38 mmol) was added. After degassing for another 1 hour, the nitrogen was removed. And the whole system was stirred overnight in dark condition. To obtain the product, toluene was first removed by rotary evaporator. Then silica gel
chromatography was done by using solvent toluene/hexane with the volume ratio of 2:1 to get our monoadduct C60.

Monoadduct C60 (350 mg, 0.38 mmol) was dissolved in ODCB (60 mL) under dark and nitrogen environment for three hours later. Then M3 (1.2 g, 3.8 mmol) and I2 (967 mg, 3.8 mmol) was added into the system. DBU (1.16 g, 7.6 mmol) was added after another half an hour’s degassing. Nitrogen was removed one hour later. The reaction took up three days. Extra I2 was removed by silica gel chromatography in pure CH2Cl2 and raw product was obtained in CH2Cl2/ethyl acetate with a volume ratio of 4:1. Target product was achieved by silica gel chromatography in toluene/ethyl acetate with a volume ratio of 12:1.

1H NMR (CDCl3, 300 MHz, ppm, δ): 4.67 (s, 20H), 4.36 (t, 2H), 3.87 (s, 3H), 2.33 (t, 2H), 1.92 (br, 2H), 1.44 (s, 90H). 13C NMR (CDCl3, 300 MHz, ppm, δ): 165.5, 162.9, 145.9, 140.8, 82.5, 78.6, 69.0, 68.7, 63.0, 53.4, 44.7, 27.9.

2.3.3 Synthesis of BNC60-alkyne

C60 (500 mg, 0.69 mmol) was dissolved in toluene (500 mL) into a round bottom flask. The solution was stirred under a dark condition with nitrogen for 3 hours to make C60 completely dissolved and no oxygen in the system. M2 (130 mg, 0.69 mmol) and I2 (177 mg, 0.69 mmol) were added into the system one by one. Another half an hour’s stirring and degassing, DBU (212 mg, 1.38 mmol) was added. After degassing for another 1 hour, the nitrogen was removed. And the whole system was stirred overnight in dark condition. To obtain the product, toluene was first removed by rotary evaporator. Then silica gel
chromatography was done by using solvent toluene/hexane with the volume ratio of 1.5:1 to get our monoadduct C₆₀.

Monoadduct C₆₀ (360 mg, 0.40 mmol) was dissolved in ODCB (60 mL) under dark and nitrogen environment for three hours later. Then M₄ (1.67 g, 4.0 mmol) and I₂ (1.01 g, 4.0 mmol) was added into the system. DBU (1.21 g, 8.0 mmol) was added after another half an hour’s degassing. Nitrogen was removed one hour later. The reaction took up three days. Extra I₂ was removed by silica gel chromatography in pure CH₂Cl₂ and raw product was obtained in CH₂Cl₂/ethyl acetate with a volume ratio of 1:1. Target product was achieved by silica gel chromatography in toluene/ethyl acetate with a volume ratio of 2.2:1.

¹H NMR (CDCl₃, 300 MHz, ppm, δ): 4.36 (s, 20H), 3.15 (s, 3H), 1.92 (br, 2H), 1.44 (s, 90H). ¹³C NMR (CDCl₃, 300 MHz, ppm, δ): 165.5, 156.2, 145.9, 140.8, 82.5, 78.6, 69.0, 68.7, 63.4, 44.7, 37.5, 27.9.

2.3.4 Synthesis of BNC₆₀-2alkynes

C₆₀ (500 mg, 0.69 mmol) was dissolved in toluene (500 mL) into a round bottom flask. The solution was stirred under a dark condition with nitrogen for 3 hours to make C₆₀ completely dissolved and no oxygen in the system. M₅ (264 mg, 0.69 mmol) and I₂ (177 mg, 0.69 mmol) were added into the system one by one. Another half an hour’s stirring and degassing, DBU (212 mg, 1.38 mmol) was added. After degassing for another 1 hour, the nitrogen was removed. And the whole system was stirred overnight in dark condition. To obtain the product, toluene was first removed by rotary evaporator. Then silica gel
chromatography was done by using solvent toluene/hexane with the volume ratio of 1:1 to get our monoadduct C_{60}.

Monoadduct C_{60} (459 mg, 0.41 mmol) was dissolved in ODCB (60 mL) under dark and nitrogen environment for three hours later. Then M4 (1.72 g, 4.1 mmol) and I_{2} (1.05 g, 4.1 mmol) was added into the system. DBU (1.25 g, 8.2 mmol) was added after another half an hour’s degassing. Nitrogen was removed one hour later. The reaction took up three days. Extra I_{2} was removed by silica gel chromatography in pure CH_{2}Cl_{2} and raw product was obtained in CH_{2}Cl_{2}/ethyl acetate with a volume ratio of 1:1. Target product was achieved by silica gel chromatography in CH_{2}Cl_{2}/ethyl acetate with a volume ratio of 2.5:1.

To get the alkyne groups, one step deprotection reaction of TMS was undertaken. The fully functionalized BNC_{60}-2TMS (300 mg, 0.09mmol) was dissolved in THF (10 ml). TBAF (0.23 ml, 0.23mmol) was dropped into the system and then the red solution turned darker. After 10 seconds, 15 drops of CH_{3}COOH was added into the solution and the solution became red again. The mixture was stirred under room temperature overnight. The product was purified by silica gel chromatography in pure CH_{2}Cl_{2} to remove the impurities. Final product was obtained in CH_{2}Cl_{2}/CH_{3}OH with a ratio of 12:1.

^{1}H NMR (CDCl_{3}, 300 MHz, ppm, δ): 4.36 (s, 20H), 3.15 (s, 3H), 1.92 (br, 2H), 1.44 (s, 90H).

2.3.5 Synthesis of BNC_{60}-4alkynes

C_{60} (500 mg, 0.69 mmol) was dissolved in toluene (500 mL) into a round bottom flask. The solution was stirred under a dark condition with nitrogen for 3 hours to make C_{60}
completely dissolved and no oxygen in the system. M6 (347 mg, 0.69 mmol) and I\textsubscript{2} (177 mg, 0.69 mmol) were added into the system one by one. Another half an hour’s stirring and degassing, DBU (212 mg, 1.38 mmol) was added. After degassing for another 1 hour, the nitrogen was removed. And the whole system was stirred overnight in dark condition. To obtain the product, toluene was first removed by rotary evaporator. Then silica gel chromatography was done by using pure toluene to get our monoadduct C\textsubscript{60}.

Monoadduct C\textsubscript{60} (450 mg, 0.37 mmol) was dissolved in ODCB (60 mL) under dark and nitrogen environment for three hours later. Then M4 (1.55 g, 3.7 mmol) and I\textsubscript{2} (0.94 g, 3.7 mmol) was added into the system. DBU (1.13 g, 7.4 mmol) was added after another half an hour’s degassing. Nitrogen was removed one hour later. The reaction took up three days. Extra I\textsubscript{2} was removed by silica gel chromatography in pure CH\textsubscript{2}Cl\textsubscript{2} and raw product was obtained in CH\textsubscript{2}Cl\textsubscript{2}/ethyl acetate with a volume ratio of 1:1. Target product was achieved by silica gel chromatography in CH\textsubscript{2}Cl\textsubscript{2}/ethyl acetate with a volume ratio of 2:1.

\(^1\text{H} \text{NMR (CDCl}_3, 300 \text{ MHz, ppm, } \delta): 4.36 (s, 20\text{H}), 3.15 (s, 3\text{H}), 1.92 (br, 2\text{H}), 1.44 (s, 90\text{H}).\}
\(^{13}\text{C} \text{NMR (CDCl}_3, 300 \text{ MHz, ppm, } \delta): 165.5, 156.2, 145.9, 140.8, 82.5, 78.6, 69.0, 68.7, 63.4, 37.5, 27.9.\)

2.3.6 Click Reaction and Deprotection Reaction

BNC\textsubscript{60}-alkyne (60 mg, 20 mmol), TC\textsubscript{60}-N\textsubscript{3} (63 mg, 24 mmol) and CuBr were added into a reaction flask. Toluene served as the solvent. Oxygen was removed in this system by three freeze-vacuum-thaw cycles. Then PMDETA was added into the reaction system under nitrogen condition. After another two freeze-vacuum-thaw cycles, the reaction was
carried out in room temperature overnight. To get our product, silica gel chromatography was done. First, CH$_2$Cl$_2$/ethyl acetate with a volume ratio of 4:1 was used to remove the excess TC$_{60}$-N$_3$. Then CH$_2$Cl$_2$/ethyl acetate with a volume ratio of 1:1 was used to get the target product BNC$_{60}$-TC$_{60}$.

$^1$H NMR (CDCl$_3$, 300 MHz, ppm, δ): 4.67 (s, 20H), 4.36 (s, 20H), 3.15 (s, 3H), 1.92 (br, 2H), 1.44 (s, 180H). $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm, δ): 165.5, 156.2, 145.9, 140.8, 82.5, 78.6, 69.0, 68.7, 63.4, 37.5, 27.9.

Deprotection aimed to obtain amino groups and carboxylic acid groups. BNC$_{60}$-TC$_{60}$ was dissolved in pure CH$_2$Cl$_2$ (3 mL) in a vial. Then CF$_3$COOH (1.5 mL) was added into the vial. The reaction was carried out in room temperature overnight. The final product NC$_{60}$-AC$_{60}$ was achieved after the solvent was removed.

BNC$_{60}$-2alkynes (30 mg, 10 mmol), TC$_{60}$-N$_3$ (56 mg, 22 mmol) and CuBr were added into a reaction flask. Toluene served as the solvent. The degas process was the same as the click reaction of BNC$_{60}$-TC$_{60}$ during which PMDETA was introduced into the system. Target product was purified by silica gel chromatography. CH$_2$Cl$_2$/ethyl acetate with a volume ratio of 4:1 was used to remove the excess TC$_{60}$-N$_3$. Then CH$_2$Cl$_2$/ethyl acetate with a volume ratio of 1:1 was used to get the final product BNC$_{60}$-2TC$_{60}$.

$^1$H NMR (CDCl$_3$, 300 MHz, ppm, δ): 4.67 (s, 20H), 4.36 (s, 40H), 3.15 (s, 3H), 1.44 (s, 270H). $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm, δ): 165.5, 145.9, 140.8, 82.5, 78.6, 69.0, 63.4, 37.5, 27.9.

BNC$_{60}$-4alkynes (20 mg, 6.1 mmol), TC$_{60}$-N$_3$ (69 mg, 28.2 mmol) and CuBr were prepared. The same click reaction was undertaken and the final product was achieved by silica gel chromatography with CH$_2$Cl$_2$/ethyl acetate=4:1 and CH$_2$Cl$_2$/CH$_3$OH=10:1.
\(^1\)H NMR (CDCl\(_3\), 300 MHz, ppm, \(\delta\)): 4.36 (s, 80H), 3.15 (s, 3H), 1.44 (s, 450H).

The deprotection reaction of both BNC\(_{60}\)-2TC\(_{60}\) and BNC\(_{60}\)-4TC\(_{60}\) were both the same as BNC\(_{60}\)-TC\(_{60}\) by using CF\(_3\)COOH and CH\(_2\)Cl\(_2\) served as solvent.

2.4 Janus particles’ Self-assembly Behaviors in Solution

The self-assembly behaviors in solution of the Janus particles were studied under different conditions.

2.4.1 Solution Self-assembly of NC\(_{60}\)-AC\(_{60}\)

Sample NC\(_{60}\)-AC\(_{60}\) (1 mg) was prepared and dissolved in deionized water (1 g) which was filtered earlier. The solution was stirred under room temperature for three days before the TEM sample was prepared.

Same quantity of the sample NC\(_{60}\)-AC\(_{60}\) was prepared. THF (0.88 g) was filtered and added in the vial. The mixture was also stirred under room temperature for three days.

2.4.2 Solution Self-assembly of NC\(_{60}\)-2AC\(_{60}\) and NC\(_{60}\)-4AC\(_{60}\)

Sample NC\(_{60}\)-2AC\(_{60}\) (1 mg) was prepared and dissolved in deionized water (1 g) which was filtered earlier. The solution was stirred under room temperature for three days.

The preparation of sample NC\(_{60}\)-4AC\(_{60}\) was as the same quantity and time as the preparation of sample NC\(_{60}\)-2AC\(_{60}\).
CHAPTER III

RESULTS AND DISCUSSION

To identify our product, MALDI-TOF mass spectrum and nuclear magnetic resonance (NMR) were the most convincing evidence. Based on the data of mass spectrum and NMR, all the targets products were obtained as expected. Six different kinds of malonates were characterized after they were synthesized by $^1$H and $^{13}$C NMR spectroscopy. The chemical shifts of the different protons and different carbons indicated the purity of the products. The spectrums are shown in appendix. Then they were used to functionalize $C_{60}$ via Bingel-Hirsch reaction.

For $TC_{60}-N_3$, the theoretical molecular weight is 2608.7 matches the molecular we get from mass spectra which is 2608.8. In $^1$H NMR spectra (shown in appendix), the peaks of chemical shift of 1.44 stand for the 90 protons of tert-butyl groups which means the functionalization succeeded. In $^{13}$C NMR spectra, three characteristic peaks corresponding to chemical shifts of 69.0 ppm, 145.9 ppm and 140.8 ppm can be obviously observed indicating this is the hexakisadduct of $C_{60}$. All of these evidence convince us that the target product was obtained.
For BNC\textsubscript{60}-alkyne, the calculation molecular weight is 2983.1. The molecular weight observed by mass spectra is 2983.2. These two numbers are really close to each other. In \textsuperscript{1}H NMR spectra (shown in appendix), the peaks of chemical shift of 1.44 stand for the 90 protons of tert-butyl groups which means the functionalization succeeded. Also, in \textsuperscript{13}C NMR spectra, hexakisadduct C\textsubscript{60}, our target product, hexakisadduct of C\textsubscript{60}, has three characteristic peaks which are sp\textsuperscript{3} carbon atoms showing up at 69.0 ppm and the only two different types of sp\textsuperscript{2} carbons having chemical shifts around 145.9 and 140.8 ppm,
respectively. There three peaks are all clearly showed in our $^{13}$C NMR spectra. Therefore, BNC$_{60}$-alkyne was achieved.

![Figure 3.3 Mass spectra of BNC$_{60}$-alkyne](image)

After “click reaction” between BNC$_{60}$-alkyne and TC$_{60}$-N$_3$, these two C$_{60}$ were linked with each other forming BNC$_{60}$-TC$_{60}$. The calculated molecular weight is 5575.8 and the molecular weight we get from mass spectra is 5575.6. In $^1$H NMR spectra (shown in appendix), the peaks of chemical shift of 1.44 stand for the 180 protons of tert-butyl groups can be obviously observed. In $^{13}$C NMR spectra, the characteristic peaks of
chemical shift of 69.0 ppm, 145.9 ppm and 140.8 ppm standing for the special carbon on our product clearly exist.

Figure 3.5 Mass spectra of BNC₆₀-TC₆₀

Figure 3.6 ¹³C NMR spectra of BNC₆₀-TC₆₀

To make sure the deprotection reaction succeeded, ¹H NMR spectrums before and after deprotection were compared. By comparing these two spectrums, clearly we could find out that before deprotection, peaks of chemical shift of 1.44 ppm standing for the protons
in tert-butyl groups show up and there were no peaks at 8.21 ppm. But after deprotection, peaks at 1.44 ppm totally disappeared while peaks at 8.21 ppm standing for amino groups appeared. And this means our deprotection reaction was successful and the final product NC$_{60}$~AC$_{60}$ was achieved.

For BNC$_{60}$-2alkynes, $^1$H NMR spectra was used to characterized once the Bingel-Hirsch reaction and deprotection reaction were finished. From the spectra, peaks peaks of chemical shift of 1.44 proved the Bingel-Hirsch reaction was successful. No peaks around 0 which are standing for the pronto in TMS group indicated that the deprotection reaction completed.

BNC$_{60}$-4alkynes was obtained after the Bingel-Hirsch reaction directly. The proton and carbon NMR spectra are shown in appendix, the peaks of chemical shift of 1.44 indicating the tert-butyl groups. The characteristic peaks in the carbon NMR spectra were observed as well.

The characterizations of click reaction between BNC$_{60}$-2alkynes and TC60-N$_3$ and BNC$_{60}$-4alkynes and TC60-N$_3$ was the same as BNC$_{60}$-TC$_{60}$ except the mass spectra due to a large amount of charges in the products. The NMR spectra of BNC$_{60}$-2TC$_{60}$ and BNC$_{60}$-4TC$_{60}$ areshown in appendix with their structures.

After all these target products were achieved, their self-assembly behaviors in solution were studied. Below two images were the results from TEM based on NC$_{60}$-AC$_{60}$ dissolved in H$_2$O and stirred for three days.

After water was added in the system, the mixture was transparent which means the product dissolved in the water. But due to the interaction between the negatively and
positively charged C₆₀, the NC₆₀-AC₆₀ pack with each other alternatively. Therefore, the twist nano-belt structure was formed in the solution and was observed under TEM.

Figure 3.7 TEM images of NC₆₀-AC₆₀ in H₂O

But when H₂O was replaced by THF, the mixture was translucent indicating the sample could not totally get dissolved in the THF solvent. This was because the NC₆₀ had extremely strong polarity making it less soluble in THF. Since H₂O is more polar than THF, the product can dissolve in H₂O. After stirred 3 days and under TEM, some vesicles were found. The different solubility of the two kinds of C₆₀ made the NC₆₀-AC₆₀ a normal surfactant. The vesicle structure is shown below as figure 3.8.
Another two samples, NC\textsubscript{60}-2AC\textsubscript{60} and NC\textsubscript{60}-4AC\textsubscript{60} were only studied in H\textsubscript{2}O condition. Since the symmetry of the charges was broken due the number of negative charges were more than positive charges, their self-assembly behaviors were different from the symmetry NC\textsubscript{60}-AC\textsubscript{60}. Instead of the twist nano-belt structures, some aggregated fiber like structure were formed and found. These two products were both well-dissolved in water therefore the interaction between the negative charges and positive charges had the dominant effect in their self-assembly process. Due to the unequal quantities of the charges, their packing was different from NC\textsubscript{60}-AC\textsubscript{60}. Taking NC\textsubscript{60}-2AC\textsubscript{60} as an example. One positively charged C\textsubscript{60} had two negatively charged C\textsubscript{60}s. The two negatively charged C\textsubscript{60}s would then pack with two positively charged C\textsubscript{60}s. Therefore, starting with one positively charged C\textsubscript{60}, four negatively charged C\textsubscript{60}s aggregated after the first step packing. Under the TEM, some fiber like structures were found as shown in figure 3.9 and 3.10 for NC\textsubscript{60}-2AC\textsubscript{60} and NC\textsubscript{60}-4AC\textsubscript{60} respectively.
Figure 3.9 Fiber like structure for NC$_{60}$-2AC$_{60}$ in water

Figure 3.10 Fiber like structure for NC$_{60}$-4AC$_{60}$ in water
CHAPTER IV

SUMMARY AND FUTURE WORK

In summary, Janus particle \( \text{NC}_{60}\text{-AC}_{60} \) has been synthesized successfully. To break the symmetry of the negative charges and positive charges, \( \text{NC}_{60}\text{-2AC}_{60} \) and \( \text{NC}_{60}\text{-4AC}_{60} \) were also obtained by changing the linkers. The principle of the molecule design is to try to synthesize a type of Janus particle that is fully hydrophilic but can form different charges when they are dissolved in water. And that’s what drives the Janus particle to self-assemble under certain condition. Therefore, \( \text{C}_{60} \) were functionalized by amino groups or carboxylic groups. The \( \text{C}_{60} \)s were differently functionalized by Bingel-Hirsch reaction. The “clickable” \( \text{C}_{60} \)s were linked with each other by the application of CuI-catalyzed Huisgen alkyne-azide cycloaddition. Every synthesis step is confirmed by MALDI-TOF mass spectroscopy, \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectrum. The self-assembly in solution was studied mostly based on water as well as THF. The charge symmetry \( \text{NC}_{60}\text{-AC}_{60} \) in water formed twist nano-belt structure while some vesicle structures were found when water was replaced by THF. When the symmetry was broken, fiber like structure was observed when \( \text{NC}_{60}\text{-2AC}_{60} \) and \( \text{NC}_{60}\text{-4AC}_{60} \) were dissolved in water. Because of the limitation of time, the self-assembly behavior of the new Janus particle is not completed and still will be under investigation. Different kind of solvents like acetone or
methanol will be used in the solution self-assembly study. Another new idea is that whether the self-assembly will change when the positive charges and negative charges are not equal in turn. So Janus particles like AC_{60}-2NC_{60} and AC_{60}-4NC_{60} will be synthesized in the future.
REFERENCES


APPENDIX

$^1$H NMR spectra of M1

$^{13}$C NMR spectra of M1
$^1$H NMR spectra of M2

$^{13}$C NMR spectra of M2
$^1$H NMR spectra of M3

![Diagram of M3 molecule with NMR peaks](image)

$^1$H NMR spectra of M4

![Diagram of M4 molecule with NMR peaks](image)
$^{13}$C NMR spectra of M4

$^1$H NMR spectra of M5
$^1$H NMR spectra of M6

$^1$H NMR spectra of TC$_{60}$-N$_3$
$^1$H NMR spectra of BNC$_{60}$-alkyne

$^1$H NMR spectra of BNC$_{60}$-TC$_{60}$
$^1$H NMR spectra of NC$_{60}$-AC$_{60}$

$^1$H NMR spectra of BNC$_{60}$-2alkynes
$^1$H NMR spectra of BNC$_{60}$-4alkynes

$^{13}$C NMR spectra of BNC$_{60}$-4alkynes
$^1$H NMR spectra of BNC$_{60}$-2TC$_{60}$

$^{13}$C NMR spectra of BNC$_{60}$-2TC$_{60}$
$^1$H NMR spectra of BNC$_{60}$-4TC$_{60}$

Chemical structure of NC$_{60}$-2AC$_{60}$