NOVEL THREE DIMENSIONAL $C_{3v}$ SYMMETRIC NANO-MOLECULES BASED
ON POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (POSS) NANO-ATOMS

A Thesis

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

Shan Mei

May, 2013
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Shan Mei

Thesis

Approved:

__________________________
Advisor
Dr. Stephen Z. D. Cheng

__________________________
Faculty Reader
Dr. Toshikazu Miyoshi

Accepted:

__________________________
Dean of the College
Dr. Stephen Z. D. Cheng

__________________________
Department Chair
Dr. Coleen Pugh

__________________________
Dean of the Graduate School
Dr. George R. Newkome

__________________________
Date
The self-assembly of individual building blocks with different shapes into close packed ordered structures is prevalent in nature and has drawn much attention of human for long. The close packing of some simple shapes such as sphere and rods has been widely learned and established while the assembly of polyhedral structures is still unsolved and being studied with numerous efforts, of which tetrahedron is one with special interest. However, many previous researches only study the assembly of the building blocks with sizes either too big (tens or hundreds of nanometers) or too small (around one nanometer). Thus, we seek to obtain a size in between by using the newly emerged nano building blocks with precisely defined structures, persistent shapes and outstanding properties, e.g. Polyhedral Oligomeric Silsesquioxane (POSS). We can predict there to be distinctive difference in the self-assembly behavior and structure between the nano-sized molecules and the traditional ones.

In this work, two novel claw-like $C_{3v}$ symmetric nano-molecules with different linkages were successfully synthesized by connecting 3 POSS nano-atoms to 1,3,5-Triphenyladmantane. The nano-molecules were carefully designed to ensure they possess enough shape persistent ability and 3-5 nm size, which fills the size gap between traditional small molecules and large colloidal particles. The crystals of the molecules were obtained via solvent evaporation method and the crystal structures would be explored. This work can not only provide us a new way of designing crystals with
Nano-sized units but also help us to deepen our understanding of the relationship between molecular structure and crystal structure.
ACKNOWLEDGMENTS

I would like to give my most sincere thanks to my advisor, Dr. Stephen, Z. D. Cheng, for giving me a chance to study and work in his research group, and for his tremendous guidance on not only how to do research in academic area but also how to be a better person in real life.

I would also thank Mr. Mingjun Huang, who gave me great help and precious instructions through the whole experiments despite his own heavy work, especially in the beginning of my research. Without his help, this work could not be completed easily and I might struggle for a long time to get start.

My thanks then go to all the members in Dr. Cheng’s group for helping me both in my research and my life in America. With their help I was able to adapt to the new life here. I would also thank Professor Wesdemiotis and his group members, Ms. Chunxiao Shi and Ms. Kai Guo for the MALDI-TOF mass spectral analysis.

Last but not least, special thanks are given to my parents and all family members. I am most appreciative of their deep love and strong support through my whole life. Whenever I am down, they are always behind me and give me the strongest support and warmest encouragement.
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CHAPTER I

INTRODUCTION

1.1 Self assembly and close packing

The self assembly of different building blocks into superstructures has long been a prevalent topic in academic as well as industrial area. The macroscopic structures and properties of the materials are closely related to the microscopic assembly of the units.\(^1\)

Yet, predicting the superstructures from the shapes and interactions of specific building blocks still remains a problem for human beings. As John Maddox announced about two decades ago “One of the continuing scandals in the physical science is that it remains impossible to predict the structure of even the simplest crystalline solids from a knowledge of their composition.”\(^2\) Thus, this area has attracted both theorists as well as experimentalists, trying to find out the relationship between the microscopic structure and the macroscopic assembly.

Self assembly is the process in which disordered components spontaneously form ordered structures.\(^3\) It covers a wide range including molecular crystals\(^4\), colloids\(^5\), lipid
bilayers, phase separated polymers, polypeptide folding into proteins and so on. The structures formed in self assembly are usually in thermodynamic equilibrium state.

Here, we would limit our discussion about the assembly within hard particles such as atoms, small molecules, hard colloidal particles etc., with certain shapes and surface interactions. In this case, we can talk a little about the thermodynamic of the assembly process. For particles with weak interactions and with relative big sizes (especially for colloidal particles), the thermodynamic behavior of hard particle assembly can be understood through entropy maximization, as discussed by Daan Frenkel. The system tend to minimize its free energy in the ordering process. Conflicting to our intuitive idea that an ordering process is energy driven (or enthalpy driven) with a decrease in entropy compensated by the decrease of internal energy, Frenkel suggested that the ordering process is entropy driven by maximizing the entropy of the system.

With this theory, it is necessary for us to pay more attention to the entropy change in the assembly process. In nature, one way to form ordered structure is close packing of the units. Close packing is a dense arrangement of units into an ordered structure with least free space. To simplify, we may regard the units as spheres and the spheres would close pack into fcc (face centered cubic) or hcp (hexagonal close packing) structure, which can be represented by copper metal and magnesium metal respectively. Both structures are close packed and are stable.
1.2 Small molecular crystal engineering

Self assembly can occur with particles in a wide size range, from small molecules of several angstroms to colloidal particles as large as micrometer scale. Previous work about self assembly mainly focused on small molecules, which has developed into a mature area called crystal engineering.

1.2.1 Intermolecular interactions

Crystal engineering deals with the design and the construction of solid state crystal structure with desired properties from organic species. For molecules, due to the small size, both entropy and enthalpy change contribute a lot to self-assembly process. Usually, the molecular design in crystal engineering is mainly based on utilizing the intermolecular interactions. Intermolecular interaction is a kind of non-covalent bond between molecules that can physically link molecules together. An analogy can be made between the covalent bond and the non-covalent bond that covalent bond links atoms to form molecules while non-covalent bond links molecules to form supramolecules. But there is distinct difference between them in which the bond energy of non-covalent bond is much lower than that of covalent bond. Intermolecular interactions cover a wide range including Van Der Walls force, hydrogen bonding, halogen bonding, π-π stacking, ion-ion force, dipole-dipole interaction, hydrophilic/hydrophobic interaction, metal-ligand coordination, etc. Intermolecular interactions also differ from each other. For example, Van Der Walls force is relatively weak and non-directional while hydrogen bonding is stronger and directional. In crystal engineering, the most widely used non-covalent bonds are hydrogen bond and metal-ligand coordination bond because of the high bond energy.
and directional property. By designing different molecular geometries and bond directions, a variety of 0D to 3D crystal structures have been obtained. An illustration of hydrogen bonding is shown in Figure 1.1

![Hydrogen Bonding Example](image1)

**Figure 1.1** Two examples of hydrogen bonding

1.2.2 Crystals with different dimensions

Crystal engineering scientists have designed a variety of crystal structures ranging from 0 dimensional to 3 dimensional. Among which 1D and 2D are relatively simple while 3D and 0D are under fast development only in recent decades. The schematic illustrations of some structures are shown in Figure 1.2.

![Examples of Crystal Structures](image2)

**Figure 1.2** Schematic representation of some of the simple network architecture form 1-D to 3-D for organic compounds. (a) 1D Zigzag Chain (b) 1D Ladder (c) 2D Honeycomb (d) 2D Square Grid (e) 3D Octahedral (f) 3D Hexagonal
For 1D structure, there are mainly structures of zig-zag chain, helix chain and ladder. And such structures can be gained via both coordination and hydrogen bonding. Su\textsuperscript{13} et al. have obtained 1D molecular ladders from T-shaped building block Co\textsubscript{2}(nbpy\textsubscript{4})(NO\textsubscript{3})\textsubscript{4} via self-assembly. Single X-Ray diffraction study revealed that 1D ladder structure was formed. The metal centers (Co) adopt a hepta-coordinated geometry: three nbpy\textsubscript{4} ligands form a "T-joint" at the metal center whose remaining coordination sites are occupied by two bidentate nitrates. The 1D ladders are generated from the T-shaped building blocks, with nbpy\textsubscript{4} acting as rungs and side rails. Kumar\textsuperscript{14} et al. obtained helical coordination chains by the self assembly of a kind of chiral molecule \{[Ni(4,4'-dipy)(ArCOO)\textsubscript{2}(MeOH)\textsubscript{2}]n\}. The helices are generated around crystallographic 41 or 43 screw axes and each coil of the helix therefore contains four residues. The distance between coils corresponds to the unit cell length, which ranges from 27.02 to 27.91 Å.

For 2D structure, things are more complicated. The strategy of exploiting metals to propagate 2D structures by coordinate with linear ligand spacers has yielded various architectures. The ratio of metals to ligands and the property of metals and ligands are two important factors that determine the topology of the network. Some mostly observed structures are brick wall, square grid, bilayer, honey comb and so on. Among which, grid is a typical sample because it is simple and commonly reported. For example, Ranganathan\textsuperscript{15} et al. has gained different 2D sheet structures (grid, honey comb, etc.) via the hydrogen bond induced self-assembly of Cyanuric acid (CA)/methylcyanurid acid (MCA) and 4,4'-bipyridine in different solvents, and they found that the hydrogen bonds and the final 2D structures are affected by the solvent. MacGillivray\textsuperscript{16} et al. has obtained rectangular grid structure using [M(4,4'-bipy)(pyca)(H\textsubscript{2}O)\textsubscript{2}]. In this structure, one Co
metal center is coordinated to two trans $\mu$-(4,4'-bipy) ligands, two trans $\mu$-pyca ions, and two trans water molecules that form a slightly distorted octahedral coordination environment. The pyca ions participate in the O-H···O hydrogen bonding with a coordinated water to help the alignment of the carboxylate group.

For 3D structure, pioneering work was done by Ermer$^{17}$ on the structure characterization of adamantane-1,3,5,7-tetracarboxylic acid. In this molecule, the four carboxylic groups are tetrahedrally oriented with an angle of 109°28'. Study showed that the molecules self-assemble via hydrogen bonding to an infinite diamondoid (diamond-like) network. Due to the relatively large size of the unit (compared to carbon atom in the real diamond), the network possesses large cavities that could accommodate other networks. Thus, five independent networks interpenetrate into each other to form a 5-fold structure so that the crystal structure is close packed. Following Ermer’s result, a flurry of work on the diamondoid network has been done with adamantane derivatives and other tetrahedral shaped molecules.$^{14-16}$ And different interpenetration degree networks with 7-fold$^{18}$, 3-fold$^{19}$ and 2-fold$^{20}$ have been obtained according to the cavity size. Recently, metal-ligand coordination bond develops fast due to the high bond energy and more importantly the various and controllable bond direction. The basic design strategy is “node and spacer” approach$^{12}$. In this approach, the nodes are metals with specific coordinating positions (usually with 2, 3, 4 and 6 positions) and spacers are usually rigid ligands that could link the nodes together. For example, diamondoid structure can also be obtained via coordination bond using tetrahedrally coordinating metal Zn or Cd as the node and cyanide ligands CN$^-$ as the spacer. Zn(CN)$_2$ and Cd(CN)$_2$ could form diamondoid networks with 2-fold interpenetration.$^{21}$
In complementary to the infinite structures, some groups, like Stang\textsuperscript{22}, Raymond\textsuperscript{23}, Fujita\textsuperscript{24} and some others have developed 0D (or discrete) finite assembly structures via metal-ligand coordination bonding. These structures are not expanded network but discrete closed structures. By using nodes and spacers with different angles, 2D polygon and 3D polyhedron structure can be made. For example, a 3D adamantanoid cage can be obtained by a combination of six 120° ditopic units with four 109.5° tritopic units. The four tritopic units are in 1,3,5,7 position of the adamantane.\textsuperscript{25} This structure is a single cage different from the diamondoid network mentioned above because all the coordination sites are occupied within the cage and no site is available to coordinate with other adamantanoid cage.

1.3 Assembly of colloidal particles

Small molecular assembly (crystal engineering) mainly uses the intermolecular interactions (hydrogen bond and metal-ligand coordination bond) to construct the supramolecular structure. When designing the molecules, we consider more about the direction of the bond and the direction in which the units are linked. For example, in the designing of diamondoid network\textsuperscript{17,21}, we use adamantane or Zn with bond direction of an angle 109.5° between each other, which mimic the bond of a real diamond structure (four sp\textsuperscript{3} bond of a carbon).

Indeed, in the self assembly of small molecules, the intermolecular interactions play an important role, but the geometry of the molecules is also important that it can affect the packing of the molecules. This geometry packing approach was proposed by
In this theory, the interactions between the molecules are assumed to be weak and lacking in direction and thus the system is isotropic. In this model, the crystallization process is governed by close packing. The most stable structure is the one that makes the most economical use of space. This model has been advocated by experimental results that some crystal structure whose overall close packing rather than specific interactions seems to be the critical determinant. In reality, however, this theory is not absolutely right and intermolecular interactions do play an important role in crystallization process.

Through the discussion above, we can have the notion that for molecular assembly both geometrical factor (molecular shape) and chemical factor (intermolecular interactions especially hydrogen bond and coordination bond) contribute to the final structure, affecting the entropy value and enthalpy value respectively. We cannot discuss the self assembly process solely on entropy (molecular geometry) or enthalpy (intermolecular interaction). However, based on the theory of Frekel, the self assembly process of hard particles is entropy driven on condition that the interactions between the particles are weak and the particle size is big enough. Luckily, recent developed colloidal particles are very close to the particles we describe. Thus, in this case, we can discuss the influence of particle shape on the self assembly process with the help of colloidal particles.

The self assembly of individual building blocks with different shapes into ordered structures is a prevalent phenomenon in nature and has drawn a lot of attention. Understanding how different shapes pack into extended arrangement is not only of scientific interest but also has practical significance, because the physical properties of a
material are closely related to the structure of the building blocks and how they 
assembled together. In recent years, much progress has been achieved in the synthesis of 
the colloidal nanoparticles, in their organization into ordered structures, in the 
characterization of the superlattice, and in the computer simulation of packing models. 

For colloidal particles, they can be roughly classified according to the shape. 
From simple to complex, they are sphere, plate, cylinder, polyhedron, etc. Each of them 
has its own assemble characters.

1.3.1 Spheres and patchy particles

Sphere is the simplest shape in nature with a homogenous and isotropic structure. 
Many of the nano scale building blocks (colloidal particles) that have been obtained are 
spheres. The close packing of spheres is also relatively simple and has been deeply 
studied and understood. The close packing of spherical colloidal particles is just similar 
to that of spherical atoms like copper atom or magnesium, which prefer to compact into 
either face-centered cubic (fcc) or hexagonal close packing (hcp) structure to minimize 
the total free energy and get a highest packing efficiency of 74.04%. Fcc and hcp 
structures are shown in Figure 1.3.

![Figure 1.3 Face center cubic (left) and hexagonal close packing (right)]
Pileni and coworkers\textsuperscript{32} reported that the spherical Ag$_2$S nano crystallites were successfully synthesized using reverse micelles by a surfactant sodium bis(2-ethylhexyl)-sulfosuccinate (AOT). The diameters of the nanocrystals were then measured by small angel x-ray scattering (SAXS) and found to be 3, 4 and 6 nm for 3 different samples, each with a 14\% size distribution. The Ag$_2$S nanocrystal monolayer was prepared by solvent evaporation of a heptane suspension. TEM image and diffraction pattern showed that the particles formed a hexagonal network. Large aggregates of the nanocrystal were also obtained by increasing the particle concentration. TEM diffraction revealed that the aggregates were 3D superlattice with a face-centered cubic (fcc) structure.

After the study of mono component spherical nanoparticle assembly, people have turned their attention to the self assembly of multicomponent nanoparticles.\textsuperscript{33} Multicomponent assembly provides us a way to design materials with much more possible structures and properties by tuning the interaction and organization of different particles. Recently, binary nanocrystal superlattice (BNSL) has drawn significant attraction because the two-component system is relatively easy to manipulate while the self assembly of binary components is much more diverse than monocomponent system. In a binary system, the close packing of the spheres is greatly dependent on the size ratio of the spheres, and there exists numbers of interactions like van der Waals, dipolar, Coulombic force that may greatly affect the arrangement.\textsuperscript{33,34} Murray and coworkers\textsuperscript{34} found that in some BNSL samples, the packing efficiency is lower than theoretic value, which should not be a stable state. Further study showed that it is due to the opposite electrical charges on the two kinds of particles. And by tuning the net charges on the nanoparticles, various BNSLs have been obtained from different combination of PbSe,
PbS, Au, Ag, Pd, Fe$_2$O$_3$, CoPt$_3$ and Bi nanoparticles. These mixed nanoparticles assembled through the evaporation of solvent and the aggregates were characterized by TEM showing different patterns. For example, the system of 13.4 nm Fe$_2$O$_3$ and 5.0 nm Au formed a NaCl unit cell. And a system of 6.7 nm PbS and 3.0 nm Pd formed a AlB$_2$ unit cell. Murray and coworkers$^{33}$ then extended the assembly of this BNSL to a much larger scale reaching centimeter size. In this work, a drop of hexane solution of a mixture of two kinds of nanoparticles with certain ratio was spread on liquid surface (diethylene glycol, DEG, which is immiscible with hexane). The hexane then evaporated in a few minutes, leaving the particle film on the DEG surface. The 15 nm Fe$_3$O$_4$ and 6 nm FePt mixture with 3:1 ratio was confirmed to form AlB$_2$ type unit cell by TEM. This work makes the BNSL practically useful in fabricating membranes for devices.

Due to the simplicity of the sphere structure, it is difficult to obtain diverse assemblies because the assembly is dominated by close packing and there are no strong forces that can alter the structures. Thus, scientists modified the particles by either decorating the surface into different patterns to get “Janus particles” or inducing specific patches on the surface to get “patchy particles”. Both two methods are introducing extra force to direct the assembly of the particles. Granick$^{35}$ and coworkers successfully synthesized a kind of “triblock Janus particle” by decorating two poles with hydrophobic domain and introducing electrical charges on the equator section. For this particle, there is electrostatic repulsion in the middle and hydrophobic attraction at the poles. The particles self-assembled into an open kagome lattice structure. This structure is thermodynamically favored with a maximized hydrophobic contact. The density of such structure is lower than that of close packed fcc or hcp lattice, and is of interests in both
scientific theory and practical applications. In another way, Pine and coworkers\textsuperscript{36} functionalized the surface of polystyrene particles by DNA with single-stranded sticky ends to form patches, and the patches on different particles can form highly directional bonds by specific DNA hybridization. The patch number can be controlled from 1-7 in certain positions to mimic the atomic orbitals like s, p, sp, sp\textsuperscript{2}, sp\textsuperscript{3}, sp\textsuperscript{3}d, sp\textsuperscript{3}d\textsuperscript{2} and sp\textsuperscript{3}d\textsuperscript{3}. The particles then assembled mimicking not only the geometry but also chemistry of molecules, to form a colloidal molecule. For example, two 1-patched particles form an A-B type molecule resembling CO, and other colloidal molecules resembling CO\textsubscript{2}, BF\textsubscript{3}, CH\textsubscript{4} are also obtained. As shown in Figure 1.4.

![Illustration of self assembly of patchy particles directed by DNA patches, mimicking CO, CO\textsubscript{2}, BF\textsubscript{3}, CH\textsubscript{4} molecules, respectively.](image)

1.3.2 Rods and plates

Rods and plates are two special shapes due to their huge anisotropy, with either large or small aspect ratio (length divided by width). These kinds of shapes are of some special interests because they can form liquid crystals.\textsuperscript{37} This has been predicted by Onsager\textsuperscript{38} that rod-like particles may form liquid crystals under entropic driven process. Liquid crystal is a kind of matter that has properties between conventional liquid and solid crystals. In liquid crystal the molecules may move with some freedom but they
align in a certain direction. In a word, liquid crystals have no positional order but have
long-range orientation order. Most liquid crystals have a unit of rod-like shape and some
with a plate shape. Traditional liquid crystals consist of organic molecules. Colloidal
particles are theoretically capable of forming liquid crystals but the polydispersity in
shape and size is a big problem. In recent years, the development in controlling shape and
size of inorganic nanocrystals makes it possible to obtain a new class of liquid crystals
with nano-size units. Lekkerkerker and coworkers\textsuperscript{37} synthesized plate like gibbsite
colloids and found that they could form liquid crystal in the suspension. A nematic to
columnar phase transition was also observed by increasing the particle concentration.
Alivisatos and coworkers\textsuperscript{39,40} synthesized a series of CdSe nanocrystal rods with
variable aspect ratios and excellent monodispersity (the widths were 3.2 and 4.2 nm with
5\% distribution, the lengths were 11, 20 and 40 nm with 10\% distribution). The rods were
confirmed to form nematic liquid crystals in the solution and same superlattice structure
can be formed on a substrate by deposition.

Although nano rods and plates are usually studied for liquid crystals, they are
more generally aligned into ordered arrays. Hyeon et al.\textsuperscript{41} synthesized uniform pencil
shaped CoO nano rods. Such nano rods could self assemble into two kinds of
superlattices on substrate. TEM images showed that both horizontally parallel
arrangements and perpendicularly hexagonal honeycomb lattice structure occurred, and
horizontally oriented lattice was more common than vertically oriented one. Further study
shows that the aspect ratio and the number of nanorods are the most important factors
that determine the lattice structure.\textsuperscript{29} Except for the two arrangements, Korgel and
coworkers\textsuperscript{42} found a kinetically favored assembly of CdS nanorods into networks of
stripes. In this case, two or three nanorods assemble side by side with the axis parallel to the stripe. The stripes then cross over each other to form a network. However such structure is not thermodynamically stable and could only be obtained in certain condition.

For nano plates, there are some different shapes of round nanodisc, triangular, square, hexagonal, etc. Due to the similarity in the morphology character (large aspect ratio of diameter to thickness), we can group them together and their assembly behaviors are indeed similar. For nanoplates, there are mainly two assemblies, edge to edge and face to face. Yan and coworkers\textsuperscript{43} reported that both structures were observed in the assembly of LaF$_3$ triangular nanoplates. In the edge to edge assembly, a hcp packing was observed with the face parallel to the substrate. In the face to face assembly, a ribbon-like array was observed in which the plates “stand” on the substrate with the face perpendicular to the surface. Korgel and coworkers\textsuperscript{44} further found that nanoplates prefer to form a face to face stack, with the face either parallel or perpendicular to the substrate.

1.3.3 Polyhedrons

The assemblies of spheres, rods and plates as we discussed above are not complicated due to the relatively simple structures and they have been well studied. Recently, people’s attention has greatly turned to the study of the assembly of a kind of more complicated shape, polyhedrons. This problem is interesting as well as difficult because polyhedron has anisotropic and various tunable structures. The anisotropic nature could give the material some special properties in magnetic, optical, electric, etc. areas.
Besides, the various shapes of the particles make the suprastructure diverse and difficult to predict. Some samples of polyhedrons are shown in Figure 1.5.

![Polyhedrons](image)

**Figure 1.5** Some examples of polyhedron (from left to right: tetrahedron, cube, octahedron, truncated tetrahedron)

The history of experimental study of the packing of polyhedron is not long due to the difficulty in synthesizing particles with controlled shape and size. But lots of theoretical work has been done including computer simulation. The assembly of hard particles is thought to be driven by entropy maximization, and the system tends to reach the highest density and the highest packing efficiency.\(^1\) For the packing of polyhedrons with plat facets, packing efficiency increases with the increase of contact area of the facets. Such requirement translates from one particle to its neighbors and the particles align in a certain direction with a maximum contact area of facets. Thus, the alignment can be regarded as driven by a kind of “directional entropy force”\(^45,46\). This force can be understood by comparing with directional bond between atoms or interactions between patchy particles. Based on this assumption and many others, lots of simulations have been done to model the packing of polyhedrons. Glotzer and coworkers\(^1\) simulated the self assemblies of 145 convex polyhedrons whose arrangements arise only on the shape. The assemblies were classified into four categories: crystals, plastic crystals, liquid
crystals and disordered solids (glasses). By exploring the relationship between the particle shape and the assembly, some principles have been discovered. Two parameters were used to analyze the shape of the polyhedron. One is the isoperimetric quotient (IQ), describing how close the shape is to sphere. The other parameter is the coordination number CN$_f$, meaning the number of nearest neighbors surrounding each polyhedron. A correlation has been made between IQ, CN$_f$ and the assembly categories. This “roadmap” can be used to predict the assembly of a polyhedron according to the particle shape and the coordination number. For example highly faceted polyhedrons which are almost spherical and have a high coordination number will assemble into plastic crystals.

However, the prediction of the structure of polyhedron is just based on our current understanding of self-assembly. Experimental results are still the most important information for us. Recent achievements in synthetic advances make it possible to generate polyhedral colloidal particles with precisely controlled size, shape and surface chemistry, and further explore the assembly of these particles. In the following, some examples of the study on polyhedrons are presented.

The tetrahedral nanoparticles have sharp corners and their self assembly may possess long range translational symmetry while the orientational order is in a short range.$^{29}$ Computational simulations have predicted that such shape would form unexpected crystal and quasicrystals.$^{28}$ Not many experiments have been done on tetrahedral, perhaps due to the difficulty and complexity of the assembly.

Cube is a relatively simple polyhedron. Fang and coworkers$^{47}$ synthesized monodispersed PbTe nanocubes. The self assembly of the particles was observed in both
2D and 3D. In a 2D lattice, the cubes close packed into square arrays. In this situation, the cubes attach face to face, minimizing the surface free energy. The 3D structure was also formed with a simple cubic superlattice dominated the whole structure. Philipse and coworkers\textsuperscript{48} synthesized novel hollow silica cubes by covering the silica on hematite templates that were then dissolved later. The cube length reached 1338 nm. The cubes also formed a square packing in a 2D sheet and a simple cubic lattice in 3D. This is the first observation of a simple cubic lattice by optical microscopy.

An octahedron is the Platonic solid P8 with 6 vertexes, 12 edges and 8 triangular faces. Huang and coworkers\textsuperscript{49} synthesized octahedral gold nanoparticles with sizes of 120 and 60 nm. And three types of self assembly structures were observed. Yang\textsuperscript{50} and coworkers synthesized uniform octahedral silver nanocrystals. The nanoparticles assembled into large, dense supercrystals by gravitational sedimentation. The assembly structure is very close to the Minkowski lattice as the densest packing. Unlike cubes, the octahedral in the densest packing is not a complete face to face contact.

The polyhedrons we discussed above are some examples of regular polyhedrons. In fact, there are numerous or even infinite kinds of polyhedrons if we look at irregular ones with different number and shape of the facets. Nowadays, one kind of these irregular polyhedrons, called truncated polyhedron, has been developed. We can think of this kind of polyhedron as a result of cutting the corners of the regular polyhedron like cube. The self assemblies of such polyhedrons have also been studied. Petit and coworkers\textsuperscript{51} synthesized platinum truncated nanocubes, and the results showed that they assembled into a close packed fcc superlattice. In Yang’s work\textsuperscript{50}, truncated octahedral Ag nanoparticles were synthesized and were observed to assembled into a space filling
Kelvin structure corresponding to a bcc lattice, and the particles were complete face to face packing.

1.4 Molecular design based on POSS

Colloidal particles are indeed good materials for the study of self assembly, and much work has been done as we discussed above. However, there are some intrinsic problems with this system. First, the particles cannot be precisely synthesized, thus it is very difficult or even impossible to get absolute identical shape and monodispersed size of the particles. But the monodispersity of the particle shape and size is very important for the self assembly. Slight difference will affect the packing and such defect may be amplified in the following packing process. Second, the size of the colloidal particles is usually big, reaching 100 nm to 1000 nm, in this size scale, the thermal fluctuation $k_B T$ is not enough to drive the assembly process. Besides, the interactions between colloidal particles are only weak van der walls interactions. So the assembly is difficult to occur even in two dimensions, and not to mention in three dimensions. Thus, extra force is required. So additional surfactant with hydrocarbon chains or polymer are usually added and attached to the particle surface to enhance the interaction. But such “functionality” is far from precise. That is the third problem with colloidal particles. Although scientists have made huge achievements in particle functionalization, like the synthesis of patchy particle, the precise control over the functional group number, position, functional area size etc. still cannot be achieved.
According to the problems, this paper aims at designing a kind of precisely synthesized 3D nano-sized molecule. In order to get such molecule, we need nano sized building block. Till now, several particles have been investigated such as fullerene, dendrimers, polyoxometalates (POM), polyhedral oligomeric silsesquioxane (POSS), etc. Among them, we are especially interested in POSS. POSS has many advantages compared with other building blocks. First, it has nano scale size of about 1 nm according to the different functionality. Second, the shape of the cage is persistent and the chemical property of the cage is relatively stable due to the inorganic character (composed of silicon and oxygen). Third, the precise functionalization methods are well established, including many different functionality. Plus, as many as eight functional positions can make contribution to the non-covalent interaction between POSS particles, which is rather an effective way to improve interaction strength. Last, its structure may provide special mechanical properties to the material. Here, we call it “nano atom” to make an analogy with traditional small atom.

1.4.1 Nano building block — POSS

POSS (polyhedral oligomeric silsesquioxane) is a compound consists of RSiO$_{3/2}$ units (called T) where R is an organic group and Si-O is typically inorganic. POSS can be classified by the repeating number of T, there are various POSS structures ranging from T$_2$ to T$_{16}$, among which the most widely used and learned is T$_8$. The structure of (RSiO$_{3/2}$)$_8$ is shown in Figure 1.6.
Figure 1.6 The structure of T₈ POSS. Left: ball and stick model, Si (yellow), O (red), R (grey). Right: chemical formula of POSS

T₈ POSS has a cubic shape cage consists of Si-O. Si is at the vertex and O is on the edge. On each Si, there is an organic group R. The size of POSS is related to the R group. For R = (CH=CH₂), the distance between the two =CH₂ carbon atoms is about 1.1 nm. POSS has a hybrid property of inorganic material and organic compounds. The inorganic cage provides POSS shape, chemical and thermal stability due to the high energy and the inert property of Si-O bond. The stability of POSS is a very important property because we want POSS to remain cubic structure in the reaction and assembly process. Thermal stability can be determined by TGA analysis that the degradation temperature of POSS and its derivatives are usually over 200°C. For example, TGA showed that the maximum evaporation of T₈(i-Bu)₈ occurs at 285°C while the complete mass loss is at 375°C. The chemical stability is easy to understand if we compare it to SiO₂, and the stability can be proved by IR spectrum. The characteristic peak of Si-O-Si is around 1100 cm⁻¹. By comparing this peak from the spectra before and after reactions, we can see whether the cage has been destroyed or not. On the other hand, the organic R group gives POSS possibility to carry out organic reactions and be practically useful in
molecular design. Nowadays, chemists can synthesize POSS with large number kinds of R groups such as –H, -CH₃, -Ph, -CH=CH₂, -(CH₂)₃NH₂, and so on. Besides, the asymmetric modification of POSS into T₈R₇R’₁ and even T₈R₇₋₅R’₅ have been successfully synthesized and separated.⁵²,⁵³

Recent study about POSS has focused on incorporating POSS with other materials to form nanocomposites. Due to the nano size, POSS is usually used to fabricate POSS/polymer hybrids. There are mainly four ways to make POSS into hybrid polymer or nanocomposites. The first is the copolymerization of organic monomer with POSS possessing the same functional group, such as copolymerizing styrene with vinyl POSS. The second method is mixing POSS with prepared polymer materials by physical blending. This hybrid does not contain covalent bond between POSS and polymer. The third is grafting a POSS with a single functional group onto a polymer chain by covalent bond. The fourth is directly linking POSS cage together into chains or network. The hybrid materials will have either improvement in properties such as thermal stability, combustion resistance, mechanical strength, etc., or novel structure phenomenon and assembly behavior. In this work, the structure and assembly behavior is more important and inspiring. Yu et al.⁵⁵ reported the synthesis and solution self assembly of a novel giant surfactant consists of a hydrophilic carboxylic functionalized POSS head and a hydrophobic PS tail as shown in Figure 1.7. This giant surfactant could self-assemble into vesicle, cylinder and sphere, like small molecular surfactant and amphiphilic block copolymer do. But it showed an interesting behavior that its size is comparable to block copolymer while the behavior is like small molecular surfactant. The conformation of the
PS tail is stretched like the stretched tail in small molecular surfactant, in contrast to the random coil conformation of normal polymers.

![Figure 1.7 Giant surfactant with a carboxylic acid functionalized POSS (APOSS) head and a polystyrene tail.](image)

1.4.2 Molecular design

With such information, we can start the bottom up assembly from the precisely designed nano-atoms. In nanotechnology, there are two ways to fabricate nanostructure: top down and bottom up. Top down is a method that uses external control to direct the nanoshape. One example is photolithography. Bottom up approach assembles small components such as atoms, molecules into larger ordered structures. This method can reach much smaller scale compared to top down method and the nanostructure is more precisely controlled.29,56,57 The basic steps of bottom up method are shown in Scheme 1.1.
Some pioneering work has been done on the nanomolecular design based on POSS. Li et al. synthesized a kind of POSS based Janus particle with one hydrophilic APOSS end and one hydrophobic BPOSS end, as shown in Figure 1.8. It was found to exhibit a bilayered lamellar morphology where the APOSS stack with APOSS and BPOSS stack with BPOSS. The molecule could crystallize with an orthorhombic unit cell (a = 1.53 nm, b = 1.43 nm, c = 4.62 nm) and a symmetry group of Pna2₁.

Figure 1.8 POSS based Janus particle with one hydrophilic POSS and one hydrophobic POSS
Ren et al.\textsuperscript{59} reported the self-assembled crystal structure of a POSS tethered perylenediimide. The molecular structure is shown in Figure 1.9. In the assembly of the molecules, the steric hindrance of POSS makes it difficult to directly stack the molecules together. Instead, two molecules pack into a dimer due to the $\pi-\pi$ interaction. The dimer acts as the building block and forms a huge triclinic unit cell ($a=6.577$ nm, $b=5.213$ nm, $c=1.107$ nm, $\alpha=93.26^\circ$, $\beta=94.85^\circ$, and $\gamma=92.73^\circ$)

![Figure 1.9 BPOSS-PDI-BPOSS molecule](image)

In these work, the dimension of the molecule is limited in one dimension. This constrains both the molecular structure as well as the possible assembly behaviors. In this work, a kind of three dimensional molecule is expected to be synthesized. In a three dimensional space, there are much more possibilities to design and modify the molecular shape. Also, it is easy to imagine that the assembly of a three dimensional structure is more complicated and this may bring unexpected structure or property for the material. In order to design the 3D nanomolecule, nano-sized building block (POSS) and a three dimensional linker are needed. The model of the molecule is shown in Scheme 1.2. The nano building block could provide the nano size and the linker could provide 3D structure. Here, we would like to emphasize the importance of the rigidity of the linker. Rigid
linker can make the whole molecule rigid and shape persistent. Only under this condition can the molecule give us a possible different packing mechanism from small molecules or separated POSSes and can we learn the relationship of shape and packing behavior.

Scheme 1.2 Synthetic strategy for POSS based three dimensional nano-molecules
2.1 Chemicals and Solvents

2.1.1 Chemicals used

ChloropropylisobutylPOSS (BPOSS-Cl, 99%, Hybrid Plastics), aminopropylisobutylPOSS (BPOSS-NH$_2$, 99%, Hybrid Plastics), 3,4:9,10-perylenetetracarboxyldianhydride (99%, Aldrich), decyl bromide (Aldrich, 99%), N-Methyl-N,N-dioccyloctan-1-ammonium chloride (Aliquat 336, Aldrich, 99%), p-Toluenesulfonic acid (PTSA, 99%, Aldrich), trimethylsilylacetylene (99%, Aldrich), N,N,N’,N’,N’’-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), Iodine (I$_2$, 99%, Aldrich), imidazole (99%, Aldrich), [bis(trifluoroacetoxy)iodo]benzene (Aldrich, 99%), Triethylamine(99%, Aldrich), Sodium azide (NaN$_3$, Aldrich, >99.5%), potassium fluoride (KF, 99%, Aldrich), CDCl$_3$ (Aldrich, 99.8% atom D) Silica gel (VWR, 230-400 mesh)
2.1.2 Solvent purification

The main aim of the purification of the solvent is to remove the moisture in the solvent (and some other impurities but not the main goal). For some reactions, water is poisonous. For example in an esterification or amidation reaction, water could greatly decrease the conversion.

Dichloromethane (CH$_2$Cl$_2$, Aldrich, 99%) was stirred with calcium hydride for at least 24 h under reflux. When used, CH$_2$Cl$_2$ was distilled directly into the pre-dried glass reactor (for example a round bottom flask).

Tetrahydrofuran (THF, Aldrich, 99%) was stirred with thin sodium film under reflux for 24 h to remove most of the moisture. When used, the THF was distilled directly to the glass reactor.

2.2 Instrumentations

All $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were acquired in CDCl$_3$ (Aldrich, 99.8% D) using a Varian Mercury 300 or Varian 500 NMR spectrometer. The $^1$H NMR spectra were referenced to the residual proton impurities in the CDCl$_3$ at $\delta$ = 7.27 ppm. $^{13}$CNMR spectra were referenced to $^{13}$CDCl$_3$ at $\delta$ = 77.00 ppm.

Infrared spectra were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by compressing the powder mixture of KBr and sample into a thin plate. The data were processed using Win-IR software.
Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker Ultraflex-III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (335 nm). All spectra were measured in positive reflector or linear mode. The instrument was calibrated prior to each measurement with external PMMA or PS standard at the molecular weight under consideration. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Aldrich, >99%) served as matrix and was prepared in CHCl₃ at concentration of 20 mg/mL. Silver trifluoroacetate served as cationizing agent and was prepared in MeOH/CHCl₃ (1/3, Vol/Vol) at concentrations of 5 mg/mL. The matrix and AgTFA were mixed with the ratio of 10/1 (Vol/Vol). The sample preparation involved depositing 0.5 μL of matrix and salt mixture on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 μL of each sample on a spot of dry matrix, and adding another 0.5 μL of matrix and salt mixture on top of the dry sample (sandwich method). After evaporation of the solvent, the plate was inserted into the MALDI source. The attenuation of the Nd:YAG laser was adjusted to minimize unwanted polymer fragmentation and to maximize the sensitivity.

2.3 Synthetic procedures

2.3.1 Synthesis of Adamantane-3BPOSS

1,3,5-tri(4-iodophenyl)adamantane 2 1,3,5-triphenyladamantane 1 (500 mg, 1.37 mmol, 1.0 equiv.) was dissolved in distilled toluene (30 mL) in a 100 mL round bottom flask. N₂ flow was induced to the system to remove the oxygen for 0.5 h. I₂ (694 mg, 2.73
mmol, 2.0 equiv.) was added under nitrogen flow and stirred for 1 h for the I$_2$ to dissolve. Then, [bis(trifluoroacetoxy)iodo]benzene (1174 mg, 2.73 mmol, 2.0 equiv.) was added and the suspension was stirred for 24 h at room temperature. The mixture was filtered to remove a purple solid. Toluene was removed by vacuum evaporation and the solid was dissolved in 50 mL chloroform. The solution was washed with a NaHSO$_3$ solution (5%, 50 mL), water (50 mL), brine (50 mL) and then dried with anhydrous NaSO$_4$. The product was recrystallized in a mixture of chloroform : methanol = 5:1 to isolate a white powder (Yield 53%). $^1$H NMR (300 MHz; CDCl$_3$): $\delta_H = 1.94$ (6 H, d, J = 2.3 Hz, Ada-CH$_2$), 2.00 (6 H, s, Ad-CH$_2$), 2.53 (1 H, m, Ada-CH), 7.17 (6 H, d, J = 8.5 Hz, Ar o-H), 7.61 (6 H, d, J = 8.5 Hz, Ar m-H) ppm.

1,3,5-tri(4-ethynylphenyl)adamantane 4 1,3,5-Tetrakis(4-iodophenyl)adamantane 2 (520 mg, 0.699 mmol, 1.0 equiv.) was dissolved in distilled toluene (20 mL) in a Schlenk bottle. Dry Et$_3$N (6 mL) was added. The system was degassed on the high vacuum line for 3 freeze-degas-unfreeze cycles. Then trimethylsilylacetylene (1188 mg, 11.01 mmol, 15.75 equiv.), Pd(PPh$_3$)$_2$Cl$_2$ (26.3 mg, 0.037 mmol, 7 mol%) and CuI (7 mg, 0.037 mmol, 7 mol%) were added under N$_2$ flow and the system was degassed once more. The reaction became black within minutes after unfrozen. The mixture was stirred under reflux for 48 h at 110 °C. The reaction was cooled to room temperature and removed of the toluene under reduced pressure evaporation. The residue was then dissolved in chloroform (50 mL), washed with an aqueous solution of HCl (1.0 M, 50 mL), water and dried over anhydrous NaSO$_4$.

The crude 1,3,5-tri(4-trimethylsilyl-ethynylphenyl)adamantane 3 was used for the next reaction (deprotection) without further purification. KF (500 mg) was added to a
suspension of the 1,3,5-tri(4-trimethylsilyl-ethynylphenyl)adamantane in methanol (20 mL) and stirred overnight at 50 °C. The reaction mixture was poured into water (20 mL), extracted with chloroform (30 mL × 3), washed with water (100 mL) and brine (100 mL). The organic layer was dried over anhydrous NaSO₄. Product (201 mg, 65% yield over two steps) was isolated after purification by column chromatography (silica gel, hexane : CH₂Cl₂ = 2.5:1). ¹H NMR (300 MHz; CDCl₃): δ = 2.00 (6 H, d, J = 3.0 Hz, Ada-CH₂), 2.07 (6 H, s, Ada-CH₂), 2.56 (1 H, m, Ada-CH), 3.05 (3 H, s, C≡CH), 7.40 (6 H, d, J = 8.0 Hz, Ar m -H), 7.47 (6 H, d, J = 8.0 Hz, Ar o -H) ppm.

azidopropylisobutylPOSS (BPOSS-N₃) 6  BPOSS-chloride 5 (1.00 g, 1.11 mmol, 1.0 equiv.) and sodium azide (217 mg, 3.33 mmol, 3.0 equiv.) were added to a 100 mL round bottom flask and dissolved by 20 mL DMF and 20 mL THF (NaN₃ did not dissolve well). The suspension was stirred for 24 h under room temperature. Solvent were evaporated under reduced pressure, the residue was dissolved in chloroform (50 mL) and washed with brine (50 mL). The product (910 mg, 90% yield) was obtained after purification by column chromatography (silica gel, hexane : CH₂Cl₂ = 2:1). ¹H NMR (300 MHz; CDCl₃): δ = 0.62 (16 H, d, J=7.1 Hz, POSS-CH₂), 0.97 (42 H, d, J = 6.5 Hz, -CH₃), 1.71 (2 H, t, J = 8.5 Hz, POSS-C-CH₃), 1.86 (7 H, m, -CH), 3.25 (2 H, t, J = 7.0 Hz, N₃-CH₂) ppm.

adamantane-3BPOSS 7 1,3,5-tri(4-ethynylphenyl)adamantine 4 (20.3 mg, 0.0463 mmol, 1.0 equiv.) and BPOSS-azide 6 (150 mg, 0.167 mmol, 3.6 equiv.) were added to a 100 mL Schlenk flask and dissolved by 15 mL purified THF. CuBr (about 5 mg) was added to the solution. The solution was degassed on the vacuum line for 3 freeze-degas-unfreeze cycles. 5 drops of PMDETA were added to the solution under N₂ flow. The
system was degassed once more. The solution was stirred at 70°C for 48h. The product adamantane-3BPOSS (144 mg 85% yield) was obtained after purification by column chromatography (silica gel, hexane : EA = 5:1). $^1$H NMR (300 MHz; CDCl$_3$): $\delta_H = 0.62$ (16 H, d, J = 7.1 Hz, POSS-CH$_2$), 0.97 (42 H, d, J = 6.5 Hz, -CH$_3$), 1.71 (2 H, t, J = 8.5 Hz, POSS-C-CH$_2$), 1.86 (7 H, m, -CH), 2.07 (6 H, s, Ada-CH$_2$), 2.18 (6 H, s, Ada-CH$_2$), 2.60 (1 H, s, Ada-CH), 4.40 (2 H, t, J = 6.8 Hz, N-CH$_2$), 7.55 (6 H, d, J = 7.8 Hz, Ar-o-H), 7.71 (1 H, s, triazole-H), 7.81 (6 H, d, J = 7.8 Hz, Ar-m-H) ppm.

2.3.2 Synthesis of Adamantane-3(PDI-BPOSS)

3,4,9,10-tetra(decyloxycarbonyl)perylene (PDI-4R) 10 3,4,9,10-perylenetetracarboxyldianhydride (PDI) 8 (7.84 g, 20 mmol), KOH (6.0 g, 106 mmol) and 100 ml deionized H$_2$O were added into a 200 mL beaker and stirred at 70 °C in an oil bath for 0.5 hour. The dark red mixture was filtered to a 250 mL round-bottom flask. The pH value was adjusted to 8-9 with 1 M HCl solution. Then ALIQUAT 336 (2.7 g, 6.0 mmol) and KI (0.5 g, 4.0 mmol) were added to the solution. The mixture was stirred vigorously for 10 minutes. Then decyl bromide (35.4 g, 33 mL, 160 mmol) was added and the solution was vigorously stirred under reflux for 2 hours. The solution was cooled down to room temperature and the product was extracted by CHCl$_3$ (200 mL × 2). The CHCl$_3$ phase was washed with 15% NaCl aqueous solution (200 mL × 3). The solution was evaporated to 150 mL. The product was precipitated by adding the solution to 600 mL methanol dropwise. Yellow powder was collected by filtration. Yield 12.85 g, 65%. $^1$H NMR (300 MHz; CDCl$_3$): $\delta_H = 0.87$ (12 H, t, J = 6.4 Hz, -CH$_3$), 1.27 (56 H, m, -CH$_2$),
1.80 (8 H, m, COOC-CH2-), 4.32 (8 H, t, J = 6.5 Hz, COO-CH2-), 8.00 (4H, d, J = 7.9 Hz, Ar-o-H), 8.18 (4 H, d, J = 7.9 Hz, Ar-m-H) ppm.

perylene-3,4-anhydride-9,10-di-(decyloxy carbonyl) (PDI-2R) 11 To a 50 mL round-bottom flask 3,4,9,10-tetra(decyloxy carbonyl)perylene (PDI-4R) 10 (6.0 g, 6.08 mmol), toluene (1.64 mL) and n-dodecane (8.2 mL) were added. The mixture was heated to 95 °C. After the yellow powder was all dissolved, p-toluenesulfonic acid monohydrate (pTsOH, 1151 mg) was added to the solution and the solution was stirred at 95 °C for 5 h. Then the dark red mixture was dissolved in 50 mL CHCl3. This solution was purified by column chromatography (Al2O3 gel, CHCl3 : Aceton = 20:1). Yield 2.94 g, 70%. 1H NMR (300 MHz; CDCl3): δH = 0.87 (6 H, t, J = 6.4 Hz, -CH3), 1.27 (28 H, m, CH2), 1.86 (4 H, m, COOC-CH2-), 4.37 (4 H, t, J = 6.1 Hz, COO-CH2-), 7.58, (2 H, d, J = 7.0 Hz, Ar-H), 7.73 (2 H, d, J = 7.0 Hz, Ar-H), 7.98 (2 H, d, J = 9.9 Hz, Ar-H), 8.45 (2 H, d, J = 5.8 Hz, Ar-H) ppm.

N-(propylisobutylPOSS)-perylene-3,4-dicarboximide-9,10-di-(decyloxy carbonyl) (BPOSS-PDI-2R) 13 To a 100 mL Schlenk flask, PDI-2R 11 (2.0 g, 2.894 mmol, 1.0 equiv.), aminopropylisobutylPOSS (BPOSS-NH2) 12 (3.29 g, 3.76 mmol, 1.3 equiv.) and 20 g imidazole were added. The mixture was purged with N2 flow for 15 min to remove oxygen. Then 8 mL orthodichlorobenzene (ODCB) was added to the flask and the flask was inserted to 120°C oil bath with vigorous stir under reflux for 5 h. The red mixture was cooled down to room temperature and dissolved by chloroform. The product was purified by column chromatography (Al2O3 gel, CHCl3 : Aceton = 20:1). Yield 4.1 g, 90%. 1H NMR (300 MHz; CDCl3): δH = 0.60 (16 H, d, J = 7.1 Hz, POSS-CH2), 0.89 (6 H, t, J = 6.4 Hz, decyl-CH3), 0.96 (42 H, d, J = 6.5 Hz, -CH3), 1.29 (28 H, m, -CH2), 1.86 (7
H, m, -CH), 4.21 (2 H, t, J = 6.2 Hz, N-CH₂), 4.36 (4 H, t, J = 7.0 Hz, COO-CH₂), 8.06 (2 H, d, J = 7.9 Hz, Ar-H), 8.33 (4 H, d, J = 8.2 Hz, Ar-H), 8.50 (2 H, d, J= 7.9 Hz, Ar-H) ppm.

N-(propylisobutylPOSS)-perylene-3,4-dicarboximide-9,10-anhydride (BPOSS-PDI) 14 To a 50 mL round bottom flask, BPOSS-PDI-2R 13 (1.0 g, 0.646 mmol), 50 mL toluene and 0.8 g TsOH were added. Then the flask was inserted to oil bath and heated to 100°C under vigorous stir for 5 h. Then the red mixture was dissolved in chloroform. The product was purified by column chromatography (Al₂O₃ gel, CHCl₃ : Aceton = 20:1). Yield 0.82 g, 82%. ¹H NMR (300 MHz; CDCl₃): δH = 0.59 (16 H, d, J = 7.1 Hz, POSS-CH₂), 0.95(42 H, d, J = 6.5 Hz, -CH₃), 1.85 (7 H, m, -CH), 4.21 (2 H, t, J = 7.4 Hz, N-CH₂), 8.69 (8 H, m, Ar-H) ppm.

Adamantane-3(PDI-BPOSS) 16 To a 100 mL Schlenk flask, 1,3,5-tri(4-aminophenyl)adamantane 15 (28.6 mg, 0.07 mmol, 1.0 equiv.), BPOSS-PDI (350 mg, 0.28 mmol, 4.0 equiv.), DMAP (16.8 mg, 0.14 mmol, 2.0 equiv.), 5 g imidazole were added. The mixture was purged with N₂ flow for 15 min to remove air. Then 8 mL ODCB was added and the flask was inserted to oil bath and heated to 120°C under vigorous stir for 5 h. The mixture was then cooled down and dissolved in chloroform. The product was purified by column chromatography (Al₂O₃ gel, CHCl₃ : Aceton = 20:1). Yield 210 mg, 55%. ¹H NMR (300 MHz; CDCl₃): δH = 0.58 (48 H, s, -CH₃), 0.93 (126 H, s, CH₃), 1.84 (21 H, m, -CH), 2.04 (12 H, s, Ada-CH₂), 4.22 (6 H, t, J = 7.4 Hz, N-CH₂), 8-9 (24 H, m, Ar-H) ppm.
2.4 Single crystal growth

2.4.1 Adamantane-3BPOSS single crystal

The Adamantane-3BPOSS sample was dissolved in 1,2-dichloroethane (CH₂ClCH₂Cl) to give a very dilute solution (~0.02 wt%). In a glass Petri culture dish, a thick flat glass was placed in and a clean thin coverglass (or carbon-coated mica) was put on the thick glass. About 5 mL 1,2-dichloroethane was then poured into the dish (do not pour on the cover glass nor immerse it), covered the dish and waited for 0.5 h for the vapor to be saturated. Then, open the cover slightly, 2-3 drops of the dilute solution were quickly dropped on the surface of the coverglass (or mica). The dish was covered and placed in a stable and flat desk to let the solvent evaporate slowly. The evaporation took about 2-3 days and the crystal formed on the surface of coverglass (or mica). The whole procedure is shown in Figure 2.1.
Figure 2.1 Slow solvent evaporation method to prepare Adamantane-3BPOSS single crystal
2.4.2 Adamantane-3(PDI-BPOSS) single crystal

The Adamantane-3(PDI-BPOSS) sample was dissolved in CHCl$_3$ to give a very dilute solution (~0.02 wt%). In a glass Petri culture dish, a thick flat glass was placed in and a clean thin coverglass (or carbon-coated mica) was put on the thick glass. About 5 mL mixture of CHCl$_3$ and MeOH (CHCl$_3$ : MeOH = 2:1 in volume) was then poured into the dish (do not pour on the cover glass nor immerse it), cover the dish and wait for 0.5 h for the vapor to be saturated. Then, open the cover slightly, 2-3 drops of the dilute solution were quickly dropped on the surface of the coverglass (or mica). The dish was covered and placed in a stable and flat desk to let the solvent evaporate slowly. The evaporation took about 2-3 days and the crystal formed on the surface of coverglass (or mica). The whole procedure is shown in Figure 2.2.
Figure 2.2 Vapor diffusion method to prepare Adamantane-3(PDI-BPOSS) single crystal
CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis of Adamantane-3BPOSS

To design a molecule of 3 dimensions, we need a 3-dimensional linker. As we discussed before, the rigidity of the molecule is also very important so that it can maintain the shape in the self-assembly process. Thus, adamantane is chosen. Adamantane has four reactive sites that are in tetrahedrally oriented position. But here, we only use three of them. Besides, adamantane is a rigid molecule, with the bonds on it in a fixed direction. To further enhance the rigidity, benzene rings are introduced to the molecule.

The synthetic route of adamantane-3BPOSS is shown in Scheme 3.1. In order to link the adamantane core and the BPOSS together effectively, “click” reaction was chosen. “Click” reaction refers to a group of reactions that have high yield, fast reactive rate and high selectivity. They include reactions such as Diels-Alder reactions, thiol-ene reaction etc. Here, we employ the Cu(I) catalyzed [3+2] Azide-Alkyne Huisgen cycloaddition. This reaction is between an azide and a terminal or internal alkyne to give
a 1,2,3-triazole. In this work, alkyne group was introduced to adamantane and azide group was introduced to BPOSS. We tried the opposite way to introduce azide group to adamantane by nitrating the para position of the phenyl with -NO$_3$ group followed by reducing into -NH$_2$ and then substituted by -N$_3$. Such synthetic route has been reported to introduce N$_3$ to benzene ring successfully. But in this case, adamantane is sensitive to extreme environment such as strong acid, strong base or high pressure H$_2$. And in the reaction most adamantane was destroyed. So alkyne group was introduced to adamantane by a relative mild reaction, Sonogashira reaction. The reason to use TMS protected alkyne in the reaction is to prevent both sides of the alkyne from reacting with adamantane core. To remove the TMS group, KF was used instead of KOH as usually reported due to the sensitivity of adamantane to base. The $^1$HNMR spectrum of 1,3,5-tri(4-ethynylphenyl) adamantane is shown in Figure 3.1. From the spectrum, we can see two doublets in 7.40 and 7.47 ppm, which represent the H in ortho and meta position, indicating that the para H has been substituted. The peak at 3.05 ppm indicates that alkyne group was successfully linked to adamantane.

The synthesis of BPOSS-N$_3$ is relatively easy. NaN$_3$ was added in excess to make sure all the chloride groups could be substituted. Due to the poor solubility of NaN$_3$, polar solvent DMF was used. The $^1$HNMR spectrum of the product is in shown in Scheme 3.1. The peaks at 0.62, 0.97 and 1.86 ppm are the hydrogen on BPOSS. The peak at 3.25 is the hydrogen beside the azide group. No peak was shown in 3.7 ppm indicating that no chloride group exists. Further evidence was shown in the FTIR spectrum (Figure 3.6) that there is a peak at 2100 cm$^{-1}$ from the vibration of azide group, indicating the success of the reaction.
The last step is to link the POSS and the adamantane together via [3+2] Huisgen cycloaddition catalyzed by Cu(I). PMDETA is a ligand that can coordinate with Cu(I), so that Cu(I) is soluble in the system. This reaction is highly efficient. But it has one flaw that it is sensitive to O\textsubscript{2}. To be more precise, it is the Cu(I) that is sensitive to oxygen. In this reaction, only Cu(I) can catalyze the reaction but the coordinated Cu(I) is easily oxidized to Cu(II) Thus the reaction is carried out on the vacuum line with a degas operation. The BPOSS-N\textsubscript{3} was added in slight excess to make sure all the adamantane is linked with 3 BPOSSs. The \textsuperscript{1}H NMR spectrum of the product is shown in Figure 3.3. From the spectrum, we can find a peak at 7.87 ppm representing the hydrogen on the triazole ring. We can also find that the peak of alkynyl hydrogen at 3.05 ppm disappeared. These two characters indicate that the reaction is successful and complete. Besides, the integration of the peak showed that each adamantane bears three BPOSSs. This can be further certificated by MALDI-TOF (Figure 3.5) and FTIR (Figure 3.6) analysis. MALDI-TOF shows that the calculated mass and the experimental mass is almost the same and there is only one peak, indicating that the molecule is correct and pure. From the FTIR spectrum, we can see that Si-O-Si vibration peak at 1100 cm\textsuperscript{-1} remains nearly the same before and after the reaction, which means that the POSS cage was not destroyed in the reaction. What’s more, the peak of N\textsubscript{3} at 2100 cm\textsuperscript{-1} disappeared after the reaction, indicating that all the N\textsubscript{3} groups reacted with the alkyne.
Scheme 3.1 Synthetic route of Adamantane-3BPOSS
Figure 3.1 $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of 1,3,5-tri(4-ethynylphenyl)adamantane

Figure 3.2 $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of BPOSS-N$_3$
Figure 3.3 $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of Adamantane-3BPOSS

Figure 3.4 $^{13}$C NMR spectrum (CDCl$_3$, 300 MHz) of Adamantane-3BPOSS
Figure 3.5  MALDI-TOF spectrum of Adamantane-3BPOSS

Figure 3.6  FTIR spectrum of BPOSS-N₃ and Adamantane-3BPOSS
3.2 Synthesis of Adamantane-3(PDI-BPOSS)

The motivation for synthesizing this molecule is that we want to make some modifications and improvements to adamantant-3BPOSS. In adamantant-3BPOSS, the linker between adamantane and BPOSS is not straight. There is an obvious bend in the five member ring. So the whole molecular shape is a little twisted. Besides, although the adamantane core is rigid, the chain between the adamantane and BPOSS is soft (aliphatic chain) and relatively free to rotate and bend. Thus, we seek to make the linker between adamantane and BPOSS more straight and rigid. Perylenediimide (PDI) provides us a good choice to fulfill the aim. The structure of PDI is shown in Scheme 3.2 compound 8. This molecule is a straight planar with a very rigid structure due to the aromatic rings. When introducing PDI into the nanomolecule, the “arm” of the molecule will be more rigid and straight, and the length will also increase. Thus, we can expect a different packing model for this nanomolecule.

The synthetic route of Adamantane-3(PDI-BPOSS) is shown in Scheme 3.2. The synthesis of PDI derivatives is a little bit complicated due to two reasons. One is the poor solubility. PDI only dissolve relatively well in CHCl₃ among common solvents, and actually the solubility is still low in CHCl₃. The second problem arises from the symmetric structure. In this work, the PDI molecule should link two different components with two sides (one for POSS and another for adamantane). So the symmetry must be broken. To solve these problems, the two anhydrides were opened with base and four alkyl groups (-C₁₀H₂₁) were linked to PDI. The four alkyl chains can greatly increase the solubility of the molecule and make the following reactions easier. Then, the two alkyl groups on one side were removed and the anhydride group reformed. In this step,
the solvent type (mixture of toluene : n-dodecane = 1:5/v:v) and amount were carefully
chosen so that once an anhydride formed, the product would precipitate to prevent further
reaction. This guarantees that most product molecules have only one anhydride. By doing
this step, the symmetry of the molecule is broken. The anhydride side can react with
amino group while the alkyl side remains inert. After reacting with BPOSS-NH₂, the
other side was converted to anhydride and reacted with adamantane-NH₂. The sequence
of linking PDI with BPOSS and adamantane should better not be changed because
BPOSS can increase the solubility of PDI due to the large amount of alkyl chains on
BPOSS. If PDI-2R was linked to adamantane first, after removing the two alkyl chains,
the molecule may not dissolve well and make the following reaction difficult.

The \(^1\)H NMR spectrum of PDI-4R **10** is shown in Figure 3.7. The peaks at 0.87,
1.27, 1.80 and 4.32 ppm represent the hydrogen on decyl group. The integration proves
that there are 4 decyl groups. And the two peaks at the aromatic region indicate that the
molecule is symmetric. The \(^1\)H NMR spectrum of product PDI-2R **11** after removing two
decyl groups from PDI-4R **10** is shown in Figure 3.8. From the spectrum we can clearly
find that the aromatic hydrogen showed four peaks, which is due to the symmetry
breaking of the molecule. The peaks of aliphatic hydrogen are almost in the same
positions. But the integration of the peak area is about half of that in PDI-4R, indicating
that half of the decyl groups were removed. The \(^1\)H NMR spectrum of BPOSS-PDI-2R is
shown in Figure 3.9. The spectrum shows character peaks of BPOSS at 0.57, 0.93 and
1.83 ppm, and a peak of the hydrogen beside the amino group at 4.18 ppm. After
removing the remaining two decyl groups, the \(^1\)H NMR spectrum of BPOSS-PDI is
shown in Figure 3.10. We can see that the peaks of decyl group at 0.86, 1.26 and 4.33
disappear (the peak at 1.83 ppm also disappears but cannot be observed directly due to its overlap with the peak of BPOSS, but it can be judged from the integration), indicating that the decyl groups have been removed completely. The last step is combining the adamantane and BPOSS-PDI. The $^1$H NMR spectrum of the final product is shown in Figure 3.11. All the peaks can be assigned, but the peaks at 4.2 and 8-9 ppm region are broad, this may be due to the low concentration of the solvent since the amount of product is too small. The product was further characterized by MALDI-TOF. The result shows only two Dalton difference from the calculated mass. Thus it can be concluded that the molecule is right.
Scheme 3.2 Synthetic route of Adamantane-3(PDI-BPOSS)
Figure 3.7 $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of PDI-4R

Figure 3.8 $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of PDI-2R
Figure 3.9 $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of BPOSS-PDI-2R

Figure 3.10 $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of BPOSS-PDI
Figure 3.11 $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of adamantane-3(PDI-BPOSS)

Figure 3.12 MALDI-TOF spectrum of adamantane-3(PDI-BPOSS)
3.3 Single crystals of two molecules

There are many ways to grow single crystals. In this work, two methods were used for the two molecules: slow evaporation and vapor diffusion. For adamantane-3BPOSS, slow evaporation was used. In this method, the sample is dissolved in a carefully selected solvent to make a very dilute solution. The solvent is controlled to evaporate slowly and the solution gradually becomes over saturated. In an over saturated condition, the molecules in the solution start to nucleate and crystals grow based on these small nucleus. Although many different factors affect the crystal growth, two factors are of special importance here, which are the solvent and evaporating rate. The best solvent in this case is the theta solvent. But it is not practical to find such theta solvent since we do not know any parameters of the molecule and it is not necessary. The aim for us is to find a solvent that has neither too good nor too bad solubility to the sample. If the solubility is too good, the solution could not reach over saturated until the end of the evaporation process, in this case, the crystallization process is too short and the molecules do not have enough time to arrange the conformation to pack orderly. On the other hand, if the solubility is too bad, the molecules in the solvent do not have good mobility and cannot pack efficiently either. Thus, a proper solvent should provide the molecules relatively good mobility as well as enough time to crystallize before the solvent evaporate completely. For another factor, evaporating rate, it is expected to be slow. The molecules have a rather big size and rigid structure, so the ordered packing is relatively difficult and requires a long time. Usually 2 days are enough for this molecule. After trying many different solvents, we chose dichloroethane for Adamantane-3BPOSS.
For another molecule, adamantane-3(PDI-BPOSS), vapor diffusion method was used. In this method, the sample is dissolved in a good solvent (for this molecule, chloroform). The solution droplets are then placed in a bad solvent vapor atmosphere (here we use methanol). Usually the boiling point of the bad solvent is a little lower than that of good solvent so that the bad solvent vapor will diffuse into the solution. The solubility of the mixed solvent will thus decrease gradually and to a critical point, the molecules begin to crystallize. And after the solvent evaporates, the crystal will be left. In this method, the rate of the diffusion is an important factor. If the diffusion is too fast, the crystallization process will be too fast for the molecules to pack orderly. If too slow, the solution will be all evaporate before the solubility reaches a critical point. Here, we controlled the diffusion rate by controlling the partial pressure of methanol. By using different mixture of chloroform/methanol, the partial pressure of methanol vapor will be different. Experiments proved that a ratio of chloroform : methanol = 2:1 (v:v) is a proper one.

The crystal images of the two samples are shown in Figure 3.13. a, b and c are crystal images of adamantane-3BPOSS. This sample forms an elliptical crystal with the length of the long axis about 50 nm. d, e and f are crystal images of adamantane-3(PDI-BPOSS). This sample forms a rod-like crystal structure with a length of about 50 nm. c and f are the picture taken under a polarizing optical microscopy showing birefringence phenomenon. Birefringence is a character phenomenon of anisotropic crystals so it is a proof that what we obtained here is crystal, not an amorphous phase.
Figure 3.13 Crystal images under polarizing optical microscopy (a,b: adamantane-3BPOSS. c: adamantane-3BPOSS with birefringence phenomenon. d,e: adamantane-3(PDI-BPOSS). f: adamantane-3(PDI-BPOSS) with birefringence)
CHAPTER V

SUMMARY

The assembly of particles with different shapes and sizes is always of great interest. In this work, two kinds of novel three dimensional nano-molecules were synthesized based on POSS nano building block, which are adamantane-3BPOSS and adamantane-3(PDI-BPOSS). Both molecules have C$_{3v}$ symmetry with shape similar to NH$_3$ molecule. Two molecules differ in the rigidity and length of the linkage, which may influence the packing of the molecules. The products were characterized by $^1$HNMR, $^{13}$CNMR, FTIR, MALDI-TOF and proved to be correct and pure. Two methods (slow evaporation and vapor diffusion) were used to grow single crystal of the molecules. The single crystals were observed under optical microscopy and birefringence phenomenon was observed.
REFERENCES


