SELF-ASSEMBLE OF NOVEL DISCOTIC NANO-MOLECULES BASED ON POLYHEDRAL OLIGOMERIC SILSESQUIOXANES

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SELF-ASSEMBLE OF NOVEL DISCOTIC NANO-MOLECULES BASED ON POLYHEDRAL Oligomericsilsesquioxanes

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Thesis

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ABSTRACT

Self-assembly is a process that components automatically form order patterns without any human intervention. The molecular self-assemble, including especially so called crystal engineering, has provided numerous of novel hierarchical structures with exceptional properties. However, due to their relatively small size, the intermolecular interactions play the vital role in the assemble process while the geometry effect is usually neglected. Recent studies of colloidal particles with size between tens of nanometers to several micrometers proved the significance of shape in the self arrangement of the molecules. Herein, we seek to engineer the self-assemble utilizing giant molecules which have precise chemical structure, symmetric discotic shape, and specially several nanometer size filling the gap between small molecules and colloidal particles.

In this work, two novel discoticnano-molecules or so call giant molecules were successfully synthesized by connecting three POSS and six POSS to Truxene and Triphenylene core respectively utilizing "Huisgen Cycloaddition" click reaction. Crystal structure of the giant molecule having three POSS attached to Truxene core was carefully investigated through X-ray diffraction and transmission electron microscope (TEM) diffraction. While for the giant molecule with six POSS cages attached to Triphenylene core, surprisingly it could show distinct self-assembly behavior in which A15 phase structure was found when POSS was not crystallized. This work could not only provide the detailed analysis
of crystal structure and unusual A15 phase structure, but more importantly, deepen our understanding of intermolecular interaction and shape effect on hierarchical structures based on such simple discotic giant molecules.
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CHAPTER I

INTRODUCTION

1.1 Molecular Self-assembly

Self-assembly is a process that components automatically form order patterns without any human intervention. This phenomenon is common in nature and has no limitation on length scale of components as long as properly conditions are met. Tiny matters such as DNA self-assemble into double helical structure while giant planets such as the sun and the earth comprise the galaxy still via self-assembly process. Generally, there are two main type of self-assembly and one of them is called the static self-assembly which requires the systems to reach an equilibrium state and do not dissipate energy.

Molecular self-assembly which is a static self-assembly surly is a free energy minimizing process. Many reasons can explain why molecular-self-assembly draw dramatic attentions from scientists. Among them, one significant issue is that molecular self-assembly make it possible to answer the question posed by Richard Feynman: “What could the properties of materials be if we could really arrange the atoms the way we want them?” An essential part of this question lies in the word "arrange", although it is impossible to place the atoms or molecules with hands just like workers pack bricks to build a house. The self-assembly principles make designing molecules to form any order structure as that scientist had already in mind no longer a dream. As every material science student have been told that structure determines the property of materials
self-assembly is a way to build the bridge connecting chemical structure and the state of aggregation of the molecules. The molecular self-assembly is fascinating for the two following main reasons. Firstly, biological cells contain numerous of structures that are formed through self-assembly of nucleic acid, protein, and other kinds of molecules. Thus, molecular self-assembly is somehow fundamental issue in understanding biological process which is closely bound up with improving and extending human life. Secondly, the advanced communication technology, brought by the Third Industry Revolution, never stops chasing smaller machines. The molecular devices which can load much more information than traditional ones in a certain area, meet the demand of miniaturization of devices.

In principle, molecular self-assembly is controlled by five characteristics. The first one is the component itself. Obviously, protein and tobacco mosaic virus show distinct self-assembly behavior both in structure and kinetics. Secondly, interactions between the molecules affect the self-assembly. Although these interactions are weak, they are the driving force for molecules to construct ordered structures. The third factor so called adjustability describe the ability that the components in the system can adjust their positions to make sure the self-assembly is a reversible process. Fourthly, since most of the self-assembly happens in solution or at the interface, the environment of the molecules certainly will affect the motion of them. In other words, the interaction between the components and their surrounding cannot be ignored. Last but not the least, the mass which closely affects the mobility of the molecules also has influence on the self-assembly behavior. For instance, heavy molecules may need relatively strong bonds to help them forming large structure.
There are many methods for further studying how these characteristics will affect the molecular self-assembly. Chemists mainly manipulate atoms and molecules which are in the 0.1 nm- 2 nm range. Thus, an approach so called bottom-up seems ideal to study molecular self-assembly since chemists are at the "bottom". Large scale of architecture can be constructed through arranging small molecules properly. Examples of bottom-up are plenty in nature where small molecules construct numbers of nano-devices that can sustain life. Two remarkable advantages of the bottom-up approach are that, specific functions can apply on the final devices through ingenious molecular design. Also, this approach provides better understanding of biological processes since it is somehow a mimic procedure.

1.2 Intermolecular Interaction and Crystal Engineering

Although the theory seems simple, controlling the self-assembly behavior of molecules by bottom-up remains a challenge. The reason is obvious. Complex factors that will affect the self-assembly lie among molecules. In fact, there are two important parameters (enthalpy and entropy) that should be taken into serious consideration, since the molecular self-assembly minimizes free energy to reach a thermodynamic equilibrium. The intermolecular interaction which contributes to the enthalpy surely be a significant issue in understanding the self-assembly behavior of molecules.

Crystal engineering, which constructs large-scale solid-state structures by small molecules, guides us to explore the role of interaction in the molecular self-assembly. Crystal can be regarded as a specific self-assembly result and in crystal engineering, the non-covalent bonding is a powerful tool because the
engineers rely on the intermolecular interactions to construct their designed structures. These bonds are weaker than the covalent bonds connecting atoms, however the "non-covalent" bonds form solid-state supermolecule lattice (crystal) through arranging molecules properly. Van Der Walls force, hydrogen bonding, metal-ligand coordination, halogen bonding, π-π stacking, ion-ion force, dipole-dipole interaction and hydrophilic/hydrophobic interaction can all be assigned to the non-covalent bonding. However, crystal engineers mainly utilize hydrogen bonding and metal-ligand coordination because of their relatively high strength and directionality. Strong bonds ensure a stable structure. Directionality ensures the orientation and position of a single molecule to be desirable for order pattern formation.

1.2.1 One dimensional structure in crystal engineering

Tremendous works had been done via smartly using hydrogen bonding and metal-ligand coordination bonds to obtain large-scale structures from zero dimension to three dimension. Although the two or three dimension networks are more directly to the crystals, zero and one dimensional ones are the basic elements that scientists can rely on to control the final crystal architecture precisely. For the so call 0D architecture, it is actually discrete solids with critical geometry. Thus, shape of the molecules in this system will affect the self-assembly behavior. The details will be discussed in the following section. For the 1D structures, zig-zag and helical chain are reported both in metal-ligand and hydrogen bonding system. Guo et al. showed a zig-zag chain of AgCN·2AgClO₄·2H₂O with cyanide units asymmetrically bonding to four silver atoms. The kink on the chain may be generated from diagonal pull on the C and N by different silver atoms. An interesting part of these chains is that they are cross-linked by hydrogen bonds
and generated elongated hexagonal channels. A 3D network was found as a result of the channel packing closely. Molecular ladder is another type of 1D structure which requires T-shape building blocks. Losier et al. reported a molecular ladder of \([\text{Co(NO}_3\text{)}_2(4,4'\text{-bpy})_{1.5}]\). In this structure, three 4,4'-bpy ligands coordinate to the Co(II) and the ladder is the result of a self-assembly of these T-shape molecules. The ligands, in this case, play the role of side rails and rungs in a ladder.

1.2.2 Two dimensional structure in crystal engineering

A Typical 2D structure which is square grid can be networks consists of metal and ligand \((1:2)\). The ligands have to be bifunctional and linear. Fujita et al. reported an open framework of square grids using bipy as spacer ligands. A number of transition metals, including Co(II), Cd(II), Ni(II) and Zn(II) are introduced to be the nodes in the square. Also, two different length of spacer ligands in a same grid were reported and the square expectably turned to rectangle. 14,15 "Brick wall" and "herringbone" are other two 2D structures which share a feature that the nodes are T-shape and have three coordination sites. Figure 1.1 shows these three structures. As a matter of fact, these structures will also be generated by hydrogen bonding if only the suitable molecule is can obtain.

![Figure 1.1](image.png)

**Figure 1.1** Three kinds of 2D networks: a. Square Grid, b. Brick Wall, c. Herringbone.
Comparing with the metal-ligand bonds, hydrogen bonding guides molecules into special 2D structures and Figure 1.2 shows one simple situation.

![Honeycomb network formed by hydrogen bonding.](image)

The bold line in Figure 1.2 represents a molecular with three symmetry groups and the dot line represents the hydrogen bonding generated between twogroups. The 1,3,5-benzenetricarboxylic acid is a perfect example.\textsuperscript{18,19,20}

1.2.3 Three dimensional structure in crystal engineering

3D structure is surly the most complicated one since the position and orientation of a single molecule are relatively flexible compare to the 2D or 1D network. In an ideal case, a 3D molecule with symmetrical intermolecular interactions may generate a fine 3D structure. In fact, research proved this prediction. Ermer\textsuperscript{21} determined that the adamantane-1,3,5,7-tetracarboxylic acid with four carboxylic acid groups in a tetrahedrally position is capable of building diamondilike lattice. In order to fill the empty cavities, one network could accommodate other networks. In this particular case, five independent networks interpenetrate into each other to form a 5-fold structure. Following this result, different interpenetrations have been obtained according to the size of the
cavities. Just like hydrogen bonds, metal-ligand coordination bonds also show potential to form diamondoid networks. For example, Cd(CN)_2 could form diamondoid networks with 2-fold interpenetration.

1.3 Geometry Effect and Self-Assembly of Nano-particles.

The strategy applied in the crystal engineering shows that the self-assembly behavior is mainly the consequence of non-covalent bondings. In this system, the molecules can be roughly treated as a point or a line. However, for molecules with large size (generally crystal engineers prepare molecules with size smaller than 1 nm), the geometry itself of these molecules affects their packing behavior. As we have discussed, the molecular self-assembly is a process of minimizing free energy, the entropy change should be also taken into consideration.

Considering the hard sphere system, copper metal for example, the crystal structure is formed by close packing of each atom. Kitaigorodskii once proposed a geometry packing approach that the crystallization process of molecules with certain shape is governed by close packing. A significant feature of this process is that each unit is "close" enough to make a full use of the space. This model may not be absolutely right, however, it alerts us the importance of the shape of the molecules. Because close packing is a dense arrangement of units, the geometry of the units surely affects the efficiency of the space usage. Also, Frenkel stressed a theory that, when the interaction between molecules is weak and the molecular size is big, the thermodynamic behavior of these hard molecules should be entropy-driven. To sum these two theories together, we believe that the geometry of the hard particles is related to the entropy change and
it is a vital factor in a self-assembly process especially for particles with relatively large size.

1.3.1 Spherical and patchy particles.

In fact, recent study on nano-particles proved the important role of shape in self-assemble. Since the nano-particles have distinct shape (usually these particles are around 10 nm), it gives us a chance to dig out the influence of the particle's shape on the self-assembly behavior. From simple to complex, the particles can be roughly classified into sphere, plate, rod, and polyhedron. For sphere system, the structure can be either face-centered cubic (fcc) or hexagonal close-packed (hcp) if the nano-particles are uniform. Also, if one introduce different sizes of spheres into a same system, 3D binary superlattice can be obtained.

Pileni and coworkers prepared a spherical Ag$_2$S nano-particle and the diameters of these spheres were determined by small angel X-ray scattering. The monolayer of Ag$_2$S was prepared by solvent evaporation of a heptane suspension. A hexagonal network was confirmed by TEM image and diffraction pattern. Larger aggregates can also be obtained by increasing the particle concentration. TEM diffraction revealed fcc structure of this aggregation.

Due to the simplicity of the sphere structure, close packing of spherical nano-particles limited the possibility of diverse assembles formation. One easy way to alter the fcc and bcc structures is to introduce strong forces between spheres. Thus, scientists modified the particles via inducing specific patches on the surface to get “patchy particles”. Then the extra force directs the assembly of the particles. Pine and coworkers functionalized the surface of polystyrene
particles by DNA which has a single-stranded sticky ends to form patches and because of the specific DNA hybridization, the patches on different particles can be regarded as highly directional bonds. The number of patches can be controlled as well as the positions to mimic the atomic orbitals like s, p, sp, sp\(^2\), sp\(^3\), sp\(^3\)d, sp\(^3\)d\(^2\) and sp\(^3\)d\(^3\). In fact the particles assembled mimicking not only the geometry but also chemistry of molecules. For example, two 1-patched particles form an A-B type molecule resembling CO, and other colloidal molecules resembling CO\(_2\), BF\(_3\), CH\(_4\) are also obtained.

1.3.2 Nano-plates and nano-rods.

For nano-plates which can be round, triangle, square or polygon, they share a same property that the ratio of diameter to thickness is large. Typical self-assembly of plates are consequences of face-to-face and edge-to-edge contact. One example is the work done by Yan\(^{30}\) et al. who reported both of the two arrangements in LaF\(_3\) nano-plates. The molecules are monodisperse triangular nano-plates with a thickness of 2.0 nm and a edge length of 16.0 nm. They shown that, this molecule can form ahcpsuperlattice via edge-to-edge contact when the nano-plates lay on the face. Also, the nano-plates can stand on the edge and form a ribbon via face-to-face contact. Similar observation was got by Korgel\(^{31}\) et al. who study the self-assembly of copper sulfide nano-plates with a diameter around 15 nm and a thickness around 6 nm. All these work shown a feature that the orientation of the final structure can be tune by control the environment like solvent or the substrate. Nano-rod is another shape with a big ratio of length to width. Liquid-crystalline-like ordering for both nematic and smectic phases were observed by Li\(^{32,33}\) et al. using CdSenano-rods with width around 3 nm and length around 60 nm. In fact, self-assembly of nano-rods is
mainly the consequence of the side by side alignment. The only difference is that
the rods can horizontally lie on the substrate or perpendicularly stand on the
substrate. However, Korgel et al. showed a stripe structure of CdSnano-rods
which surly has head to tail contact besides the side-by-side stacking.

1.3.3 Nano-polyhedron.

Polyhedron nano-particles recently draw much attention. They are more
complicated because of their anisotropic and various tunable structures. One
relatively simple case maybe the cubic nano-particle which is a Platonic solid with
6 square faces, 8 vertices and 12 edges. It is easy to imagine that the nano-cubes
can closely pack into square arrays via face-to-face contact. Fang et al.
demonstrated this thought using cubic PdTe. Not only 2D square arrays was
obtained but also 3D simple cubic super structure was generated by the
self-assembling of monolayer in certain direction. At the mean while, they found
that the long-range order would be lost if the cubic PdTewas covered by a
quasi-cubic shell. This phenomenon somehow stressed the importance of the
face-to-face contact in self-assembly behavior of nano-cubes.

Another less complicated polyhedron is the octahedron which has 6
polyhedron vertices, 12 polyhedron edges and 8 equivalent equilateral triangular
faces. Fang et al. showed three types of 2D monolayer structures in In$_2$O$_3$
octahedral samples. The only difference between these three is the orientation of
the samples on the substrate. Also, Yang et al. reported that large-scale
superstructure of silver octahedron could be generated through densest packing.

In fact, the experimental study of the self-assembly of polyhedron is not
long due to the challenge in synthesizing uniform polyhedron molecules.
However, computer simulation have already provided potential structures of complex polyhedrons. Glotzer et al. simulated the self-assembly of 145 convex polyhedrons and summarized the results into four categories: crystals, plastic crystals, liquid crystals and disordered solids (glasses). A roadmap was proposed by them for predicting the assembly results of polyhedrons. Since they hold a principle that, shape was the only factor that contribute to the self-assembly behavior. Two parameters which described the shape of the polyhedrons were used in this map. One was the isoperimetric quotient (IQ), describing how close the shape was to sphere. The other was the coordination number (CN) showing the number of nearest neighbors surrounding each unit. With these predictions, experiments will have more guidance since recent developments in synthetic advances make it possible to generate polyhedral colloidal particles with precisely controlled size, shape and surface chemistry.

1.4 Superlattice and Micro-phase Separation

According to the discussion in the former sections, one possible destination of molecular self-assembly is to form crystal structure of these small molecules. Actually this is not the whole story. Generally, atoms or single molecules construct the crystal unit cell so the crystal structure is periodic at atom-scale in all three dimensions. So crystal order requires three basic conditions: all atoms, periodic and all three dimensions. If any of the three conditions are not satisfied, the order structure is attributed to superlattice structure. Take micro-phase separation which is a phenomenon usually observed in diblock copolymers system as an example. Diblock copolymers are composed of two polymer blocks not only have distinct compositions but also distinguish properties.
To describe the difference, scientists introduce the interaction parameter $\chi_N$. When $\chi_N$ reaches a certain threshold, phase separation between the two incompatible polymer blocks will take place. However, limited by the strong covalent chemical bonds connecting the two different blocks, this phase separation can only happen at a nano-scale or micro-scale instead of macro-scale which is observed in the water-oil system. The separated domains at micro-scale or nano-scale in certain cases can form ordered structures such as lamellae, double gyroid, cylinder and BCC sphere structure. In lamellae or cylinder order structure, the order is only periodic along one or two dimensions. Besides, there exists no atom level order inside structure, only relatively disordered molecular assembles, which also occurs in BCC sphere structure. Although the superlattice has no precisely crystal structure, it is still an order pattern which contain the intermolecular interaction between molecules. Generally, the smallest unit in superlattice order structure is often beyond several nanometers, therefore the geometry of molecular shape plays more important role in self-assemble process.

1.5 Molecular Design Based on Polyhedral Oligomeric Silsesquioxane (POSS)

To summarize the two typical systems mentioned in the former section which are crystal engineering of small molecules (< 1 nm) and self-assembly of nano-particles (beyond 10 nm). It is worthy to mention self-assembly based on nano-particles or giant molecules is more desirable in understanding the fundament of self-assembly behavior. The reason is simple. Molecular self-assembly is a minimizing free energy process, thus both enthalpy and entropy are equally important. Small molecules which have a neglected geometry effect self assemble mainly via enthalpy change (intermolecular interaction). While the
nano-particles with certain shapes were driven into order structures by entropy change. Although this type of system is good for the study of entropy driven self-assembly, two problems are remained to develop this system. Firstly, particles with mono-disperse size and shape are still a challenge in synthesis. Without well-defined structure of building blocks, self-assembly of the particles will become much more complicated. Large order pattern will become difficult to obtain since a fluctuation in size or shape may generate defects in the final structure. Another drawback of these nano-particles is their relatively large size. Larger size actually means more energy is needed to provide the driving force for assembly. Thermal fluctuation alone is not enough to drive the system into order structures. Thus, external force such as magnetic force or mechanical force should be introduced.

For the first problem, which is preparing mono-disperse and precisely defined giant molecules in size and shape, it can be solved by connecting suitable nano-building blocks through high efficiency and selective reactions. In the synthetic route part, this problem will be discussed in details. To solve the second problem, our group has already provide an excellent way. By combing different shaped and functionalized nano-building blocks utilizing covalent bond, we can create a bank of giant molecules with size in 3 nm to 10 nm range. This exactly fills the size gap between traditional small molecules and colloidal particles. But in this work, giant molecules with relatively simple geometry was covered which is figured out in Figure 1.3. The model has a triangle shape with three fold symmetry. Surprisingly, such a simple geometry could provide a rather complicated self-assemble behavior. By changing the number of building blocks in each vertex and covalent linkage in between, different crystal structure and
superlattice structures could appear. Here, it is worth mention the similar work by Balagurusamy. He and his coworkers synthesized monodendrons with tapered fan shape or cone shape. They proved that these monodendrons could form cylinder and sphere respectively and further generate a superlattice order structure. The cylinder in fact could further self-assembly into columnar hexagonal structure and the sphere could pack together, generating cubic supramolecular assembly such as A15.

The following question after proposing a model is to find ideal nano-size building block. Till now, many nano-particles have been investigated and among them the polyhedral oligomeric silsesquioxane (POSS) is an ideal choice for three remarkable properties. Its size, stability and well defined functionality all contributes to its great interests in research. To understand the attraction of POSS, we should take a look at its chemical structure at first. POSS is a compound consists of $RSiO_{3/2}$ unit (called T) where R is an organic group. Different structure of POSS can be obtained and among them, a widely used and learned is so called $T_8$. The structure of $(RSiO_{3/2})_8$ is shown in Figure 1.4
Figure 1.4 The cage structure of T₈ POSS.

It is clearly shown in the figure that, the T₈ POSS has a cubic shaped cage. In the cage, 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 example, if R = (CH₃), then the size is about 1 nm. Except for the small size, another important property of POSS cage is that, it is stable. TGA analysis shows a good thermal stability. And the chemical stability can be proved by IR spectrum. Therefore, a nano-particle with well defined shape and relatively small size can be generate via this POSS cage. In fact, our group already reported some self-assembly behaviors of the POSS cage. Li et al. synthesized a kind of Janus particle with one hydrophilic end and one hydrophobic end like Figure 1.5 shown. Such giant molecules was found to exhibit a bilayer morphology where the same kind of POSS will stay with each other.

Figure 1.5 POSS based Janus particle
Ren et al. reported the self-assembly of POSS-nanoparticle-tethered perylenediimide molecules. The molecular structure is shown in Figure 1.6. Via π-π stacking, two giant molecules can form a dimmer. Each triclinic unit cell contains six dimmers, and finally grows into a nano-belt shaped crystal.

![Figure 1.6BPOSS-PDI-BPOSS](image)

These two pioneer works deliver a message that, the POSS, especially the BPOSS tend to aggregate together and has the potential to crystallize. Also, by introducing π-π stacking between molecules, the crystallization of BPOSS will be affected. Applying these two rules in the design model, two different molecules were prepared. The first one has a functionalized Truxenen core which had six short alkyl chain at symmetric positions. These alkyl chains can eliminate the π-π stacking so that how the shape of the molecule affects the crystallization of BPOSS can be investigated. The second molecule is based on Triphenylene core which has a strong π-π stacking. Thus, when the BPOSS cannot crystallize well, what kind of order structure will form? Finding out the answer to these two simple questions is the objective for the whole project.
CHAPTER II

EXPERIMENT

2.1 Preface

At the end of the introduction, the chemical structures of the giant molecules in this project were briefly discussed. They have two parts: center core and nano atoms at vertex. The first triangle central molecule in this work is called Truxene. It is a heptacyclicpolyarene with available functionalization at C-2, -7, -12 positions and at C-5, -10, -15 positions. The second core, which is Triphenylene, is a flat polycyclic aromatic hydrocarbon consisting of four fused benzene rings. The nano atoms in this work are POSS with 7 iso-butyl groups on the R position. The two parts will be combined through [3 + 2] Huisgencycloaddition reaction. It is a kind of click reaction with a high efficiency and can form 5-member ring between azide and alkyne group catalyzed by Copper (I). In conclusion, the strategy to prepare these molecules can be divided into three parts. Firstly, alkyne groups have to been introduced to the core on symmetrical position. Then, azide group is attached to the POSS cage. Finally, the two parts can generate the giant molecules via click reaction.
2.2 Materials and Instrumentations

1-Indanone (99 +%, Acros Organics), Acetic acid (Fisher), Hydrochloric acid (concentrated, Fisher), Acetone (Fisher), Tetrahydrofuran (THF, 99%, Aldrich), n-BuLi (2.5 M solution in n-hexane, Aldrich), Bromoethane (Aldrich), Dichloromethane (CH₂Cl₂, Fisher), Bromine (Aldrich), Sodium bicarbonate (EMD), Silica gel (VWR, 230-400 mesh), Pd(PPh₃)₂Cl₂, CuI, Triethylamine (≥99%, Aldrich), Toluene (Fisher), Trimethylsily acetylene, Methanol (Fisher), Potassium hydroxide (Fisher), CuBr, N,N,N′,N″-pentamethyldiethylenetriamine (PMDETA, Aldrich), ChloropropylisobutylPOSS (BPOSS-Cl, 99%, Hybrid Plastics), NaN₃ (Aldrich), Dimethyl Formamide (DMF, Fisher), 2,3,6,7,10,11-Hexahydroxytriphenylene Hydrate (> 95.0 %, TCI AMERICA), ChlorobenzylIsobutyl POSS (BPOSS-Ar-Cl, Hybrid Plastics), Bromoethyne (Aldrich)

All the ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were acquired in CDCl₃ (Aldrich, 99.8% D) using a Varian Mercury 300 NMR spectrometer. The ¹H NMR spectra were referenced to the residual proton impurities in the CDCl₃ at δ 7.24 ppm. ¹³C NMR spectra were referenced to ¹³CDCl₃ at δ 77.00 ppm.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a BrukerUltraflex III TOF/TOF mass spectrometer (BrukerDaltonics, Billerica, MA), equipped with a Nd:YAG laser emitting at a wavelength of 355 nm. All spectra were measured in positive reflector mode. The instrument was calibrated externally with a polystyrene standard, prior to each measurement. Dithranol 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, v/v) at concentrations of 5 mg/mL. The sample was dissolved in CHCl3 at 5 mg/mL. The matrix and AgTFA were mixed with the ratio of 10:1 (v/v). 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, S3 depositing 0.5 μL of each sample on a spot of dry matrix, and adding another 0.5 μL of dithranol and salt mixture on top of the dry sample (sandwich method). Data analyses were conducted with Bruker’sfflexAnalysis software.

Two-dimensional wide angle X-ray diffraction (WAXD) patterns were recorded on a Rigakua 18 kW rotating anode X-ray generator with Cu Kα radiation (0.154 nm) in transmission mode with an R-AXIS-IV image plate system detector. The exposure time was 15 to 20 min. The peak positions were calibrated using silicon crystals. Background scattering was subtracted from the sample pattern. One-dimensional WAXD patterns were obtained by azimuthal integration of 2D WAXD patterns.

Small angle X-ray scattering (SAXS) was conducted on a RigakuMicroMax 002+ instrument equipped with a CCD detector and a high-intensity anode tube Cu X-ray generator with a wavelength of 0.154 nm. The working voltage and current for the X-ray source are 45 kV and 0.88 mA, respectively. A small piece of sample was immobilized with Kapton tape on the sample holder. The collection time for each data was 5 to 10 min, depending on the scattering intensity. The instrument was calibrated using silver behenate with the primary reflection peak (1.067 nm-1). Data were analyzed with the Rigaku software SAXSgui.
TEM experiments were carried out with a Philips Tecnai 12 using an accelerating voltage of 120 kV. Selected area electron diffraction (SAED) patterns with different crystal orientations were obtained using a tilting stage to determine the crystal structure parameters. The d-spacings were calibrated using a TiCl₃ standard. The tilting angle was defined as positive if the tilting direction was clockwise and negative for counter-clockwise.

2.3 Synthetic Procedures

All the synthetic procedures of molecules in this project were listed below and these procedures were modified methods found in literatures.

2.3.1 AzidopropylisobutylPOSS (1).

BPOSS-chloride (1.0 g, 1.11 mmol) and sodium azide (217 mg, 3.33 mmol) were dissolved by 14 mL DMF and 4 mL THF. The solution was stirred for 24h under room temperature. Solvent were evaporated under reduced pressure, the residue was extracted with CH₂Cl₂. The product was obtained after removing the solvent. ¹H NMR (300 MHz, CDCl₃, ppm) δ 0.60 (m, 18H), 0.95 (m, 42 H), 1.86 (m, 7H), 3.22 (t,2H)

2.3.2 10,15-Dihydro-5H-diinden[1,2-a;1′,2′-c]fluorene (Truxene) (2).

The synthesis of truxene was based on a patent proposed by Duvall et al.¹⁶¹-Indanone (5.0 g, 37.88 mmol) was added into a mixture of acetic acid (22 mL) and concentrated hydrochloric acid (11 mL). The mixture was agitated at 96°C for 16 hours. Then the precipitate was filtered off, the solid material was washed with water twice. Then, the crude product was washed by acetone to give
truxene as light yellow solid. $^1$H NMR (300 MHz; CDCl$_3$) δ 4.27 (s, 6H), 7.34-7.97 (m, 12H).

2.3.3 5,5΄,10,10΄,15,15΄-Hexaethyltruxene (3).

The synthesis of this compound as well as the next were based on Yuan and coworkers' paper.$^{47}$ Stirred Truxene (2.5 g, 7.22 mmol) in THF (100 mL) under nitrogen, then n-BuLi (2.5 M solution in n-hexane, 12.0 mL, 30 mmol) was added over a 30 min period and the temperature was maintained at 0° C. Then the solution was naturally warmed to room temperature and stirred for another 30 min. Then, Bromoethane (5 mL, 46.45 mmol) was added at 0 °C. After stirring for 4h at room temperature the second portion of n-BuLi (2.5 M solution in n-hexane, 12.0 mL, 30mmol) and bromoethane (5 mL, 46.45 mmol) was added in the same way like former procedure. After stirring for 12 h, the mixture was poured into water and extracted with dichloromethane. After removing the solvent, the product was purified by column chromatography on silica gel, eluting with hexane.

$^1$H NMR (300 MHz, CDCl$_3$, ppm) δ 0.16-0.23 (t, 18H), 2.09-2.19 (m, 6H), 2.96-3.05 (m, 6H), 7.32-7.47 (m, 6H), 8.31-8.37 (d, 3H). $^{13}$C NMR (300 MHz, CDCl$_3$, ppm) δ 153.06, 144.09, 140.78, 139.04, 126.70, 126.18, 124.68, 122.49, 56.89, 29.58, 8.67.

2.3.4 2,7,12-Tribromo-5,5΄,10,10΄,15,15΄-hexaethyltruxene (4).

Compound 3 (1.50 g, 2.94 mmol) was added to a stirred dichloromethane (30 mL), then, bromine was added (0.5 mL) at room temperature. After 12 h, the reaction mixture was washed with 5% sodium bicarbonate solution and dried over magnesium sulfate. After removing the solvent, the crude product was purified by
column chromatography on silica gel, eluting with hexane. $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ 0.14-0.26 (t, 18H), 2.02-2.17 (m, 6H), 2.84-3.94 (m, 6H), 7.47–7.57 (m, 6H), 8.11-8.18 (d, 3H).

2.3.5 2,7,12-Triethynyl-5,5',10,10',15,15'-hexahexyltruxene (5).

This synthesis is a modification on previous work. Compound 4 (1.14 g, 1.52 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (59.25 mg, 0.075 mmol) were mixed with toluene–Et$_3$N (20 mL/5 mL) in a 100 mL Schlenk flask. The solution was degassed on the vacuum line for 3 freeze-degas-unfreeze cycles. CuI (14.25 mg, 0.075 mmol) and Trimethylsilyl acetylene (0.90 g, 9.16 mmol) were added to the mixture under nitrogen flow. After degassed for another 15 min, the solution was warmed and stirred at room temperature for 24 h. Then, solvent was stripped off under reduced pressure. The residue was purified by column chromatography on a silica gel column, eluting with hexane. The product (compound 5*) was dissolved in THF (50 mL). Then, MeOH (30 mL) and aq KOH (4 mL, 20%) were added at room temperature. The reactant was stirred at room temperature for 10 h. It was then poured into H$_2$O (20 mL) and extracted three times with Et$_2$O. The combined organic extracts were dried over MgSO$_4$ and then filtered. The solvent was stripped off, and the product was purified by column chromatography on silica gel, eluting with hexane to give the compound 5 as a yellow solid.

Compound 5*: $^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 8.27 (d, 1 H), 7.57–7.46 (m, 2 H), 3.01–2.82 (m, 2 H), 2.21–2.03 (m, 2 H), 1.36–1.19 (m, 12 H), 0.91–0.83 (t, 6 H), 0.34–0.12 (m, 13 H)
Compound 5: $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ 8.30 (d, 1 H), 7.56 (d, 1 H), 7.54-7.49 (d, 1 H), 3.16 (s, 1 H), 2.99–2.87 (m, 2 H), 2.21–2.05 (m, 2 H), 1.89–1.78 (12 H, m), 0.28–0.09 (m, 10 H) ppm.

2.3.6 2,7,12-TriBPOSS-5,5',10,10',15,15'-hexahexyltruxene (6).

Compound 1 (50 mg, 0.086 mmol) and 5 (308.93 mg, 0.34 mmol) were added to a 100 mL Schlenk flask and dissolved by 10 mL purified THF. CuBr (about 2 mg) was added to the solution. The solution was degassed on the vacuum line for 3 freeze-degas-unfreeze cycles. 5 drops of PMDETA was added to the solution under N$_2$ flow. The system was degassed once more. Then the solution was stirred at room temperature for 48h. The product was obtained after purification by column chromatography on silica gel eluting with hexane: EA (2:1). $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ 8.40 (d, 3H), 8.04 (s, 3H), 7.81 (s, 3H), 7.79-7.74 (d, 3H), 4.51-4.34 (m, 6H), 3.14-2.90 (m, 5H), 2.35-2.15 (m, 5H), 2.14-2.01 (m, 7H), 1.92-1.76 (m, 25H), 1.11-0.79 (m, 163H), 0.76-0.50 (m, 65H), 0.31-0.18 (m, 21H) $^{13}$C NMR (300 MHz, CDCl$_3$, ppm) δ 153.62, 147.97, 144.36, 140.66, 138.54, 129.02, 124.96, 123.90, 119.32, 57.07, 53.46, 52.49, 29.48, 25.68, 24.27, 23.83, 22.5, 19.29, 8.67

2.3.7 2,3,6,7,10,11-Hexa-Alkyne-Triphenylene (7).

To a solution of 2,3,6,7,10,11-Hexahydroxytriphenylene (100 mg, 0.308 mmol) in THF (10 mL) was added CaCO$_3$ (100 mg) suspended in THF (10 mL). A solution of Bromoethyne (293.47 mg, 2.464 mmol) in THF (10 mL) was then added to the mixture. The resulting mixture was stirred at room temperature overnight. The reaction extracted with MeOH. The organic layer was washed with
brine, dried over Na$_2$SO$_4$ and concentrated. The residue was purified on a silica gel column chromatography to get the compound 7. $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ 8.10–8.08 (s, 6H), 4.99–4.95 (d, 12H), 2.60–2.57 (m, 6H).

2.3.8 Azidebenzyl Isobutyl POSS (8).

BPOSS-Ar-Cl (1.0 g, 1.06 mmol) and sodium azide (207 mg, 3.18 mmol) were dissolved by 14 mL DMF and 4 mL THF. The solution was stirred for 24h under room temperature. Solvent were evaporated under reduced pressure, the residue was extracted with CH$_2$Cl$_2$. The product was obtained after removing the solvent. $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ 7.75–7.65 (d, 2H), 7.39–7.31 (d, 2H), 4.42–4.32 (s, 2H), 2.01–1.79 (m, 7H), 1.15–0.90 (m, 42H), 0.78–0.59 (m, 14H). $^{13}$C NMR (300 MHz, CDCl$_3$, ppm) δ 137.34, 134.50, 131.96, 127.26, 54.79, 25.73, 23.72, 22.37

2.3.9 2,3,6,7,10,11-Hexa-BPOSS-Ar-Triphenylene (9).

Compound 8 (250 mg, 0.263 mmol) and 7 (17.16 mg, 0.033 mmol) were added to a 100 mL Schlenk flask and dissolved by 10 mL purified THF. CuBr (about 2 mg) was then added to the solution. The solution was degassed on the vacuum line for 3 freeze-degas-unfreeze cycles. 5 drops of PMDETA was added to the solution under N$_2$ flow. The system was degassed once more. Then the solution was stirred at room temperature for 48h. The product was obtained after purification by column chromatography on silica gel eluting with hexane: EA (2:1). $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ 8.23–8.14 (s, 6H), 7.84 (s, 6H), 7.70–7.62 (d, 12H), 7.32–7.24 (d, 12H), 5.56–5.48 (d, 12H), 1.96–1.79 (m, 42H), 1.02–0.90 (m, 252H), 0.67–0.60 (m, 84H). $^{13}$C NMR (300 MHz, CDCl$_3$, ppm)
δ148.12, 144.59, 136.54, 135.77, 134.78, 132.55, 127.18, 124.04, 123.58, 30.26, 25.83, 23.77, 22.47

2.4 Sample Preparation For X-ray and Transmission Electron Microscope (TEM)

In this project, both wide angle and small angle X-ray were used to found the structure information of the molecule's packing. Also, TEM was used to observe the image as well as the diffraction of the molecular self-assembly. For each molecule, different instrument was used so that the sample preparation was distinct.

2.4.1 Sample preparation of Truxene-3BPOSS

The sample evaporated from CHCl₃ solvent was put into a DSC pan, then annealed at 160 °C for 12 h under the N₂ gas. After cooled down, the sample was taken out for WAXD measurement. To prepare the TEM samples for SAED experiments and morphological investigation, a dilute solution of Truxene-BPOSS was prepared in CHCl₃ (0.02% w/v). The solution was sprayed onto mica. After solvent evaporation, the mica was subject to the identical thermal treatments as the samples prepared for WAXD experiments. Then sample was transferred to copper grids from mica.

2.4.2 Sample preparation of Triphenylene-6BPOSS

The bulk sample was place on a hot stage under protection of the nitrogen gas. Then set the temperature at 160 °C and maintained for 12 hours. After cooled down, the sample was taken out for SAXS and WAXD measurement. To prepare the sample thin enough for TEM image, the annealed sample was embedded into
epoxy resin. Then, trimmed sample in epoxy was cut using microtome to get slice of sample with thickness around 100 nanometer, after which the slices were transferred onto copper grids.
3.1 Chemical Structure Characterization

All the chemical structures of the molecules were determined by $^1$H NMR and $^{13}$C. Herein, only the final giant molecule's structures are discussed.

3.1.1 Chemical structure of 2,7,12-TriBPOSS on Truxene core

Scheme 3.1 Synthetic route of Truxene-3BPOSS
Based on the discussion in the INTRODUCTION part, preparing well defined giant molecules both in shape and size is one object of this project. Thus, rigid Truxene core and stable POSS cage were chosen to maintain a discotic shape at around 3 nanometer in diameter and 1 nanometer in thickness. At the meanwhile, in order to get mono-disperse molecules, click chemistry or specifically the 3+2 Huisgencycloaddition reaction was used to combined the two parts, because of its high efficiency and selectivity. The details of the synthetic route of this molecule were shown in Scheme 3.1 and the $^1$H NMR of this molecule was shown in Figure 3.1 The peak at 8.04 shown a successful of the click reaction and the product is quiet pure since all the peaks can assigned to certain proton. And the chemical shift as well as the integration of each peak can be confirmed by the previously work of the truxene core$^{46,47}$ and the BPOSS cage. $^{43}$The peak at 7.27 ppm is the CDCl$_3$ signal and 1.55 ppm is the water peak.$^{49}$

Figure 3.1 $^1$H NMR of 2,7,12-Tri-BPOSS-truxene
Figure 3.2 shows the $^{13}\text{C}$ NMR of the molecule. This result, showing 19 strong peaks, further confirmed the chemical structure of the molecule.

Figure 3.2  $^{13}\text{C}$ NMR of 2,7,12-Tri-BPOSS-truxene
3.1.2 Chemical structure of Hexa-BPOSS on Triphenylene core

When consider the factors affecting the self-assembly of the giant molecules, intermolecular interaction, obviously, is an important one. The molecule discussed in the former part of this chapter, was designed to reduce the intermolecular interaction as low as possible by introducing six alkyl chains onto the Truxene core just like Scheme 3.1 shown. These alkyl chains can eliminate the π-π stacking between the Truxene cores which are conjugate molecules. In fact, in the Ren and his coworkers' pioneer work, which linked two BPOSS with a conjugate molecule. Because of the strong π-π stacking, this type of molecule can form dimmer and the crystal structure is no longer similar to pure BPOSS packing. Based on the knowledge of this work, a new design of discotic molecules is synthesized and Scheme 3.2 shown the synthetic route and the chemical structures of them.

Scheme 3. 2 Synthetic route of Triphenylene-BPOSS
Although the π-π stacking has a strong attraction between conjugate molecules, if the size and weight of the molecule becomes bigger, this attraction will surely be weakened. At this time, the crystallization of BPOSS will be more easier than the Ren's work or in another words since the Triphenylene core and the BPOSS will pack with their own kind and repel others, mirco-phase separation like behavior may be happen to generate order structures. According to the discussion above, two different molecules were prepared and the Triphenylene core here introduce a strong π-π stacking in this system. Also, two type of BPOSS building block were used. One of them has a relatively soft linker with the core which may give the BPOSS more space and freedom to pack while another is rigid linking to the core so that the shape of the whole molecule can be maintain well. When compared with the Truxene-BPOSS, which almost has no π-π stacking, both shape and intermolecular interaction in molecular self-assembly can be investigated. More importantly, nicely ordered phase structure of the Triphenylene-BPOSS may be generate. Because the strong π-π stacking bring a relatively huge difference on the attraction between homogenous and heterogenous part of the final molecules. Again, considering the requirement of mono-disperse, 3+2 Huisgencycloaddition reaction was used to combined the core and the nano-building blocks.
Figure 3.3 shown the proton NMR result of the Triphenylene-Ar-BPOSS. Except for all the labeled peaks which can be assigned to the proton for the molecule, there are several more peaks. This impurity will draw much attention because the uncertainty it brings to the self-assembly process of the molecules. Thanks to the great work of Fulmer\textsuperscript{49} again which points out that the Toluene will have three peaks in CDCl$_3$ at 2.34, 7.15 and 7.24 ppm respectively. Based on the chemical structure, the integration at around 7.28 ppm and 7.66 ppm should be identical, however, in Figure 3.3 the peak labeled as "d" is bigger than peak "e" which means that there should be another peak merged in the "d" range. Thus, the peaks at 2.26, 7.00 and 7.27 ppm happened match the Toluene's peaks in CDCl$_3$. 
This supposition were further confirm by the carbon NMR result shown in Figure 3.4 which has four irrelevant peaks with ppm value higher than 100. These peaks have a quite similar ppm value with the Toluene in CDCl$_3$. At the meanwhile, the peaks at ppm lower than 77 had several irrelevant ones which were sharp.

![13C NMR of 2,3,6,7,10,11-Hexa-BPOSS-Triphenylene](image)

Figure 3.4  13C NMR of 2,3,6,7,10,11-Hexa-BPOSS-Triphenylene

These sharp peaks suggest a relatively simple chemical environments of the carbon which means these peaks came from the small molecules rather than the Triphenylene-Ar-BPOSS. Also, this small molecules as well as the Toluene can be washed and dried over in vacuum, thus this impurity can be got over and should have no serious effects on the self-assembly behavior of this nano-molecule.

3.2 Self-assembly Behavior Analysis

The Truxene-3BPOSS and the Triphenylene-6BPOSS shown distinct self-assembly results. For the Truxene core molecule, single crystal had been
successfully prepared for X-ray and TEM diffraction experiment while the giant molecule with Triphenylene core could hardly be crystallized. However, after thermal annealing at 160°C for several hours, an A15 phase was found, which indicate that these molecules though cannot pack regularly at atom-scale, still had possibility to self-assembly into nano-scale order structures.

3.2.1 Crystal structure determination of Truxene-3BPOSS

Following the procedure in the former chapter, crystal of this sample was carefully generated and TEM diffraction experiment was done to determine the unit cell parameters of the sample's crystal structure. The diffraction pattern of this sample was shown in Figure 3.5. This diffraction pattern indicated that the unit cell was probably orthorhombic. If we assumed it was orthorhombic and labeled the $a^*$ and $b^*$ axis as Figure 3.5 shown we can then work on the unit cell parameters. Since the product of d-spacing and its corresponding distance on the pattern should be a constant under certain camera length. Thus, through the diffraction pattern of TiCl$_4$ standard with known d-spacing, the d-spacing of Truxene-3BPOSS crystal can be calculated by measuring certain distance. In order to determine "a" and "b", the distance of (600) point and (010) point were measured and the unit cell parameters of "a" and "b" were calculated as 32.55 Å and 10.78Å respectively.
Figure 3.5 Selective area diffraction pattern of Truxene-BPOSS with labeled d-spacing for the a* and b* axis.

Figure 3.6 Tilting pattern of Truxene-BPOSS. (a) and (b) had tilting angle 0 and 45 degree along a* axis. (c) was the enlarge view of selective area in (b).
The determination of "c" was done by analysis of the tilting pattern which was shown in Figure 3.6 where the sample was tilted along a*-axis. Through the enlarge view in (c), we clearly saw two layer of points which represents the lattice plane at different height, \((h \ k \ l)\) and \((h \ k \ l+1)\). Thus, through measuring this distance, we can calculate the real space distance \(d\) with the same method in calculation of "a" and "b". Since we tilted for 45 degree, thus \(c^2\) should equal to 
\[2d^2,\]
so that the unit cell parameter "c" then can be calculated as 53.33 Å.

To exam the calculation of unit cell parameters, we tilted the diffraction pattern along b* axis at different angle which was shown in Figure 3.7.

Figure 3.7 Tilting patterns of Truxene-BPOSS. (a), (b) and (c) had tilting angle 0, 11 and 30 degree along b* axis corresponded to [001], [103], [101] zones.

The determination of "a" and "b" were exactly the same method in former part, by measuring distance of certain points in the (a) in Figure 3.7, the d-spacing can be calculated through comparing with diffraction pattern of standard sample. However, in order to exam the "c" value, we can measure the distance of point \((1 \ 0 \ l)\) and calculated the d-spacing of this point (the "l" here is an integer). Since we assumed that this unit cell was orthorhombic, the d-spacing and unit cell parameters should satisfy an equation that, 
\[1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2,\]
the d here is the d-spacing of the point \((h \ k \ l)\), and "a", "b" and "c" are the unit cell parameters.
Through this equation, we could find out suitable value for "l" and check whether
the calculated "l" value was an integer. Besides, we can also confirm the
calculation through another method. Since we knew the value of c axis, we could
then calculate how many degrees we need to tilt to get other zones in three
dimensional reciprocal lattice, and compare the calculated values with
experimental ones. For example, when we tilt along b* axis for 11degree and 30
degree starting from [001], we could acquire [103] and [101], matched very well
with the calculated about 11 degree and 30 degree. This means our calculation
about c axis was rather precise.

![Figure 3.8 Powder pattern and integration figure of Truxene-3BPOSS](image)

The crystal sample of Truxene-3BPOSS was then prepared for the WAXD
experiment and Figure 3.8 showed the results. With the unit cell parameters we
already calculated, the peaks can be assigned to certain point.

To summarize the preliminary results, parameters of the unit cell was
determined as "a", "b" and "c" equal to 32.55 Å, 10.81 Å and 53.33 Å respectively.
The unit cell was orthorhombic so all the angle of the unit cell equal to 90 degree.
The measured density was 1.12 g/cm³, so that the Z value was calculated as 4,
which means each unit cell contains four giant molecules. The exactly molecular
packing in a single unit cell was being tried on Cerius² and this work is still undergoing.

3.2.2 Order structure determination of Triphenylene-BPOSS

Single crystal growth on Triphenylene-BPOSS molecules was unsuccessful to show any interesting self-assembly results. These failed experiments bring a new thought that, if crystal ordered structure cannot be formed, then how about superlattice order structure? The mechanism has been discussed in the INTRODUCTION part, and in order to prove this theory, the sample was thermal annealing at 160°C for 12 hours.

![SAXS and WAXD profile of the Triphenylene-6BPOSS](image)

Figure 3.9  SAXS and WAXD profile of the Triphenylene-6BPOSS

At this temperature, the BPOSS was seldom crystallized because it already exceeded the melting temperature of BPOSS. This can be proved by the WAXD result showed in Figure 3.9. There was no any crystal diffraction peak, only amorphous halo. To dig out the whether there was formation of order structure, SAXS experiment was done and Figure 3.9 showed the results. It was surprise to find out three clear and sharp peak as Figure 3.9 showed which indicated an order structure was formed by the Triphenylene-6BPOSS sample. Thus, following question was to distinguish this structure. Through literature review, identical
example of such SAXS experimental results were found in Percec's work where they determined there were three peaks coming from a cubic phase called A15. A15 is the most widely occurring micellar thermotropic phase with eight "micelles" in each unit cell. The packing of these "micelles" is so unique that not only are the each vertex and body center of the cubic have a "micelle" but also each face have two "micelles". The "micelles" here can be supramolecular dendrimers which formed spheres in advance and the spheres can further packing into the A15 structure. A feature of this phase is that it is the result of sphere packing and the TEM image of the Triphenylene-6BPOSS in Figure 3.10 happen showed regular packing of spheres. This phenomena was more obvious when the original TEM image was filtered by Fourier Transform.

![TEM image of Triphenylene-6BPOSS](image)

(a) The original TEM image (b) TEM image after Fourier filter

Thus, through the characteristic triplet of strong peaks with indices (200), (210) and (211) and TEM image, we can determined the order structure of Triphenylene-6BPOSS as A15 cubic structure and the dimension of this cubic
lattice was calculated to be $a = 6.54 \text{ nm}$. The formation mechanism for this molecule was not precisely defined however the roughly route was that since each discotic molecule has six POSS cages and a center core with $\pi-\pi$ stacking, although these discs tended to stack on each other, the huge number of POSS cages made plain stacking difficult. In other words, the linkages between POSS cages and core would bend so that the cages can fully take the space around the core. This made formation of sphere possible and according to density measurement of this sample, each sphere contained four Triphenylene-6BPOSS. The details of the packing of these four giant molecules were still under investigation with Cerius$^2$. 
CHAPTER IV

CONCLUSION AND FUTURE WORK

In conclusion, novel discoticnano-molecules were successfully prepared. The chemical structure of these molecules were confirmed by $^1$H NMR and $^{13}$C NMR. These molecules shown distinct self-assembly behavior. Until now, the Truxene-BPOSS sample was successfully form orthorhombic crystal structure with the parameters of unit cell determined. Computer simulation is undergoing for this molecules to further prove how the geometry of this molecules affects the close packing of them. The Triphenylene-Ar-BPOSS sample form A15 structures with four single molecules generate sphere at first and these spheres then pack together to the cubic phase. However, the specific mechanism of this self-assembly was unknown and more importantly, the possibility of these samples to form other order structure is remained a question which need more effort in the future.
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