CRYSTAL ENGINEERING OF GIANT MOLECULES BASED ON PERYLENE
DIIMIDE CONJUGATED POLYHEDRAL Oligomeric Silsesquioxane
NANO-ATOM

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Dissertation

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ABSTRACT

Molecular architectures and topologies are found contributing to the formation of supramolecular structures of giant molecules. Dr. Cheng’s research group developed a diverse of giant molecules via precisely controlled chemistry synthetic routes. These giant molecules can be categorized into several different families, namely giant surfactants, giant shape amphiphiles and giant polyhedron. By analyzing the hierarchical structures of these carefully designed and precisely synthesized giant molecules, the structural factors which affect, or even dominates, in some cases, the formation of supramolecular structures are revealed in these intensive researches. The results will further contribute to the understanding of dependence of supramolecular structures on molecular designs as well as molecular topology, and providing a practical solution to the scaling up of microscopic molecular functionalities to macroscopic material properties.

Molecular Nano Particles (MNPs), including fullerene (C$_{60}$), POSS, Polyoxometalate (POM) and proteins etc., is
defined and applied as a specific type of building blocks in the design and synthesis of giant molecules. The persistence in shape and symmetry is considered as one of the major properties of MNPs. This persistence will support the construction of giant molecules for further supramolecular structures’ study by introducing specific shapes, or precisely located side groups which will facilitate self-assembling behaviors with pre-programmed secondary interactions.

Dictating material physical properties by its chemical composition is an attractive yet currently failed approach in the study of materials. However, the pursuit of determining material properties by microscopic molecular level properties is never seized, and found its solution when the idea of crystal engineering is raised: should each atom in the material is located exactly where it is designed to be and is properly bonded, the property of the material is hence determined. In such “bottom-up” approach, the precise fabrication of 2 nm ~ 100 nm nanostructures, is of great research interest. In this thesis, crystal engineering of giant molecules based on PDI conjugated POSS Nano-Atom (PDI-BPOSS) nano-atoms via self-assembly is performed and studied.
I received precious and irreplaceable help from many during my pursuit of this honored doctoral degree. I would like to take this opportunity to present my sincere thankfulness to those who supported and instructed me towards higher level of scientific achievements.

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characterizations regarding to GISAXS and computer simulation. I would like to take this opportunity to deliver my gratitude to him. Dr. Mingjun Huang deserves my deepest gratitude for providing me with samples and assisted my experiments.

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CHAPTER I
INTRODUCTION

Molecular architectures and topologies are found contributing to the formation of supramolecular structures of giant molecules. Dr. Cheng’s research group developed a diverse of giant molecules via precisely controlled chemistry synthetic routes. These giant molecules can be categorized into several different families, namely giant surfactants, giant shape amphiphiles and giant polyhedron. By analyzing the hierarchical structures of these carefully designed and precisely synthesized giant molecules, the structural factors which affect, or even dominates, in some cases, the formation of supramolecular structures are revealed in these intensive researches. The results will further contribute to the understanding of dependence of supramolecular structures on molecular designs as well as molecular topology, and providing a practical solution to the scaling up of microscopic molecular functionalities to macroscopic material properties.
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Dictating material physical properties by its chemical composition is an attractive yet currently failed approach in the study of materials. However, the pursuit of determining material properties by microscopic molecular level properties is never seized, and found its solution when the idea of crystal engineering is raised: should each atom in the material is located exactly where it is designed to be and is properly bonded, the property of the material is hence determined. In such “bottom-up” approach, the precise fabrication of 2 nm ~ 100 nm nanostructures, is of great research interest. In this dissertation, crystal engineering of giant molecules based on PDI conjugated POSS Nano-Atom
(PDI-BPOSS) nano-atoms via self-assembly is performed and studied.

Supramolecular structures and self-assembling behaviors of one giant shape amphiphile and two tetrahedra will be discussed. This dissertation will be divided into three parts. For the following first part, Chapter II, a background introduction will be given. This section will be covering 1) general introduction to state of matters and crystal engineering, followed by 2) the discussion of supramolecular structure and a practical strategy by introducing “Molecular Nanoparticles” through which the purpose of designing and modulating supramolecular structures would be realized; 3) the three major types of giant molecules which were precisely designed and synthesized are specifically introduced by presenting previous works.

Various experimental techniques were applied to determine the supramolecular structures of the synthesized samples discussed in this dissertation. The experimental part, Chapter III will be presenting the applied techniques and procedures.

A giant shape amphiphile $m$-phenyl-(PDI-BPOSS)$_2$, which is constructed by PDI and BPOSS building blocks and a non-linear 2-vertices node, were synthesized and its crystalline
properties were performed in Chapter IV, where a triclinic unit cell were determined and discussed for \( m \)-phenyl-(PDI-BPOSS)\(_2\).

Chapter V and Chapter VI cover the synthesis and study of two PDI-BPOSS based giant tetrahedra samples. The samples are differentiated by their linkers between PDI and BPOSS units: one is a rigid phenyl linker while the other is an alkyl soft linker. By determining the orthorhombic crystal structure for R-(PDI-BPOSS)\(_4\) and demonstrating the hexagonal super lattice for S-(PDI-BPOSS)\(_4\), the difference between the supramolecular structures of the samples resulted from the variation of rigidity of linkers applied in the designing of giant molecules via “node-spacer-vertex” strategy are presented.
2.1 State of Matter and Phases

State of matter and phase are two terms introduced in the studies of materials. Our daily life observes four typical states of matter: solid, liquid gas and plasma, while the term phase are characterized by uniform chemistry, distinct physics. The concepts of order and symmetry are needed in the description of the state of matters and phases. "Order" or "disorder" is defined as a description of the existence of certain degree of symmetry. In general, the level of order is an opposite to that of symmetry: a highly ordered crystal, always possess a higher order and a lower symmetry than those of a disordered amorphous system.

The understanding of states and phases is essential in the study of material science and engineering. The four typical phases, as well as many other known phases can be described and identified by their thermodynamic properties.\(^1\) Matters can be considered as assemblies of particles.
Microscopically, these particles are arranged according to certain symmetry. Order and symmetry are therefore two characteristics that could be introduced to describe and categorize different phases. As described previously, the higher symmetry a system possesses, the lower order it will be. For gas and liquid, where the particles are arranged randomly, i.e., with lowest order, when subjected to all symmetrical operations including rotation, reflection, translation, etc. both states are statistically invariant. While on the other hand, a matter with an ordered structure will only be persistence when undergoes certain symmetrical operations. This will result in an increase in order and decrease in symmetry comparing to liquid and gas phases.

The study of microscopic ordered structures involves three aspects: 1) positional order, the periodic arrays of motifs; 2) bond orientational order, the alignment of directional vectors determining lattice axis and 3) molecular orientational order, the alignment of motifs with respect to particular directional vectors. It is revealed that ordered structures may decay with the elongation of distance, and consequently the idea of long-ranged order, short-ranged order and quasi-long-ranged order, according to how the correlation function decay with increasing distance. Figure.2.1 presents an illustration of the three types of
variation of order with distance. For long-ranged function, the ordered structure decays according to a step function. For short-ranged and quasi-long ranged order, the ordered structure decay within a finite range, following an exponential or a power function, respectively. Diffraction patterns are related to the order of materials. With the decrease of order in the sequence of long-ranged, quasi-long-ranged and short-ranged order, a variation from sharp single peaks to broaden single peak and then broaden halos can be observed.

Figure 2.1 Illustration of the decay functions of long range, quasi-long range, and short range order with distance and corresponding diffraction pattern.\textsuperscript{3}
2.2 Crystal and crystal engineering

Unlike amorphous solids, where molecules are arranged in an irregular manner, crystals, by definition, are solids with three-dimensionally periodic ordered spatial atomic structure under thermal equilibrium state.\textsuperscript{4}

Ordered structures of crystals grants them with unique properties, thus made the study of crystal growth and properties an important aspect of material science. Homogeneity is one of the major properties of crystals. Well defined crystals possess a highly ordered structure, where all the properties: including physical properties, such as transparency, density, heat capacity etc.; physicochemical properties, take solubility, absorption coefficient, etc. as examples, of a crystalline matter are invariant throughout the material. Anisotropy is another important property of crystals which contributed to variations of some properties of crystals with directions, including elasticity, strength, electrical and thermal conductivity, etc.

For crystalline materials, since their anisotropic properties are dependent of their crystal structures, the design and realization of the control over crystal structures would be a good solution of the pursuit of material properties modification. Therefore, the idea of determining or
predicting crystal structure from their chemical composition becomes attractive. However, such control over crystal structures is, to our best of knowledge, currently impossible: “one of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition”, as is stated by Maddox.⁵ To circumvent the difficulties in determining material properties by predicting their crystal structures with their chemical composition solely, a second thought is the pursuit of precisely arrange every atom in a material to “produce” a matter with desired structure.⁶ Among all the fruitful studies towards the realization of precisely arrangement of atoms in crystals, molecular self-assembly holds a promising future for its possible control over supramolecular architectures, and therefore, was summarized and developed into a concept: crystal engineering. Crystal engineering is an idea first proposed by Schmidt in 1971,⁷ proposing that the intensive study of intermolecular forces, including van der Waals forces, hydrogen bonds, coordination ionic interactions, etc., which are controlling molecular packing behavior, is leading to a new developing strategy of material study: through precisely controlled molecular architecture, supramolecular structures could be further defined via non-covalent
interactions and consequently construct materials with desired properties.

The realization of crystal engineering, will alter the traditional way of the growth of a crystal, where the process can be considered as simple as fulfill a space by atoms, or “avoid a vacuum”, taking a series of processes when all atoms or functional groups are to be recognized and further self-assembled. As is proposed by Dunitz, crystal can be referred to as “supermolecule(s) par excellence”. Further development of crystal engineering goes beyond the concept of crystals, especially when implicated to organic materials, crystal engineering finds its similarity with another field of great research interest: supramolecular chemistry, which will be discussed in later sections.

It is also noteworthy that, when considering the properties, i.e. physical and chemical properties of a crystalline solid material, the consideration of the properties of individual molecules are of the same importance as the distribution of these molecular components. To this context, the scaling up of microscopic molecular functionality to macroscopic material properties finds its new and promising solution.
The differences between crystal engineering and crystal structure prediction should be stressed. Generally speaking, crystal structure prediction refers to a process which will contribute to a precise construction of the crystal structure, including space group and exact detailed packing scheme of a well-known molecule. While for crystal engineering, it is dealing with molecules that are not necessarily well-known, predicting or sometimes, designing the phases, supramolecular structures, networks, etc.

2.3 Supramolecular Structure and Supramolecular Isomerism

Supramolecular structure is a concept describing the structures formed with multiple molecules via intermolecular non-covalent interactions. The interactions here includes, but not limited to van der Waals forces, hydrogen bonds, π-π interactions, ionic interactions, coordination interactions. A good example of supramolecular structure could be given by firstly proteins, and secondly DNA double helix. For the assembly of protein, the first order structure is the chemical sequence of amino acids. Hydrogen bonds would form between amino acid residues and generate intramolecular structures, which is also known as secondary structures. While for certain functioning proteins, like collagen, where 3 protein chains are packed together via intermolecular interactions, a
supramolecular structure is consequently constructed. For DNA, the breaking through discovery of double helix also revealed a supramolecular structure constructed via hydrogen bonds formed between the two corresponding base pairs located one in each of the two chains.

Lehn provided us with an analogy of the relationship between supramolecular structures and molecules. In general, supramolecular structures are constructed by different molecules, just like the molecules are constructed by different atoms. The interaction between units in supramolecular structures are non-covalent interactions, while the interaction between atoms in molecules are covalent bonds. According to Lehn, since the modification of these intermolecular interactions acts in the same manner as what we do to the covalent bonds in molecular chemistry, such modification could be considered as “supramolecular chemistry”.

Supramolecular structures are realized by molecular self-assembly. These self-assembly behaviors require the generation of non-covalent bonds at designed positions of given molecules in a controlled manner. Thus, the study of supramolecular chemistry will cover 1) the design and synthesis of molecules with potential linkage points; and 2)
the realization of programmed formation of non-covalent intermolecular interactions.

Each unit or motif in a supramolecular structure could be one single molecule or multiple molecules. Through aforementioned procedure, the designed motif will assemble via non-covalent bonding to give supramolecular structures. Since these connections are physical bonds with lower bond energy compared to that of covalent bonds, the thermal stability of such structures will be limited to a relatively lower level, leading to a high sensitivity of the structures to temperature.

The existence of multiple supramolecular structure, networks, phases, etc., for a same molecule has come to general notification. In analogy to the polymorphism in crystalline materials, this concept can be described by the statement that one molecule would give multiple possible supramolecular structure, and is known as supramolecular isomerism.\textsuperscript{15-16} The study of supramolecular polymorphism offers great scientific significance, and may also provide clues in pharmaceutical developments.\textsuperscript{17-22} The control over supramolecular isomers and supramolecular polymorphs, according to Moulton, is one of the essential concept of crystal engineering when designing solids. However, the
understanding of this phenomenon is still to be further developed: “very little understanding concerning even the existence of supramolecular isomers, never mind how to control them”.12

It has been a great research interest to pursue the control over material properties via scaling up microscopic molecular functionalities. The supramolecular chemistry provides us with a practical strategy in achieving this target: by synthesizing molecules with carefully designed linking points where could accommodate desired secondary bonds, supramolecular structures could be formed in a preferred manner which will contribute to a desired architecture and properties.

2.4 Molecular Nanoparticles (MNPs) and Supramolecular Structures

The study of small molecules self-assemble into supramolecular structures has been intensively conducted, and contributed creative progress. At the meantime, if macromolecules are taken into consideration, it will generate even more creative and innovative ideas. As what have been discussed previously, the study of self-assembly of protein and DNA do provides us with a close view into the study of nature and human life. Macromolecules, which would enable
multi-positional chemical modification from chemistry point of view, as well as hydrophobicity or all kinds of shape or interaction anisotropy programming and tuning from molecular architecture point of view, would provide scientists tremendous possibilities and opportunities to study and realize various controlled supramolecular structures. Such expansion in research focus from small molecule to macromolecule also provides us with a strategy that could contribute to a success in scaling up microscopic functions to macroscopic properties. With the knowledge that physical properties could be predicted via analyzing their hierarchical arrangements of the motifs: atoms, molecules, etc., designing and realizing material properties via the control over molecular arrangements at various length scale, especially ~100nm scale would be more efficient and attractive. It is familiar to people that materials are constructed in this way: atoms are bonded together to form molecules, and molecules are arranged to give matters. At the meantime, we could also do another analogy, describing a roadmap of how materials with desired properties can be generated, as is shown in Figure 2.2: if we could consider functional building blocks in a macromolecule as an “atom”, and these “atoms” were bonded together via covalent bonds to give macromolecules, then the packing of these macromolecules
will give well defined supramolecular structures at hundreds of nanometer scale via secondary interactions. In order to achieve the target of precisely control and study of the supramolecular structures, the precision of the synthesis of the macromolecule would be the first and foremost essential step. Currently, the first choice for well-controlled synthesizing macromolecules with repeating functioning motifs is through the well-developed living or controlled polymerization. However, polymerizations could always involve polydispersity or tacticity. Therefore, in order to gain full control over desired repeating motif sequence with definite size and specific topology, precision chemistry synthesis is of disparate need.\textsuperscript{25-26}

Figure 2.2 Illustration of a novel strategy of scaling up microscopic functions to macroscopic properties\textsuperscript{27}
Synthesizing such macromolecules with precisely defined motif sequence and large amount of functional groups through traditional synthetic route would definitely undergo a series of complex reactions, which would face huge challenge in purification and dispersity. A solution has been raised regarding such challenges: by introducing size, shape and functional groups persisting building blocks, people will design and synthesis macromolecules by selecting favorable building blocks and bond them together through precision chemistry.28-30

The aforementioned building blocks, which are characterized by persistence in shape and symmetry, would be the key to the control over interaction positions as well as anisotropic properties of the macromolecules, and were named “nanoatoms” or molecular nanoparticles (MNPs).27, 31-33 Herein, a clearer definition of “giant molecule” is introduced, differentiate itself from macromolecule by its precisely defined molecular architecture.

In the design and realization of the precisely defined giant molecule, the first step is to construct an invariant building block or molecular nanoparticle (MNP), in both chemical and physical properties, possesses shape and volume persistence and specific symmetry.34 Three different
categories of such MNPs are intensively studied in Dr. Cheng’s research group: [60] fullerene (C₆₀)³⁵, polyhedral oligomeric Silsesquioxane (POSS)³⁶ and polyoxometalate (POM)³⁷-³⁹. All three types of MNPs possess ~1nm sized cages with specific symmetry: spherical (C₆₀), cubic (POSS) or octahedral (POM). The summary of the basic properties and scheme of these three MNPs are shown in Figure 2.3.

![Figure 2.3 Illustration and summary of basic properties of C₆₀, POSS and POM.][1]
2.4.1 C\textsubscript{60} as Nanoatoms

[60]Fullerene (C\textsubscript{60}), also named buckyball after Buckminster Fuller, is a spherical (diameter of 7.1 Å) organic molecule with \(I_h\) symmetry. It is cage shaped, and formed by 12 five member and 20 six member rings of carbon atoms. Kroto, Curl, and Smalley were awarded Nobel Prize in Chemistry for their achievement in the synthesis and development of C\textsubscript{60}.\textsuperscript{41} For their application as MNPs, C\textsubscript{60} would undergo a series of well-developed functionalization strategies, such as the Bingel-Hirsch reaction, (Figure 2.4) the Prato reaction (Figure 2.5), and azide addition (Figure 2.6), etc.\textsuperscript{42-46} C\textsubscript{60} chemical reactions often yield mixed products of unreacted, mono- and multi- adducted C\textsubscript{60}s. Therefore, except for a few cases where the reactions stops when C\textsubscript{60}s are mono adducted, the separation and purification of the monoadduct will be an important step in the preparation of functionalized C\textsubscript{60} units.

Dr. Cheng’s research group have developed a series of C\textsubscript{60} derivatives with interesting self-assemble behaviors which will result in well-defined hierarchical architectures. A few examples will be discussed in later sections.
Figure 2.4 Illustration of a typical Bingle-Hirsch Reaction.\textsuperscript{45}

Figure 2.5 Illustration of a typical Prato Reaction.\textsuperscript{46}

Figure 2.6 Illustration of a typical azide addition reaction.\textsuperscript{43}

1. R = OCH\textsubscript{2}CH\textsubscript{2}SiMe\textsubscript{3}
2. R = C\textsubscript{6}H\textsubscript{5}
3. R = 4-C\textsubscript{6}H\textsubscript{4}-OMe
4. R = 4-C\textsubscript{6}H\textsubscript{4}-Br
2.4.2 POSS as Nanoatom

Silica nanoparticle POSS is a family of cage compounds with size varies around ~ 1 nm. Substituted POSS with functional groups would provide us an organic-inorganic material composed of an inner inorganic framework $(\text{SiO}_{1.5})_x$ and an outer shell of organic functional groups. Typically, a POSS will possess outstanding thermal stability, etching selectivity and could undergo feasible chemical decoration. Among all POSS compound, cubic T8-POSS (Figure 2.7 (L1)) is widely applied as nanoatoms in giant molecules and the derivatives of which is the research focus of this thesis.

POSS with various side groups were developed, however, the major type of the side groups are limited to a few simple ones, like isopropyl, phenyl, vinyl, etc. These side groups could be functionalized to favor further chemical reactions. In order to create well-defined giant molecules, the selective functionalization of the eight possible reaction sites of POSS would be taken into serious consideration. This can be achieved by using proper precursors with reactive functional groups at one or a few of the 8 sites. Another solution to achieve selective addition is through stoichiometry controlled reactions like thiol-ene reactions as reported by Yiwen Li et al.\textsuperscript{47}
Tert-butyl POSS (BPOSS) is one of the widely studied POSS MNPs, and involved in many of recent studies of giant molecules. The crystallographical study of BPOSS by Bassindale et al provided us with crystal unit cell structures of BPOSS (triclinic, \(a = 9.988\ \text{Å}, \ b = 10.818\ \text{Å}, \ c = 10.954,\ \alpha = 96.54^\circ, \ \beta = 91.27^\circ, \ \text{and} \ \gamma = 99.44^\circ\)) which will be of great significance in further studies regarding the understanding of self-assemble behaviors of giant molecules with BPOSS MNPs.\(^{48}\)

**Figure 2.7** Illustration of POSS cages with different composition \((\text{SiO}_{1.5})_x : x = 8, 10, 12\) (Left to Right)\(^{49}\)

**Figure 2.8** Selective addition through stoichiometry controlled thiol-ene chemistry.\(^{47}\)
2.5 Giant Molecules Based on Molecular Nanoparticles

Giant molecules are specifically designed for their promising assembly into complex but priori designed structures. It is the anisotropy in shape, interaction, etc. of the giant molecule that would lead to the programmed self-assemble behavior.\textsuperscript{23, 50} This provides us with a strategy by which the aforementioned long pursuit of precisely control over giant molecule self-assembly can be achieved, noticing that in the first place, the MNPs, i.e., nanoatoms, are of different shape, and can be functionalized by different functional groups; second, the development of giant molecules will enable the realization of a diverse molecular design.

Recent studies have revealed the relationship between shape and interaction anisotropy and the assembled complexed structures. The synthesis of these anisotropic nanoparticles and colloidal building blocks can be achieved through a variety of chemical, biological and physical methods: selective crystallization and deposition as chemical methods;\textsuperscript{51-54} plant extraction, fungi as biological methods;\textsuperscript{55-56} and for physical methods, selective deposition, surface templating, lithography, electrified jetting, to name a few.\textsuperscript{57-60} A large number of nanoparticles with different shapes, like cubes,\textsuperscript{61} triangles,\textsuperscript{62} tetrahedra,\textsuperscript{63} striped particles,\textsuperscript{64}
tripods and many else were synthesized via these well-developed methods. All these shapes would be incorporated into specific superlattice structures and hierarchical architectures due to their unique shape and interaction anisotropy, which is shown in Figure 2.9.

Figure 2.9 Examples of nanoparticles with different shape anisotropy (classified in rows) and the supramolecular structures formed by the self-assembly of nanoparticles (increase in length scale from left to right)
It has been demonstrated that by adding designed shape or interaction anisotropy to nanoparticles will further increase possible packing schemes to the motifs in their self-assembly process. Therefore, the understanding of how individual anisotropy scales up to build complex structures are of desperate desire for designing creative particles to be transformed into materials with favored properties.

Precisely defined giant molecules are providing a substantial enrichment of the library of nanoparticles with unique shape and interaction anisotropy for the reason that the freedom in selecting and functionalizing MNPs when constructing giant molecules will provide numerous possibilities.

Dr. Cheng’s research group developed and followed a philosophy of the construction of giant molecules, which is named “Node-Spacer-Vertex” method, and is shown in Figure 2.10. For a desired giant molecule blue print, the first step is to select an appropriate node, which would possess different number of functional groups, different shape and different size. Via the selection of different nodes, giant molecules with different 3-dimensional shape would be generated. The next step is to select a spacer which would be of different rigidity, and length as well. The spacer would
control the rotation or positioning of the different MNPs in the giant molecule. The last step is to select an MNP. The MNPs in a giant molecule would be functionalized to gain appropriate functional groups to accommodate further secondary interaction spots and anisotropic properties.

Through the “Node-Spacer-Vertex” method, a variety of giant molecules were designed and synthesized, the properties of which were intensively studied. Such studies would contribute to the enrichment of a “library”, holding the information of a wide range of giant molecules with different shapes, symmetry, properties and their self-assembly behaviors. Three different categories of giant molecules are of great research interest: giant surfactants, giant shape amphiphiles and giant polyhedra. Wen-Bin Zhang, et al. in an invited perspective paper discussed these giant molecules (Figure 2.11) intensively.27
Figure 2.10 Illustration of the “Node-Spacer-Vertex” method in the design of giant molecules.
Figure 2.11 Illustration of typical giant molecules: (A) giant surfactants, (B) giant shape amphiphiles, and (C) giant polyhedra, which also include nano-Janus grains.27
2.5.1 Giant Surfactant

Surfactants, by definition, are chemicals that would lower surface tension between two phases, either liquid-liquid or liquid-solid. In general, small molecule surfactants are organic molecules composed of hydrophilic heads and hydrophobic tails. Since such molecules would facilitate the dispersion of oily phase in watery phases, they are widely applied as detergents, emulsifiers, or wetting agents, etc.

Amplifying small molecule surfactants to macromolecules would give new materials with distinctive properties. Typically, a macromolecule surfactant would be constructed by covalently bonded hydrophilic head and a hydrophobic polymer chain.

Introducing certain functionalized MNPs with shape and symmetry persistence would present a giant surfactant with unique properties. Giant surfactants as a member of giant molecules are precisely synthesized molecule that retains the key factors of small molecule surfactants: a head-tail structure that possesses different hydrophilicity. The enlarged size and increase in the number of possible functional groups grants giant surfactants versatile
modifications towards precise structural modification that favors supramolecular structures formation.

As is shown in Figure 2.11 (A), giant surfactants have been developed into quite a few interesting categories: one (or multiple) head(s) with multiple (or one) tails. In giant surfactants, functionalized MNPs would act as heads, while polymer chains may act as tails. Chemical decoration would further define the hydrophobicity of the heads or tails by introducing hydrophobic or hydrophilic functional groups to either part of the giant surfactant molecules.\textsuperscript{79-81} Giant surfactants were firstly reported by connecting a hydrophilic polymer chain, poly(ethylene oxide)(PEO) or poly(acrylic acid)(PAA) with a POSS unit with hydrophobic functional groups.\textsuperscript{82-83} Such architecture is an inverse to the traditional small molecule surfactants until Xinfei Yu et al. reported hydrophilic APOSS head (POSS with carboxylic acid-functional groups) bonded with a hydrophobic polystyrene (PS) chain.\textsuperscript{84} Comparison of this APOSS-PS giant surfactant, a block copolymer (PS-b-PEO) with small molecule surfactant is made and summarized in Figure 2.12. Comparing to the “random-coil-like” block copolymer surfactant, the giant molecules is constructed by shape and symmetry persisting MNPs and a linear hydrophobic polymer chain. Such configuration gives a good mimic of the small molecule surfactants. The self-assemble
behavior of giant surfactant would be modified by tuning the balance of hydrophilicity and hydrophobicity.

Figure 2.12 Structural comparison of (a) a typical small-molecule surfactant, sodium dodecyl sulfate; (b) a giant surfactant, PS-APOSS; and (c) a typical amphiphilic block copolymer, PS-b-PEO.84

Figure 2.13 Giant surfactants with hydrophilic POSS or C60 heads and hydrophobic polymer tails. Library 1 and 2 shows molecules with one head and one tail; Library 3 and 4 shows those with one head and two tails; Library 5 shows giant surfactant with 3 heads and one tail.34
Xinfei Yu et al. have reported a study of a series of giant surfactants. (Figure 2.13) The reported giant surfactants are categorized by differences in functional groups of two types of polar heads (POSS or \( C_{60} \)) and differences in number of tails or heads. Admittedly, applying polymer chains as tails in giant surfactant will introduce polydispersity in molecular weight and thus contradicts with the definition of giant molecule, it is noteworthy that the MNPs with far larger molecular weight and well defined structure will greatly suppress the polydispersity.

Phase separation and self-assemble behaviors are observed for the prepared samples due to their anisotropic nature induced by difference in hydrophobicity: the MNPs heads are substituted by hydrophilic functional groups while the tails are hydrophobic polystyrene chains. One dimensional small angle x-ray scattering (1D-SAXS) studies reveal phase information of the bulk samples in Library 1, where POSS cage is decorated by hydroxyl groups (Figure 2.14 A). The ratio between scattering vector \((q)\) values of the peaks in each diagram shows a change in phase with the change of PS chain length. As a conclusion, DPOSS-PS\(_{23}\) presents a Lamella phase; DPOSS-PS\(_{35}\) gives a Double Gyroids phase; DPOSS-PS\(_{91}\) renders a Hexagonal phase, while DPOSS-PS\(_{140}\) will self-assemble into a body-centered cubic phase. From 8.1nm for DPOSS-PS\(_{23}\) to 11.6nm
for DPOSS-PS$_{140}$, an increase in featured structure dimension can also be observed. Transmission Electron Microscopic (TEM) images of these obtained phases further confirm this relationship between PS chain length and self-assemble behavior.

Figure 2.14 Results for the study of self-assembly behavior of the reported giant surfactants.  

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For the study of the architecture of giant surfactant, as was introduced previously, other than changing the length of the polymer chain, the modulation of molecular structures via changing functional groups of the MNPs, changing the number of polymer chains or MNP heads would also be of research interest and will provide us with information of the effect of molecular topology on supramolecular structures.

For multi-head and single tail, 3-headed giant surfactant, 3DPOSS-PS$_{19}$ (Figure 2.14B), would be a good example which presents an inverted-hexagonal phase.

To emphasize the change of number of tails while maintaining an identical volume fraction of the hydrophobic PS chains, a comparison between AC$_{60}$-PS$_{44}$ and AC$_{60}$-2PS$_{23}$ (Figure 2.14C) is conducted. The resulting phases are Lamella and Hexagonal, respectively. Noticing that the total number of styrene units are almost identical, the volume fractions of PS chain ($V_{ps}$) are identical. The same trend would also be observed when comparing the phase structures of DPOSS-PS$_{35}$ and DPOSS-2PS$_{17}$, where the former one is double gyroid, while the later one is hexagonal (Figure 2.15). The difference in structures is attributed to the difference in molecular topology. Thus, the geometrical properties, i.e. cross-
sectional area ratio, should also be taken into consideration for phase structure analysis.\textsuperscript{34}

Thin film samples of DPOSS-PS\textsubscript{35} (Figure 2.16 A) and DPOSS-PS\textsubscript{75} (Figure 2.16 B) are casted and grazing incidence small angle x-ray scattering (GISAXS) and TEM are applied to study self-assemble behaviors. For DPOSS-PS\textsubscript{35}, thin film was casted, and studied after solvent annealing. The TEM pattern presents a layered structure with a width of 2.5 nm, while the GISAXS pattern suggested a hexagonal packing of cylinders. For DPOSS-PS\textsubscript{75}, which will form a Face Centered Orthorhombic (FCO) structure, displaying a packed dots with a sphere diameter of 4.0 nm in TEM images.

These giant surfactants are featured with a high self-assemble rate due to their high diffusion mobility of MNPs and their polymer chains with low entanglement. Thus, the application of these molecules would be promising in thin-film nanopatterning. The sharp interface and well defined structures indicated in previous experimental results will facilitate the precisely controlled nanopatterns at \textasciitilde20 nm scale.
Figure 2.15 SAXS patterns of DPOSS-PS$_{35}$ and DPOSS-2PS$_{17}$ presenting the self-assembled structures.$^{34}$

Figure 2.16 Self-assemble structure analysis by TEM images and GISAXS patterns for DPOSS-PS$_{35}$ (A) and DPOSS-PS$_{75}$ (B).$^{34}$
2.5.2 Giant Shape Amphiphiles

As is shown in Figure 2.11 (B), giant shape amphiphiles are typically giant molecules constructed by building blocks with unique shapes and competing interactions.23, 50, 80, 89 One example of giant shape amphiphiles is the “patchy particles”, which are formed by adding polymeric tethers to nanoparticles, as discussed by Glotzer, et al.50 The early studies of shape amphiphiles are originated from the study of biomaterials. The pursuit of pre-determined guidance of self-assembly behaviors finds its solution by designed and precisely decorated particle surfaces: an idea inspired by the precisely self-assembled structures of viruses and organelles.90 Further studies revealed that, when selective interactions are introduced by controlling the polymeric building blocks attached to the nanoparticles, these patchy particles formed will potentially possess the self-assembling behaviors of giant surfactants as well as the formation of intricate ordered phase as in liquid crystals (Figure 2.17).79, 91 The guideline of the design of patchy particles is later developed to the conjugation of nanoparticles with specific shapes, like spheres, cubic, disc, rods, octahedral, etc. The illustration of some representative giant shape amphiphiles constructed by MNPs with specifically defined structures
could be find in Figure 2.11 (B): cube-plane-cube,
92 sphere-cube,
93 sphere-disk, to name a few. It is noteworthy that, the
wide range of the selection of building blocks with different
shapes and symmetry as well as the vast variety of chemical
modification for the functional groups will grant the
designed giant shape amphiphiles with huge potential in the
engineering towards self-assembled structures.
Figure 2.17 Illustration of self-assembled structures. From left to right, (A-E): Twisted wires; Tetrahedron; Icosahedron; Ring structures; Micelle.\textsuperscript{50}

Scheme 2.1 Synthetic route of the BPOSS-PDI-BPOSS compound.\textsuperscript{92}
Ren et al. reported their work of a shape amphiphile in the year 2010. A giant shape amphiphile with cubic- and disk-shaped shape-persistent MNPs: BPOSS and Perylene Diimide (PDI), respectively, was synthesized and studied. The molecular structure of the giant molecule as well as its synthetic route is shown in Scheme 2.1. The compound (2BPOSS-PDI) is synthesized by covalently linking a BPOSS unit to the both sides of a planner shaped PDI unit through a rigid linker: a phenyl ring. The resulted molecule will have a precisely defined dumbbell-like molecular structure. Single crystal was grown for the molecular via slow solvent evaporation method, and the crystal was studied for its crystal structures by wide angle x-ray scattering (WAXS), TEM bright field (BF) mode and selected area electron diffraction (SAED).

When single crystal was grown from a diluted tetrahydrofuran (THF) solution, a nano-belt shaped structure would be observed. The single crystal structure was studied by electron diffraction and a triclinic crystal unit cell parameters of \(a = 6.577 \text{ nm}, \ b = 5.213 \text{ nm}, \ c = 1.107 \text{ nm}, \ \alpha = 93.26^\circ, \ \beta = 94.85^\circ, \ \text{and} \ \gamma = 92.73^\circ\) was determined for the single crystal.

UV-vis spectra are taken for solution of 2BPOSS-PDI with increasing concentration (Figure 2.18). The appearance and
strengthen of peaks at ~585nm in the spectra gives a good indication of π-π interaction, and suggests the packing of 2 PDI units from 2 molecules. Therefore, for the self-assemble of 2BPOSS-PDI should start with a dimer-formation, with a twisted angle due to the stereo-hindrance of the bulky BPOSS unit. And 13 of the dimers will further give the triclinic unit cell with the previously discussed parameters (Figure 2.19).

The packing scheme of 2BPOSS-PDI could be accounted for the anisotropic nature of the molecular structure. Such anisotropic would lead to the anisotropic crystal growth from solution along different axis.

Figure 2.18 UV-VIS absorption spectra (a) and fluorescence spectra (b) of 2BPOSS-PDI diluted solution indicating the existence of π-π interaction between assembled molecules.2

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Figure 2.19 Illustration of the formation of 2BPOSS-PDI dimers (a) and the unit cell computer simulation (b)\textsuperscript{92}

Scheme 2.2 Synthetic route of the BPOSS-C\textsubscript{60} compound
Another example of giant shape amphiphiles comes from a work of Sun et al. In this work, a POSS-C₆₀ dyad was synthesized (Scheme 2.2). The resulted giant molecules shows good solubility in organic solvent hexane, THF and chloroform, etc. When single crystals are grown from diluted solution via solvent evaporation method, it is revealed that crystal structure would alter with the change of substrates: glass (orthorhombic, Figure 2.20 (a)) or carbon coated mica (hexagonal, Figure 2.20 (d)).

Both of the two types of single crystals were analyzed by TEM BF and SAED. For crystals grown on glass substrate, a crystal with orthorhombic lattice ($a = 2.10$ nm, $b = 1.05$ nm and $c = 3.62$ nm) is obtained. The asymmetry in molecular architecture and the immiscibility between C₆₀ and POSS will render the formation of an alternating bilayer structure: a layer of BPOSS on the glass substrate followed by another of C₆₀ (Figure 2.21 (a)-(c)). For crystals grown on carbon coated mica, differ from glass substrate where BPOSS will have stronger interaction with, C₆₀s will tend to be packed on the substrate to form the first layer, and thus create a bilayer structure start with a C₆₀ layer followed by a BPOSS layer (Figure 2.21 (e)-(g)).
In this case of BPOSS-C₆₀ giant shape amphiphile, the packing scheme and the resulting hierarchical structure is determined by the molecular symmetry as well as the immiscibility of the two MNP building blocks. Furthermore, the scheme could be controlled by the interaction between the molecule and the substrate.
Figure 2.20 TEM BF images of BFOSS-C₆₀ different single crystals grown on different substrates: glass (a) and carbon coated mica (b); ED patterns of different single crystals: orthorhombic grown on glass (b) and (c) and hexagonal grown on carbon coated mica (e) and (f)⁹³

Figure 2.21 Computer simulation of the packing scheme of the orthorhombic (a), (b) and (c) and hexagonal (e), (f) and (g) crystal lattice model and the corresponding simulated diffraction patterns, (d) and (h).⁹³
The supramolecular structures formed through self-assembly of giant shape amphiphiles gives an alternating bilayer structure: a conductive C\textsubscript{60} and an insulating BPOSS layer. This would make the material applicable in some electronic applications. Wang et al. provided another creative study of a shape amphiphile that has found its promising application in electronics. A sphere-disc shape amphiphile, porphyrin-C\textsubscript{60} was synthesized and studied.\textsuperscript{94-95} The porphyrin ring are substituted by a C\textsubscript{60} unit at one of the four functional groups, while the rest three sites are occupied by alkyl chain substituted phenyl rings, aiming at increasing solubility Figure 2.22 (A). WAXS and selected area electron diffraction (SAED) studies facilitated the determination of the crystal structure, presenting a hexagonal packed 129\textsubscript{44} columns (Figure 2.22 (B)), where porphyrins are located at the center while the C\textsubscript{60} units will be surrounding the column (Figure 2.23 (b),(c)).

This unique supramolecular structure was found to benefit electron transportation in electronic devices. As was designed, the resulted supramolecular architecture possess two channels: porphyrin for hole and C\textsubscript{60} for electron transportation, and thus favors the boost of device performance. Device fabrication and performance analysis were carried out and providing a satisfying power conversion.
efficiency (PCE) of 3.36% with a fill factor (FF) of 0.38 when this porphyrin-C₆₀ is applied as an electron acceptor.

Figure 2.22 (B).

Figure 2.22 Self-assembly of a Porphyrin-C₆₀ derivative into double-cable structure gives unique electronic properties: Molecular structure (A); J-V characteristics of a solar cell fabricated by applying the porphyrin-C₆₀ as electron acceptor (B); Illustration of columnar packing of the porphyrin-C₆₀ forming a 129₄₄ helix (C); Hexagonally packed columns will present two electron conducting channels, (1) C₆₀ surrounding the column and (2) porphyrin in the center (D).⁹⁴–⁹⁵

Figure 2.23 Illustration of the 129₄₄ helix structure (a); Enlarged top view (b) and side view (c) of the helix, (omitting the alkyl chains for clarity).⁹⁴
Li et al. reported a cubic-cubic giant shape amphiphile in the year 2011 (Figure 2.24 (s1)). In this paper, a series of giant molecules constructed by POSS units substituted by different functional groups are synthesized and studied.

For BPOSS-APOSS, since BPOSS is substituted by hydrophobic tert-butyl groups while the functional groups of APOSS is ended with hydrophilic carboxyl groups, the resulting molecule will present a symmetry breaking Janus particle. Furthermore, the excluding two building blocks due to hydrophobicity will render a bilayer structure while self-assembling. The crystal structure as well as the self-assemble behavior is studied by TEM, SAED and WAXS experiments. The TEM BF image Figure 2.24 (a)) of the typical stacked lamellar morphology with a flat-on arrangement of a thermal annealed film. Tilting SAED analysis (Figure 2.24 (b)-(d)) contributed to the determination of unit cell parameter. The unit cell is decided to be orthorhombic with dimension of $a = 1.53$ nm, $b = 1.43$ nm, $c = 4.62$ nm. Figure 2.25 presents the computer simulation of the crystal structure of BPOSS-APOSS. A bilayer structure is revealed with alternating BPOSS-BPOSS layer and APOSS-APOSS layer.

The examples presented well-emphasizes the fact that well defined giant shape amphiphiles would contribute to the
formation of controlled supramolecular structures and the scaling up of microscopic functionality and anisotropy to macroscopic properties.

Figure 2.24 The molecular structure of XPOSS-XPOSS molecules (s1); TEM BF of the layered BPOSS-APOSS crystal (a); Tilting SAED patterns of the single crystal at various angles (b)-(d).96

Figure 2.25 Computer simulation of the packing scheme of BPOSS-APOSS (a), (b) and (c) and the corresponding simulated diffraction patterns, (d).96
2.5.3 Giant Polyhedra

As previously discussed, the studies of giant surfactants are focusing on the hydrophobicity while those of giant shape amphiphiles are focusing on the shape, symmetry and competing interactions between the MNP building blocks. Besides these two types of giant molecules, giant polyhedra is a third type of giant molecules that attracts great research interest, which is mainly developed for their unique topology, geometry and symmetry.

Figure 2.11 (C) presents a cartoon illustration of different types of giant polyhedra. Giant polyhedra can be categorized into two types by their different constructions: Type I is constructed by building blocks which are polyhedra themselves, like the cube-cube model in Figure 2.11 (C) while Type II is constructed by organizing multiple smaller MNPs into one giant molecule. For the second type, the geometry of the giant polyhedron is controlled by constructing a certain polyhedron framework via the aforementioned "Node-Spacer-Vertex" strategy. By selecting node with proper geometry, the models presented in Figure 2.11 (C) would be successfully generated: for example, a tetrahedron node will give a tetrahedron; a 2-D node will give a wide range of giant polyhedra varies from triangular, tetragonal... shaped giant
molecules while a linear node with polyhedra as vertex will lead to linear giant polyhedra. This giant molecule, is actually also a giant shape amphiphile. It is noteworthy that, all the discussed three types of giant molecules are unique, but not thoroughly independence.

The node of giant polyhedra will gain the control over molecular geometry, while the linker will contribute and assist in the tuning of molecular physical properties including rigidity, etc. By selecting a rigid linker, like PDI, it is likely that the resulting polyhedra will possess a high degree of shape-persistence, and further affects the self-assembling behavior of the giant polyhedra.

Tetrahedron is an important member of the family of polyhedra. A study in 2009 revealed that shape (tetrahedron) itself can produce remarkable structure complexity, and inspired the study of quasicrystals formed by tetrahedron. The authors adopted computer simulation to study the phase transition of a fluid of rigid tetrahedra. The tetrahedral were found to pack into quasicrystal with a 12-fold symmetry and a packing fraction of 0.8324, which is a densest packing known. The computer simulated model is shown Figure 2.26.

Figure 2.27 (a) presents a connected network of one slice from the quasicrystal formed by rigid tetrahedral. Triangles
and squares as tiles could be packed and fulfill a plane. The simulated diffraction pattern which presents significant strong 12-fold Bragg peaks indicates the existence of a long ranged ordered structure. Figure 2.27 (b)-(c) is an illustration of how tetrahedral will be packed into a quasicrystal. First, 12 tetrahedra will form a 12-membered ring; and then, a pentagonal bipyramid will sit on top to form a single unit. The packing of these units will form “Logs” (Figure 2.27 (b)). These logs will be packed into squares or triangles and further to a 3-D close packed quasicrystal with additional tetrahedra units. (Figure 2.27 (c)).
Figure 2.26 Illustration of close packed ($\phi = 0.8324$) rigid tetrahedral simulated via Monte-Carlo method. (a): model viewed along y-axis; (b): model viewed along z-axis, and the white overlay revealing the 12-fold symmetry.\textsuperscript{97}

Figure 2.27 Structural characterization of the dodecagonal quasicrystal. (a) Connected network viewed along the 12-fold axis. (b) Construction of logs by the packing of rigid tetrahedral. (c) Logs with additional tetrahedral pack into quasicrystal.\textsuperscript{97}
Mingjun Huang et al published a paper discussing the selective assemblies of giant tetrahedra recently.\(^9\) In this paper, a series of precisely defined giant tetrahedra are synthesized and studied. In these giant tetrahedra, POSS units with different side groups are placed at the vertices of a tetrahedral framework. Highly ordered super lattice structures were formed and observed. Among them, the observation of a Frank-Kasper A\(_{15}\) phase, an essential structural feature of certain metal alloys, implicates great significance to this paper.

In this study, the giant tetrahedra are categorized by the difference in POSS units: each molecule may contain hydrophobic POSS (with isobutyl groups) MNPs or 0~3 hydrophilic POSS (with different hydrophilic side groups) MNPs. The synthesized giant tetrahedra are studied for their super lattice structures. Among them, the giant tetrahedra with 1 hydrophilic and 3 hydrophobic POSS (Figure 2.28 (2a~2c)) are found to give A\(_{15}\) phases as is shown in Figure 2.29.

SAXS and WAXS are applied to characterize the supramolecular structures of 2a grown from tetrahydrofuran (THF)-acetonitrile (MeCN) mixed solvents at room temperature (RT). A \(q\) value ratio of 1:2:3 suggesting a lamella lattice can be found in the combined profile shown in Figure 2.30 (A).
The strong peak with $d$-spacing of 10.9 Å is assigned to the characteristic diffraction peak of crystalline BPOSS.\textsuperscript{48} TEM BF image of microtomed samples is presented in Figure 2.30 (B) where the lamella lattice can be clearly observed. Layer thickness (~4.5 nm) can be estimated from the TEM BF image, suggesting a packing scheme of 1 layer of hydrophilic POSS and 2 layers of BPOSS frustrated lamellae.\textsuperscript{99}

Figure 2.28 Molecular structure of giant tetrahedra with 1 hydrophilic and 3 hydrophobic POSS MNPs. Intercept cartoon shows simplifications with blue spheres representing hydrophilic POSS MNPs while red spheres the hydrophobic ones.\textsuperscript{98}

Figure 2.29 Schematic illustration of the assembly mechanism of giant tetrahedra that gives A15 lattice.\textsuperscript{98}
Figure 2.30 Characterization of molecule 2a self-assemble behaviors by multiple methods and conditions: SAXS and WAXS (A), TEM BF mode (B), SAXS after annealing (C), TEM BF mode after thermal annealing and staining by RuO₄ (D), Fourier filtered image of D (E) and magnified E with inverted colors. ⁹⁸
The 2a samples were subjected to thermal annealing. The samples were heated to 180°C and immediate cool down to 140°C for a 12-hour annealing. SAXS, WAXS and TEM images suggest the formation of a brand new supramolecular lattice. As is indicated in Figure II.31 (C), a series of peaks with $q$ ratio of $\sqrt{2} : \sqrt{4} : \sqrt{5} : \sqrt{6} : \ldots : \sqrt{14} : \sqrt{16}$ can be identified well matching the characteristic peaks of an A15 phase. The original and processed TEM BF images (Figure II.32 (D)-(F)) present a clear view of the A15 structure consists of two types of spheres packed with coordination number (CN) of 12 and 14, for the smaller and the larger spheres, respectively. The dimension of a single cell is measured to be 13.2 nm. Calculations based on the size of the two types of spheres revealed that the spheres are constructed by 38 and 50 molecules, respectively.

Experimental results of 2b and 2c also indicate the formation of A15 phases by presenting virtually identical patterns, while at the meantime suggesting a relationship between collective hydrogen-bonding strength with the number of giant tetrahedra in each sphere.

The formation of these A15 phases can be illustrated by Figure II.33. Upon melting and thermal annealing, the frustrated lamella disassembles. The hydrogen bonds will facilitate the assembling of hydrophilic POSS units into
spherical aggregates, guiding the hydrophobic BFOSS MNPs, which were originally forming the upper and lower layer of the three-layered frustrated lamella, to scroll and result in an outer shell. The spheres formed will be further packed into the A15 supramolecular lattice to maximize entropy and minimize interfaces.101-104

This study of the self-assemble behavior of precisely defined giant tetrahedra demonstrated a well-developed strategy in designing giant molecules, specifically giant tetrahedra, with tunable architecture, core structure and functionalities that favor the self-assembly into complex structures.
CHAPTER III
EXPERIMENTAL

The study of crystal structure analysis starts with sample recrystallization (section 3.2). X-ray scattering (section 3.3 and section 3.4), electron diffraction and transmission electron microscope (TEM) methods (section 3.5), grazing incidence x-ray scattering (section 3.6) and polarized light microscopy (section 3.7) are employed to obtain experimental results. UV-vis analysis is conducted to gather information regarding the possible formation of π-π stacking (section 3.8). Besides, computer simulation (section 3.9) is also conducted as the basic methodology to determine crystal structures. Density of recrystallized samples are measured in order to confirm the obtained models (section 3.10).

3.1 Sample Compounds

Figure 3.1 presents an illustration of the molecular structure of the samples studied in this dissertation: m-phenyl-(PDI-BPOSS)_2 (a), S-(PDI-BPOSS)_4 (b) and R-(PDI-BPOSS)_4.
In $m$-phenyl-$(\text{PDI-BPOSS})_2$, a phenyl ring is applied as the core of the giant shape amphiphile. A PDI is covalently linked to a BPOSS MNP through a soft alkyl linker. While in $S$- and $R$-$(\text{PDI-BPOSS})_4$, a tetrahedral core is applied to generate a giant tetrahedra. The difference between $S$- and $R$-$(\text{PDI-BPOSS})_4$ lies in the linker between the PDI units and BPOSS units: for $S$-, an alkyl soft linker is applied while in $R$-, the PDI and BPOSS units are connected by a rigid linker, phenyl ring.

![Molecular structures](image)

**Figure 3.1** Illustration of the molecular structures of the three compounds in this thesis: giant shape amphiphile $m$-phenyl-$(\text{PDI-BPOSS})_2$ (a); giant tetrahedra $S$-$(\text{PDI-BPOSS})_4$ (b) and $R$-$(\text{PDI-BPOSS})_4$ (c).
3.2 Sample Preparation for Crystal Structure Analysis

At room temperature, the three samples are soluble in organic solvent THF and chloroform, while insoluble in water and methanol. For crystal structure analysis, multiple methodologies were applied, and recrystallized samples were prepared accordingly: powder samples for X-ray diffraction (section 3.2.1) and single crystal samples for TEM and ED (section 3.2.2).

3.2.1 Powder Crystal Samples

In a 20mL vial, each sample is dissolved in chloroform (filtered by Whatman® 0.45μm PTFE membrane syringe filter). Methanol is added to the solution, accommodating chloroform: methanol (v/v) = 2:1. The vial is sealed afterwards and placed at a steady stage. The solution will gradually become saturated as solvent evaporates and the chloroform: methanol ratio decreases. Crystal powders are collected after the solvent is thoroughly evaporated, and are dried for future x-ray diffraction analysis and density measurements. The samples are also grinded and staffed into Kapton tubular sample holders for x-ray scattering study at beamline 11-BM at Argonne National Lab.
3.2.2 Single Crystal Samples on Substrates

Single crystal samples were prepared on carbon coated mica substrates.\textsuperscript{105} 5mL THF solvent was added to a petri dish where a glass stage was placed holding a piece of carbon coated mica substrate. After one hour during which a saturated THF atmosphere was generated, a drop of diluted sample solution in THF (0.01 wt\%) was casted on the substrate. The petri dish was placed on a steady stage with a heavy load on top to help sealing the cap for 24 hours. Single crystals were grown during the slow evaporation of solvent as time went by. The obtained samples were checked under PLM to pick out the ones with high quality single crystals. Selected carbon coated mica substrates were subjected to hydraulic floating method to peel off the carbon films with single crystals.

Single crystals were also grown on glass substrates for \textit{m-phenyl-(PDI-BPOSS)}\textsubscript{2}. Using glass substrates instead of carbon coated mica and follow the previously introduced method will result in single crystal samples grown on glass substrates. A carbon film was thermal deposited (thermal evaporator: model JEE-4C JEOL) on top of the single crystal layer. One drop of poly(acrylic acid) (PAA) aqueous solution (25 wt\%, purchased from Polysciences, Inc. CAS# 9003-01-4)
was casted on the carbon layer. After total solidification, the carbon coated film will be peeled off with the PAA film. Carefully place the film on water surface with the carbon coated film facing up, after 20 min, the PAA film will be dissolved in water, leaving carbon coated film floating on the water.

Carbon films floating on the surface of water were collected by TEM copper and nickel grids. The grids were dried under vacuum at RT to prepare TEM and ED samples.

3.3 Small Angle X-ray Scattering

Powder samples were prepared for small angle x-ray scattering (SAXS) experiments on a Rigaku MicroMax 002+ and a Rigaku S-Max3000 with additional chamber. Cu sources are applied in both systems to provide an X-ray with wavelength of 1.54 Å. The two systems works at different current and voltage. For the former one, a voltage of 45 KV and a current of 0.88 mA is applied, while for the latter one, the voltage and current are 50 KV and 06 mA, respectively. Silver behenate (AgC_{22}H_{43}O_{2}) was used to calibrate the scattering vector (q). Data collection periods were determined according to the scattering intensity of each sample. Data collected from Rigaku MicroMax 002+ covered q range between 0.2~2.0 nm^{-1}. The additional sample chamber attached to the Rigaku S-Max3000
allows a selection from different data collection range: the front chamber allows collection of data within the scattering range of 2θ = 2° ~ 3° while for the rear chamber, the range is up to 10°. Resulted data collected from the two equipment were further analyzed by Rigaku SAXSgui software, respectively.

3.4 Wide Angle X-ray Scattering at Argonne National Lab

Beamline 11-BM and Beamline 8-ID-E at Argonne National Lab (ANL) provided this work with precious opportunity performing synchrotron x-ray diffraction experiments. Powder samples were filled in a Kapton tube and subjected to wide angle x-ray scattering (WAXS) experiments. Data collected were analyzed by GIXGUI Matlab software set transmission mode provided by ANL.

3.5 Electron Diffraction

Single crystal samples were studied by TEM and ED experiments. These experiments were performed on the Philips (Tecnai 12) TEM equipped with a Gatan 780 DualView CCD camera @ 120 KV electron acceleration voltage. Single tilting stage was applied for tilting experiments to give detailed crystal structural information. The beam stops lies in the beam path
provided a reference when locating the tilting axis direction which is approximately parallel to the beam stop.

For R- and S- (PDI-BPOSS)$_4$, cross-sectional TEM images were also taken under TEM bright field mode. Samples were embedded in epoxy resin and microtomed (PowerTome PC/CR-X cryosectioning system (RMC)).

3.6 Grazing Incidence Small Angle and Wide Angle X-ray Scattering

Grazing incidence small angle x-ray scattering (GISAXS) and grazing incidence wide angle x-ray scattering (GIWAXS) experiments were performed in beamline 11-ID-E at ANL, providing thin film morphology information.

3.7 Polarized Light Microscopy

Samples were observed under polarized light microscope (PLM) (Olympus BX51 research system microscope equipped with Mettler Hot Stage) and images were taken through a CCD camera.

3.8 UV-vis Spectrophotometry

UV-vis Spectrophotometry was conducted to identify π-π stacking in order to facilitate supramolecular structure determination. The samples were dispersed in mixed solvent of chloroform and methanol (v/v = 1:2) with different
concentration (\(5 \times 10^{-5} \text{M}, 2 \times 10^{-5} \text{M}, 1 \times 10^{-5} \text{M}, 5 \times 10^{-6} \text{M}, 2 \times 10^{-6} \text{M}, 1 \times 10^{-6} \text{M}\)) and examined by Hewlett Packard Model 8453 UV/VIS Spectrophotometer.

3.9 Computer Simulation

Accelrys Cerius² program (v4.6) assisted the construction of molecular packing model and crystallographic simulation. Initial model was built based on the unit cell parameters calculated from the experimental results from the methods discussed in previous sections. ED and x-ray diffraction (XRD) patterns can be simulated from this model, and will be compared by the experimental data. Modifications of atomic positions will be made accordingly as a molecular packing model refinement.

3.10 Density Measurements

The density measurements of the powder samples were conducted by dispersing them in water and sequentially adding saturated potassium iodide (KI) aqueous solution. However, serious dewetting is observed for \(m\)-phenyl-(PDI-BPOSS)\(_2\) and introduced significant error to the density measurement. In order to overcome the dewetting issue, a bad solvent with a high density and will help eliminating the dewetting phenomenon should be introduced. Dimethyl sulfoxide (DMSO) is
a solvent that meet these requirements. It has a relatively high density (1.10g/mL) and will not dissolve the sample. Samples were dispersed in methanol, KI solution is dropped in the suspension until the powder in the stabilized suspension neither rose nor sank. 5 mL of the solution was extracted and weighed and the density of the solution is calculated afterwards.
CHAPTER IV
CRYSTAL STRUCTURE OF PDI-BPOSS BASED SHAPE AMPHIPHILE

In this chapter, the study of \textit{m-phenyl-(PDI-BPOSS)}\textsubscript{2} sample will be introduced, including the synthesis, the crystal structure determination and the supramolecular hierarchical architecture model construction.

4.1 Molecular Design and Molecule Synthesis

This section will be discussing the molecular design and synthesis of this giant shape amphiphile based on a BPOSS MNP and PDI unit. As is shown in Figure 4.1, this shape amphiphile contains a phenyl core and two substituting groups located at \textit{meta} position of the phenyl ring. Each substituting group is consist of a PDI unit and a BPOSS unit which are covalently linked together by a soft 3C alkyl chain.

Compound \textit{m-phenyl-(PDI-BPOSS)}\textsubscript{2} was synthesized by the synthetic routed described as follows:

1: 3,4,9,10-perylenetetracarboxyldianhydride (1 equiv.) and potassium hydroxide (KOH) (5 equiv.) were added to a flask filled with 100mL deionized water, heated to 70°C, stirred
for 0.5 hr. PH value was adjusted to 8~9 by HCl afterwards. Potassium iodide (KI) and Aliquat were added to the flask followed by decyl bromide (8 equiv.) after stirring for 10 min. Products were collected after 2 hours' reaction under vigorous stirring by extraction with chloroform. Methanol was added to the NaCl washed chloroform solution to precipitate the yellow solid 1 (Scheme 4.1).\textsuperscript{107}

Figure 4.1 Illustration of molecular structure of \textit{m-phenyl-(PDI-BPOSS)}$_2$ I

\textsuperscript{107}
Scheme 4.1 Synthetic route of perylene-3,4-anhydride-9,10-di-(decyloxy carbonyl) 2.107

Scheme 4.2 Synthetic route of m-phenyl-(PDI-BPOSS)2 I.
2: 1 (1 equiv.), 0.5mL toluene and 2.5mL n-dodecane were added to a round flask and heated to 95°C to have 1 well-dissolved. p-Toluenesulfonic acid monohydrate (PTSA) was added to the flask afterwards. The solution was stirred 5 hours for reaction. The product was purified by column chromatography to give dark red solid 2 (Scheme 4.1).\textsuperscript{107}

3: To a 100 mL Schlenk flask, perylene-3, 4-anhydride-9,10-di-(decyloxycarbonyl) (2, 2.0 g, 2.89 mmol, 1 equiv.), aminopropylisobutylPOSS (3.29 g, 3.76 mmol, 1.3 equiv.) and 20 g imidazole were added. The mixture was purged with N\textsubscript{2} flow for 15 min. Then 4 mL 1, 2- dichlorobenzene (ODCB) was added to the flask and heated to 125 °C with vigorous stir for 5 hours. The red mixture was cooled to 90 °C and 60 ml methanol was added. The crude product was separated by filtration and further purified by column chromatography (silica gel) using 20/1 (v/v) CHCl\textsubscript{3}/Acetone as the eluent (Scheme 4.2). Yield: 4.1 g, 90% (dark red solid). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, ppm, \(\delta\)): 8.35 (d, 2H, PDI-Ar), 8.10 (t, 4H, PDI-Ar), 7.95 (d, 2H, PDI-Ar), 4.37(t, 4H, CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}), 4.21 (t, 2H, SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}N), 2.00–1.75 (m, 13H, SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3} + SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}N + CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}), 1.52 –1.25 (m, 28H, CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}(CH\textsubscript{3})\textsubscript{7}CH\textsubscript{3}), 0.96 (d, 42H, SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}H\textsubscript{6}), 0.88 (t, 6H, -CH\textsubscript{3}), 0.75 (t, 2H, SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}N), 0.65–0.55 (m, 14H, SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}H\textsubscript{6}). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}, ppm, \(\delta\)): 168.16, 163.16, 134.90, 131.79, 130.95, 130.12, 129.03, 128.80,
4: A 50 mL round bottom flask was charged with 3 (1.0 g, 0.646 mmol), 30 mL toluene and PTSA (0.27 g, 1.40 mmol). Then the flask was capped and heated to 100 °C under vigorous stir for 5 hours. Volatiles were removed on a rotary evaporator, and the solid residue was washed by methanol twice and acetone twice. The solid product after filtration was further purified by column chromatography (silica gel) using 20/1 (v/v) CHCl₃/Acetone as the eluent (Scheme 4.2). Yield: 0.82 g, 82% (orange solid). ¹H NMR (300 MHz, CDCl₃, ppm, δ): 8.71-8.62 (m, 8H, PDI-Ar-\( \text{H} \)), 4.21 (t, 2H, SiCH₂CH₂CH₂-N), 2.00-1.75 (m, 9H, SiCH₂CH₂H₆ + SiCH₂CH₂CH₂N), 0.96 (d, 42H, SiCH₂CH₂H₆), 0.77 (t, 2H, SiCH₂CH₂CH₂-N), 0.75-0.60 (m, 14H, SiCH₂CH₂H₆). ¹³C NMR (75 MHz, CDCl₃, ppm, δ): 162.99, 159.90, 136.35, 133.78, 133.52, 131.84, 131.40, 129.34, 126.79, 126.33, 124.15, 123.86, 123.18, 119.11, 42.98, 25.66, 23.83, 22.50, 22.42, 21.58, 9.78.

I: To a 50 mL Schlenk flask, m-phenylenediamine (8.64 mg, 0.080mmol, 1 equiv.), 4 (250 mg, 0.20mmol, 2.5 equiv.), 4-Dimethylaminopyridine (DMAP, 24 mg, 0.20mmol, 2.5 equiv.), and 3.0g imidazole were added. The mixture was purged with N₂
flow for 15 min. Afterwards 3 mL ODCB was added and the flask was inserted to oil bath kept at 130 °C for 12h. The red mixture was cooled to 90°C and 30ml methanol was added. The solid was collected by filtration, washed by methanol twice and acetone twice. Dark red product was yielded after further purified by column chromatography (neutral Al₂O₃ gel) using CHCl₃ as the eluent. The final product was characterized by ¹H-NMR as shown in Figure 4.2.

Figure 4.2 ¹H-NMR spectrum of m-phenyl-(PDI-BPOSS)₂
4.2 Sample Preparation

\( m\text{-Phenyl-(PDI-BPOSS)_2} \) compound was recrystallized for crystal structure studies. Single crystal samples were prepared for Selected Area Electron Diffraction (SAED) experiments. As was described in section 3.2, \( m\text{-phenyl-(PDI-BPOSS)_2/THF} \) solution was drop casted on glass substrate and placed in a closed petri dish with saturated THF atmosphere overnight to allow slow solvent evaporation, during which single crystal growth takes place. Sample were prepared for the grown crystal following the procedure discussed in Chapter III.

4.3 Crystal Structure Investigation

Recrystallized samples were studied by TEM BF, SAED, WAXS experiments to investigate the single crystal structure and determine the unit cell parameters.

4.3.1 Unit Cell Determination from Selected Area Electron Diffraction Data

Figure 4.3 is a typical SAED pattern for \( m\text{-phenyl-(PDI-BPOSS)_2} \) single crystal sample. The patterns, together with tilted angle images indicate a triclinic unit cell. The inset is a bright field image showing the region from which the diffraction pattern was obtained.
Figure 4.3 A typical diffraction pattern of $m$-phenyl-(PDI-BPOSS)$_2$ single crystal, with the inset presenting the TEM BF image of the sample.
In order to determine the unit cell parameters of the
unit cell, tilting was performed away from the original 0’
tilted pattern one degree after another until an integral
zone is reached with the indication of a strong-weak-strong
diffraction intensity variation is observed. A set of
sequentially tilted diffraction patterns (Figure 4.4) was
obtained for unit cell calculation.

On the basis of the principle for unit cell determination
that the base vectors, i.e., a, b and c axis, would be of the
largest d-spacing while of the shortest reciprocal a*, b* and
c* length, 25’ pattern is picked up for its shortest base
vector which was further assigned b* axis. Attempt to index
this set of diffraction patterns was made by assigning the
second shortest vector in 25’ pattern with \( h \) and \( l \in [0, 1] \). Calibrating with a beef liver catalase crystal standard from
SPI supplies®, \( b^* \) is measured to be 4.35nm and the angle
between the two basic vectors in this diffraction pattern to
be 76.74°.
Figure 4.4 SAED pattern of $m$-phenyl-(PDI-BPOSS)$_2$ single crystal samples, tilted along indicated axis, with zone axis labeled: $[1\bar{1}2]/0^\circ$, $[2\bar{1}3]/11^\circ$, $[101]/25^\circ$ and $[211]/41^\circ$. 
For triclinic unit cells, the $d$-spacing of a given $hkl$ plane could be calculated following (Equation 4-1. The patterns obtained via sequentially tilting experiments are stacked to construct a 3-D reciprocal lattice with Matlab®, which assisted in the determination of unit cell parameters. By assigning each base vectors in the diffraction patterns, measuring the $d$-spacing and angles, the unit cell parameters are then calculated to be $a=5.1\,\text{nm}$, $b=4.9\,\text{nm}$, $c=4.7\,\text{nm}$, $\alpha=62.9^\circ$, $\beta=70.0^\circ$ and $\gamma=78.2^\circ$.

\[
\frac{1}{d^2} = \frac{h^2}{a^2 \sin^2 \alpha} + \frac{2kl}{bc} (\cos \beta \cos \gamma - \cos \alpha) + \frac{k^2}{b^2 \sin^2 \beta} + \frac{2hl}{ac} (\cos \alpha \cos \gamma - \cos \beta) \\
+ \frac{l^2}{c^2 \sin^2 \gamma} + \frac{2hk}{ab} (\cos \alpha \cos \beta - \cos \gamma) / V
\]

(Equation 4-1)

where $V=\left(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma \right)$

With the unit cell parameters, it is calculated that [321], [223] and [111] zones are 47°, 9° and 22° away from [112] zone when tilted along proper axis, respectively. This is confirmed by SAED tilting experiments, the results of which are shown in Figure 4.5.
Figure 4.5 Tilting along different axis for unit cell parameter (a=5.1nm, b=4.9nm, c=4.7nm, α=62.9°, β=70.0° and γ=78.2°) confirmation: 47° tilting along [11̅1] direction for [11̅1] zone; 9° and 22° for [2̅2̅3] and [11̅1], respectively.
Figure 4.6 Synchrotron WAXD powder pattern obtained at beamline 8-ID-B of Argonne National Lab, with major peaks assigned with the calculated unit cell parameters.

\[ \begin{align*} 
\alpha &= 62.9^\circ, \\
\beta &= 70.0^\circ, \\
\gamma &= 78.2^\circ. 
\end{align*} \]

\[ \begin{align*} 
a &= 51 \text{ Å}, \\
b &= 49 \text{ Å}, \\
c &= 47 \text{ Å}. 
\end{align*} \]

- (311) 13.2 Å
- (002) 20.1 Å
- (021) 23.5 Å
- (110) 32.1 Å
- (001) 40.2 Å
- (100) 46.7 Å
4.3.2 X-ray Diffraction for Crystal Structure Determination

X-ray diffraction experiments were conducted to further characterize crystal structure of $m$-phenyl-(PDI-BPOSS)$_2$ samples. Powder sample were grown for WAXS characterization with synchrotron beam source at Argonne National Lab. The obtained diffraction pattern is presented in Figure 4.6. The major peaks were labeled on the basis of the calculated unit cell parameters.

4.3.3 Computer Simulation of Molecular Packing in Unit Cell

Molecular packing scheme of $m$-phenyl-(PDI-BPOSS)$_2$ molecules in unit cell is performed with Cerius$^2$ on the basis of the calculated unit cell parameter ($a=5.1\text{nm}$, $b=4.9\text{nm}$, $c=4.7\text{nm}$, $\alpha=62.9^\circ$, $\beta=70.0^\circ$ and $\gamma=78.2^\circ$).

Noticing that $\alpha$ angle is 62.9°, the supplementary angle of which is ~120° and coincides that of the angle between meta substituted phenyl ring side groups, an assumption that a molecule would be occupying the corresponding corner.

Two possible packing schemes of the molecules are raised: firstly, the molecules would repeat itself periodically along the bisector direction of the angle between the two PDI-BPOSS units; while the second one is a 3₁ helix (Figure 4.7), which is proved to be a more reasonable model which will on one
hand allow a proper π-π stacking of PDI groups and on the other hand further be applied in unit cell construction. In Figure 4.7 (a), an illustration of the top viewed trimer is presented, where the PDI units in the three molecules are colored with different colors: the bottom layer is colored with red/blue, the second layer is not specifically colored, and the top layer is colored with green/pink. In (a), a slight displacement between 1 and 2, 2 and 3 is observed due to the rigidity of the center core.

Figure 4.7 Schematic illustration of the packing of 3 molecules into a trimer: (a) top view of the model with color-differentiated molecules; (b) side view of the model with color-differentiated molecules and (c) side view of the model without specific coloring.
Figure 4.8 Schematic illustration of the locating of molecule in 001 plane: (a) the molecular stacking model and (b) corresponding packing scheme.

Figure 4.9 Schematic illustration of the 3-D packing of molecules in a unit cell: (A) Projected views of the unit cell of 001, 100 and 010 zone; (B) 3 trimer units stacking into a 9-unit column, 3 of which are assembled into a unit cell.
A rhombohedral can be estimated since b and c are of similar length. In addition, the measured density of 1.153g/cm³, which suggests a total number of 27 molecules within the unit cell. A 9 layered structure with 3 molecules in one single layer would thus be considered as a reasonable model, as is shown in Figure 4.8. One the basis of the three molecules located on the 100 plane, columns propagate along a-axis until three trimers are assembled for each column: A unit cell would thus be created (Figure 4.9).

As a brief summary, a giant shape amphiphile based on PDI spacer and BPOSS MNP is synthesized. Single crystal was grown for the giant molecule, and was characterized for its crystal structure. A triclinic unit cell is determined with parameters of a=5.1nm, b=4.9nm, c=4.7nm, α=62.9°, β=70.0° and γ=78.2°.
CHAPTER V
CRYSTAL STRUCTURE OF PDI-BPOSS BASED GIANT TETRAHEDRA WITH A RIGID LINKER

In this chapter, the study of R-(PDI-BPOSS)$_4$ sample will be introduced, covering the synthesis, the crystal structure determination and supramolecular hierarchical architecture model construction.

5.1 Introduction

This chapter will be discussing the study of compound R-(PDI-BPOSS)$_4$. The molecular design and synthesis of compound R-(PDI-BPOSS)$_4$ will be introduced as the first section (section 5.2). This giant tetrahedra is constructed by a methane core substituted by four PDI-phenyl-BPOSS units located at the four vertices. The crystal structure analysis will be the second part of this chapter. Samples were carefully prepared and the preparation procedure will be introduced in section 5.3. On the basis of the experimental results obtained from small angle X-ray scattering (SAXS), wide angle X-ray scattering (WAXS), transmission electron
microscopy bright in field mode (TEM BF) and selective area electron diffraction (SAED) and grazing incidence wide angle x-ray scattering (GIWAXS), the crystal structure is determined. The results were confirmed by density measurements and computer simulation by Ceris². It is concluded that, crystalline R-(PDI-BPOSS)₄ possesses an orthorhombic unit cell with lattice parameters as follows: a=163.98Å, b=98.11Å, c=50.00Å α=β=γ=90°.

5.2 Molecular Design and Molecule Synthesis

This section will be discussing the molecular design and synthesis of this giant shape amphiphile based on a BPOSS MNP and PDI unit. As is shown in Figure 5.1, this shape amphiphile contains a tetrapod core and four substituting groups are located along the vertices axis of the tetrapod. Each substituting group is consist of a PDI unit and a BPOSS unit which are covalently linked together by a phenyl ring.

Compound R-(PDI-BPOSS)₄ was synthesized by the synthetic routed (Scheme 5.1) described as follows:

5: To a 100 mL Schlenk flask, 2 (0.878 g, 1.27mmol, 1 equiv.), p-aminophenyl-isobutylPOSS (1.50 g, 1.65mmol, 1.3 equiv.), DMAP (198 mg, 1.65mmol, 1.3 equiv.), and 10 g imidazole were added. The mixture was purged with N₂ flow for 15 min. Then 2 mL ODCB was added and the mixture was kept at
125 °C under vigorous stir for 5 hours. Afterwards the red mixture was cooled to 90 °C and 50 ml methanol was added. The solid residue was separated by filtration, and further purified by column chromatography (silica gel) using 20/1 (v/v) CHCl₃/Acetone as the eluent. Yield: 1.51 g, 75% (dark red solid). ¹H NMR (300 MHz, CDCl₃, ppm, δ): 8.61 (d, 2H, PDI-Ar), 8.38 (t, 4H, PDI-Ar), 8.09 (d, 2H, PDI-Ar), 7.88 (d, 2H, Si-Ar₀-H), 7.40 (d, 2H, Si-Ar₉-H), 4.37 (t, 4H, CO₂CH₂CH₂), 4.21 (t, 2H, SiCH₂CH₂CH₂N), 2.00-1.75 (m, 11H, SiCH₂CH₆CO₂CH₂CH₂), 1.52 - 1.25 (m, 28H, CO₂CH₂CH₂(C₂H₅)₇CH₃), 0.96 (d, 42H, SiCH₂CH₂C₂H₆), 0.88 (t, 6H, -C₃H₃), 0.75-0.58 (m, 14H, SiCH₂CH₂CH₂H₆). ¹³C NMR (125 MHz, CDCl₃, ppm, δ): 168.17, 163.61, 137.04, 135.85, 135.18, 132.71, 132.10, 132.01, 131.71, 130.33, 129.58, 129.21, 129.07, 127.83, 126.15, 122.76, 122.18, 121.88, 65.89, 31.89, 29.55, 29.30, 28.58, 26.01, 25.70, 23.87, 22.66, 22.53, 22.46, 14.08.

6: A 100 mL round bottom flask was charged with 5 (1.50 g, 0.952mmol), 40 mL toluene and p-toluenesulfonic acid monohydrate (PTSA, 0.380 g, 2.0mmol). Then the flask was capped and heated to 100 °C under vigorous stir for 5h. Volatiles were removed on a rotary evaporator, and the solid residue was washed by methanol twice and acetone twice. The solid product after filtration was further purified by column chromatography (silica gel) using 20/1 (v/v) CHCl₃/Acetone as
the eluent. Yield: 0.73 g, 60% (orange solid). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, ppm, δ): 8.85-8.65 (m, 8H, PDI-Ar-H), 7.88 (d, 2H, Si-Ar\textsubscript{o}-H), 7.38 (d, 2H, Si-Ar\textsubscript{m}-H), 2.00-1.75 (m, 7H, SiCH\textsubscript{2}CH\textsubscript{2}H\textsubscript{6}), 0.96 (d, 42H, SiCH\textsubscript{2}CH\textsubscript{2}H\textsubscript{6}), 0.75-0.60 (m, 14H, SiCH\textsubscript{2}CH\textsubscript{2}H\textsubscript{6}). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}, ppm, δ): 163.26, 159.85, 143.80, 135.26, 133.59, 131.91, 131.68, 130.93, 129.88, 127.73, 127.58, 126.82, 124.47, 123.94, 123.42, 121.03, 119.27, 25.71, 23.87, 22.43.
Figure 5.1 Illustration of molecular structure of $\text{R-}(\text{PDI-BPOSS})_4$ II

Scheme 5.1 Synthetic route of $\text{R-}(\text{PDI-BPOSS})_4$ II.
II: To a 50 mL Schlenk flask, tetrakis(4-aminophenyl)methane (26.6 mg, 0.070 mmol, 1 equiv.), 4 (404 mg, 0.315 mmol, 4.5 equiv.), DMAP (37.8 mg, 0.315 mmol, 4.5 equiv.), and 4.0 g imidazole were added. The mixture was purged with N₂ flow for 15 min. Afterwards 3 mL ODCB was added and the flask was inserted to oil bath kept at 125 °C for 5 h. The red mixture was cooled to 90 °C and 30 ml methanol was added. The solid was collected by filtration, washed by methanol twice and acetone twice. Dark red product was yielded after further purified by column chromatography (neutral Al₂O₃ gel) using CHCl₃ as the eluent. Yield: 202 mg, 53% (dark red solid). The product was characterized by ¹H NMR, as is shown in Figure 5.2 and MALDI-TOF, as is shown in Figure 5.3 (Calc. for C₂₅₇H₃₁₆N₈O₆₄Si₃₂: 5438.44. Found: 5461 (M+Na)⁺).
Figure 5.2 $^1$H-NMR spectrum of R-(PDI-BPOSS)$_4$ II

Figure 5.3 MALDI-TOF spectrum of R-(PDI-BPOSS)$_4$ II
5.3 Sample Preparation

R-(PDI-BPOSS)₄ compound was recrystallized for crystal structure studies. This section will be introducing the sample preparation for further experiments, further information can be found in section 3.2.

Samples of R-(PDI-BPOSS)₄ were prepared for crystal structure studies through two methods (Scheme 5.2):

1) In a 20mL vial which was placed on a steady shelf, the compound precipitate by solvent diffuson. R-(PDI-BPOSS)₄ was dissolved in chloroform. Methanol was slowly added on top of the solution. A clear interface was generated between the two phases. The vial was sealed and kept steady for 24 hours during which methanol will diffuse into chloroform solution and sample precipitation took place. The suspension was filtered and the resulting solid was dried for further experiments (Scheme 5.2a). The resulted solid was dried and wrapped in epoxy resin and subjected to microtome. The sample was studied by TEM experiments;

2) In a 20mL vial, the compound is dissolved in chloroform (filtered by Whatman® 0.45μm PTFE membrane syringe filter). Methanol is added into the solution, creating a solution of R-(PDI-BPOSS)₄ in a mixed solvent chloroform: methanol (v/v) = 2:1 (Scheme 5.2b). The vial is sealed
afterwards and placed at a steady stage, as was described in experimental section 3.2.1. The sample was dried for x-ray scattering experiments.

Scheme 5.2 Powder sample preparation via solution growth: precipitation by bad solvent diffusion (a) and solvent evaporation (b)
5.4 Crystal Structure Investigation

Recrystallized R-(PDI-BPOSS)$_4$ samples were studied by TEM BF, scanning electron microscopy (SEM), SAED, SAXS, WAXS and GIWAXS experiments to investigate the ordered phase information and unit cell parameters. Solution grown powder sample was microtomed and observed under TEM BF mode, presenting an ordered phase. This ordered phase can be described by a superlattice constructed by close packed columns. In addition, the unit cell parameters was calculated from the diffraction patterns of tilting SAED and x-ray scattering experiments.

5.4.1 Morphological Investigation

To understand the morphology of the recrystallized samples, TEM BF and SEM experiments were firstly conducted. Microtomed samples were observed under SEM for their morphological information in the first place. Figure 5.4 (c) and (d) are presenting two typical view of crystals found in SEM experiments: top-viewed and side-viewed hexagonal columns with dimensions of 10-20 μm.

Figure 5.4 (a) and (b) presents two typical TEM BF images taken for the microtomed powder sample. Analysis of these images revealed that the superlattice packing of R-(PDI-BPOSS)$_4$ is constructed by closely packed columns. When viewed
from the top (c-axis), the intersection of the lattice can be observed (Figure 5.4 (a)), where hexagonally packed columns can be clearly identified. The diffraction pattern taken from c-axis is presented as the inset of Figure 5.4 (a), confirming a 6-fold symmetry of the lattice. A layered structure can be observed in Figure 5.4 (b), showing a side-view of the superlattice packing of R-(PDI-BPOSS)₄. The layer thickness can be measured to be ~5nm, which will provide a piece of evidence and reference in further crystal structure determination.

5.4.2 Unit Cell Determination from Selected Area Electron Diffraction Data

Figure 5.5 shows typical ED pattern of solution grown R-(PDI-BPOSS)₄ single crystals. The rectangular lattice which is observed in Figure 5.5(a) suggested that the crystal unit cell may either be an orthorhombic or a monoclinic. Diffraction patterns obtained by tilting along c* +/-30° may provide further evidence for deciding the crystal unit cell.
Figure 5.4 TEM BF and SEM images of hexagonally packed R-(PDI-BPOSS)$_4$ columns with 6-fold symmetry: (a) TEM BF image presenting the hexagonal packing of columns (top view of the crystal intercept as is shown in the SEM image (c)), with the inset presenting the diffraction pattern; (b) presenting a layered morphology (side view of crystal as is presented in the SEM image (d)).
Figure 5.5 ED pattern of solution grown single crystal of R-(PDI-BPOSS)$_4$: (a) diffraction pattern of [100] zone, diffraction spots form a lattice with base vectors c* and 010 corresponding to d-spacing of 5.0 nm and 4.9 nm, respectively; (b) diffraction pattern of [110] zone with base vector 120 corresponding to d-spacing 4.20 nm after tilting 30° along c* axis; (c) diffraction pattern of [110] after tilting 30° reversely
As is shown in Figure 5.5(b) and (c), the identical rectangular diffraction patterns suggests the crystal unit cell is more likely to be an orthorhombic one instead of a monoclinic. The shorter and longer base vectors in Figure 5.5(a) are identified as \( c^* \) and 020, with \( d \)-spacing of 5.0nm and 4.9nm, respectively. While in Figure 5.5(b), the \( d \)-spacing of 220 is measured to be 4.2nm, from which \( a^* \) axis \( d \)-spacing can be thus calculated to be 16.4nm. As a brief summary, an orthorhombic unit cell is characterized for the solution grown crystal sample with \( a=16.4\text{nm}, b=9.8\text{nm} \) and \( c=5.0\text{nm} \).

5.4.3 X-ray Diffraction Data for Unit Cell Parameter Refinement

X-ray diffraction experiments were conducted to further characterize and refine single crystal unit cell parameters. Experiment results from Small Angle X-ray scattering (SAXS), Wide Angle X-ray scattering (WAXS) and Grazing Incidence X-ray Small Angle X-ray scattering (GISAXS) were obtained to refine unit cell parameters.

SAXS spectrum of the powder sample is presented in Figure 5.6, showing a strong peak with 42.17Å and 40.80Å \( d \)-spacing, corresponding to 220 and 400 plane.
Figure 5.6 SAXS spectrum of R-(PDI-BPOSS)$_4$, indicating $d$-spacing of 42.17Å and 40.80Å.
Figure 5.7 WAXS Spectrum of R-(PDI-BPOSS)$_4$ from Synchrotron @ Argonne National Lab, with diffraction peaks indexed on the basis of orthorhombic unit cell with $a=163.98\,\text{Å}$, $b=98.11\,\text{Å}$, $c=50.00\,\text{Å}$. 
Figure 5.8 WAXS Spectrum of R-(PDI-BPOSS)$_q$ from Synchrotron @ Argonne National Lab, with diffraction peaks indexed on the basis of orthorhombic unit cell with $a=163.98\text{Å}$, $b=98.11\text{Å}$, $c=50.00\text{Å}$. 
Figure 5.7 is the diffraction spectrum of R-(PDI-BPOSS)₄ with peaks labeled with theta ranging within 0~20°. In order to identify the halo peaks, samples were prepared and performed WAXD experiments with synchrotron beam source. Figure 5.8 is the WAXS Spectrum of R-(PDI-BPOSS)₄ obtained from Synchrotron @ Argonne National Lab. Refinement was performed on the basis of previous discussed ED pattern, and was firstly utilized to fit the primary peaks in the SAXS data. The refined parameters are as follows: a=163.98Å, b=98.11Å, c=50.00Å. The major peaks in WAXS spectrum are labeled as shown in the figure, and the calculated/experimental 2θ and d-spacing are summarized and presented in Table 5.1.
Table 5.1 Summarized Calculated and Experimental data of labeled peaks in R-(PDI-BPOSS)$_4$ WAXS Spectrum. Data calculation were performed with: 1) wavelength of 1.54Å; 2) unit cell parameters of $a=163.98\text{Å}$, $b=98.11\text{Å}$, $c=50.00\text{Å}$.

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5.4.4 Solution UV-Vis Absorption Analysis

UV-Vis Spectrum was taken for R-(PDI-BPOSS)$_4$ in CHCl$_3$/Methanol (v/v = 1:2) mixed solvent with different concentration. As is shown in the UV-Vis spectrum Figure 5.9, the three peaks with wavelengths of 465nm, 498nm and 532nm are attributed to the absorption of PDI units. While with the increase of solution concentration, R-(PDI-BPOSS)$_4$ will tend to aggregate. Furthermore, a slight red shift of these peaks can also be observed. Therefore, it would be reasonable to consider the appearance and strengthen of the multiple peaks located within 330~400nm wavelength range as an outcome of molecular aggregation which give rise to the π-π stacking of benzene rings.$^{108}$
Figure 5.9 UV-Vis Spectra of R-PDI-BPOSS4 in CHCl₃/Methanol (1:2) Solution with different concentration; The appearance and increase in indicated absorbance as well as the slight red shift of peaks within 330~400nm wavelength range suggest the strengthen of π-π stacking with the increase of solution concentration.
5.4.5 Computer Simulation of Unit Cell Molecular Packing

Computer simulation is performed to assist the determination and confirmation of the structure of solution grown R-(PDI-BPOSS)$_4$ single crystal. The R-(PDI-BPOSS)$_4$ has a tetragonal shaped molecular structure with the dimension of ~4.8nm along the edge. The rigid and planar PDI spacer as well as the bulky BPOSS units requires dislocation of one molecule ontop of the other while stacking upwards along c axis of the column. The rotating angle is limited to avoid not reasonable crossing of PDI spacer located in a prior unit with one in a later unit. Furthermore, the $2_1$ symmetry along c-axis of an individual molecule allows an even dividing of $180^\circ$ for a total of 13 units in a single helix, which renders a $13.85^\circ$ rotation. The rotation and translation of molecules during the formation of the helix resulted in a column with the core and PDI units in the center and POSS units ascending along the packing direction (Scheme 5.3). 13 units in one column while 8 columns in one unit cell gives a density of 1.17g/cm$^3$; the density was experimentally measured to be 1.16g/cm$^3$, which is in well agreement with the calculated density.
Scheme 5.3 Illustration of the packing of R-(PDI-BPOSS)$_4$ molecule into a column: (a) side view and (c) top view of the column; (b) rotational and translational factors of the packing scheme.
Figure 5.10 Simulated molecular packing model projected image shown with (1×1×2) scale: (I) ab-plane, (II) bc-plane, (III) ac-plane; and (IV) the 8 columns in one unit cell (shaded area, ab-plane) are categorized into 4 families, columns in each family are: (1) 0°, (2)+90°, (3)+45° and (4)-45° clockwise rotated along c axis.
Figure 5.10 is presenting the simulated molecular packing model by plotting a 3-D projection, where (I) $ab$-plane, (II) $bc$-plane, (III) $ac$-plane can be found. There are 8 columns that can be divided into 4 groups located in one unit cell. The columns are shifted from one another, and thus differentiate themselves. As is shown in Figure 5.10 (IV), Group 1 is set to be 0° phase, while Group 2 is +90° away from 1. Similarly, Group 3 and Group 4 are +45° and -45° rotated.

Simulated ED pattern is generated by Cerius², and is presented Figure 5.11 (b). The simulated pattern generally agrees the experimental pattern in terms of positions of diffractions in the reciprocal lattice, indicating that the model can be expected to possess the key features of the molecules in the unit cell.

As a brief summary, the synthesis and characterization of a tetrahedral giant molecule- $R$-(PDI-BPOSS)₄ is discussed. Single crystal was solution grown and characterized for its crystal structure. An orthorhombic unit cell with cell parameters of $a=163.98\text{Å}$, $b=98.11\text{Å}$, $c=50.00\text{Å}$. 
Figure 5.11 Experimental and Simulated [100] zone ED pattern of R-(PDI-BPOSS)$_4$ single crystal.
In this chapter, the study of S-(PDI-BPOSS)$_4$ sample will be introduced, covering the synthesis and the supramolecular hierarchical architecture model construction. By examine solution precipitated S-(PDI-BPOSS)$_4$ powder sample and drop casted thin film sample by X-ray diffraction experiments, a hexagonal superlattice is found. With structural information provided by UV-Vis spectroscopy which suggested π-π interaction resulted from the packing of PDI and phenyl groups located in the core of the molecule, a column-peripheral BPOSS model was proposed.

6.1 Molecular Design and Molecule Synthesis

This section will be discussing the molecular design and synthesis of this giant shape amphiphile based on a BPOSS MNP and PDI unit. As is shown in Figure 6.1, this shape amphiphile contains a tetrapod core and four substituting groups are located along the vertices axis of the tetrapod. Each
substituting group is consist of a PDI unit and a BPOSS unit which are covalently linked together by a soft 3C linker.

Compound S-(PDI-BPOSS)$_4$ was synthesized by the synthetic routed (Scheme 6.1) described as follows:

3: To a 100 mL Schlenk flask, perylene-3, 4-anhydride-9,10-di-(decyloxy carbonyl) (2, 2.0 g, 2.89 mmol, 1 equiv.), aminopropylisobutylPOSS (3.29 g, 3.76 mmol, 1.3 equiv.) and 20 g imidazole were added. The mixture was purged with N$_2$ flow for 15 min. Then 4 mL 1, 2-dichlorobenzene (ODCB) was added to the flask and heated to 125 °C with vigorous stir for 5 hours. The red mixture was cooled to 90 °C and 60 ml methanol was added. The crude product was separated by filtration and further purified by column chromatography (silica gel) using 20/1 (v/v) CHCl$_3$/Acetone as the eluent (Scheme 4.2). Yield: 4.1 g, 90% (dark red solid). $^1$H NMR (300 MHz, CDCl$_3$, ppm, $\delta$): 8.35 (d, 2H, PDI-Ar), 8.10 (t, 4H, PDI-Ar), 7.95 (d, 2H, PDI-Ar), 4.37(t, 4H, CO$_2$C$_2$H$_2$CH$_2$), 4.21 (t, 2H, SiCH$_2$CH$_2$CH$_2$-N), 2.00-1.75 (m, 13H, SiCH$_2$CH$_2$H + SiCH$_2$CH$_2$N + CO$_2$CH$_2$CH$_2$), 1.52 - 1.25 (m, 28H, CO$_2$CH$_2$CH$_2$(CH$_2$)$_\gamma$CH$_3$), 0.96 (d, 42H, SiCH$_2$CHC$_2$H$_5$), 0.88 (t, 6H, -CH$_3$), 0.75 (t, 2H, SiCH$_2$CH$_2$CH$_2$-N), 0.65-0.55 (m, 14H, SiCH$_2$CHC$_2$H$_5$). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm, $\delta$): 168.16, 163.16, 134.90, 131.79, 130.95, 130.12, 129.03, 128.80, 128.75, 125.57, 122.27, 122.00, 121.48, 65.85, 31.90, 29.57,
4: A 50 mL round bottom flask was charged with 3 (1.0 g, 0.646 mmol), 30 mL toluene and PTSA (0.27 g, 1.40 mmol). Then the flask was capped and heated to 100 °C under vigorous stir for 5 hours. Volatiles were removed on a rotary evaporator, and the solid residue was washed by methanol twice and acetone twice. The solid product after filtration was further purified by column chromatography (silica gel) using 20/1 (v/v) CHCl₃/Acetone as the eluent (Scheme 4.2). Yield: 0.82 g, 82% (orange solid). ¹H NMR (300 MHz, CDCl₃, ppm, δ): 8.71-8.62 (m, 8H, PDI-Ar-H), 4.21 (t, 2H, SiCH₂CH₂CH₂-N), 2.00-1.75 (m, 9H, SiCH₂CH₂CH₆ + SiCH₂CH₂N), 0.96 (d, 42H, SiCH₂CHCH₆), 0.77 (t, 2H, SiCH₂CH₂CH₂-N), 0.75-0.60 (m, 14H, SiCH₂CHCH₆). ¹³C NMR (75 MHz, CDCl₃, ppm, δ): 162.99, 159.90, 136.35, 133.78, 133.52, 131.84, 131.40, 129.34, 126.79, 126.33, 124.15, 123.86, 123.18, 119.11, 42.98, 25.66, 23.83, 22.50, 22.42, 21.58, 9.78.
Figure 6.1 Illustration of molecular structure of S-(PDI-BPOSS)$_4$ III.

Scheme 6.1 Synthetic route of S-(PDI-BPOSS)$_4$ III.
II: To a 50 mL Schlenk flask, tetrakis(4-aminophenyl)methane (26.6 mg, 0.070 mmol, 1 equiv.), 4 (394 mg, 0.315 mmol, 4.5 equiv.), DMAP (37.8 mg, 0.315 mmol, 4.5 equiv.), and 4.0 g imidazole were added. The mixture was purged with N₂ flow for 15 min. Afterwards 3 mL ODCB was added and the flask was inserted to oil bath kept at 125 °C for 5 h. The red mixture was cooled to 90 °C and 30 ml methanol was added. The solid was collected by filtration, washed by methanol twice and acetone twice. Dark red product was yielded after further purified by column chromatography (neutral Al₂O₃ gel) using CHCl₃ as the eluent. Yield: 186 mg, 50% (dark red solid). The product was characterized by ¹H NMR (Figure 6.2), and MALDI-TOF, as is shown in Figure 6.3(Calc. for C₂₄₅H₃₂₄N₈O₆₄Si₃₂: 5304.0. Found: 5308).
Figure 6.2 $^1$H-NMR spectrum of S-(PDI-BPOSS)$_4$.

Figure 6.3 MALDI-TOF spectrum of S-(PDI-BPOSS)$_4$. III
6.2 Sample Preparation

S-(PDI-BPOSS)$_4$ compound was precipitated for supramolecular structure studies. This section will be introducing the sample preparation for further experiments, further information can be found in section 3.2.

Powder samples of S-(PDI-BPOSS)$_4$ were prepared through the following method (Scheme 5.2a):

In a 20mL vial, the compound is dissolved in chloroform (filtered by Whatman® 0.45μm PTFE membrane syringe filter). Methanol is added into the solution, creating a solution of S-(PDI-BPOSS)$_4$ in a mixed solvent chloroform: methanol (v/v) = 2:1 (Scheme 5.2b). The vial is sealed afterwards and placed at a steady stage, as was described in experimental section 3.2.1. The sample was dried in vacuum for x-ray scattering experiments. The solution of S-(PDI-BPOSS)$_4$ in a mixed solvent chloroform: methanol (v/v) = 2:1 was also drop casted on to silicon wafer to prepare thin film sample for GIWAXS experiments.

6.3 Supramolecular Structure Investigation

In the bulk, the carefully designed and precisely synthesized giant tetrahedra tend to undergo self-assembly into hierarchical architectures. It is of great research
interest to understand the self-assembly of these giant molecules to provide detailed information which will benefit the realization of materials with dictated physical properties by pre-determining their microscopic architectures. Herein, precipitated tetrahedra S-(PDI-BPOSS)₄ powder samples were studied by TEM-BF, SEM, SAXS, WAXS; and thin film samples prepared via drop casting were analyzed by GIWAXS experiments to investigate the ordered phase information.

6.3.1 Morphological investigation

To understand the morphology of the precipitated samples, microtomed samples were observed under SEM in the first place. Figure 6.4 is presenting images taken from PLM and SEM experiments, showing a fabric appearance with millimeter scale in size.
6.3.2 X-ray diffraction of powder sample

SAXS and WAXS diffraction patterns were obtained for S-(PDI-BPOSS)$_4$ powder sample. However, few information were obtained to determine superlattice structures for the sample. As is shown in Figure 6.5, both the SAXS spectrum and the WAXS spectrum are showing a major peak of ~3.60nm. Different from the previously discussed crystalline R-(PDI-BPOSS)$_4$ sample, the halo shown in WAXS spectra of S-(PDI-BPOSS)$_4$ indicates an amorphous state instead.

Further information were gathered by carefully preparing samples for GIWAXS with synchrotron at Argonne National Lab.
The thin films prepared by drop casting solution on silicon wafer present two typical images as is shown in Figure 6.6 (a) and (b). In Figure 6.6 (b), the d-spacing of the three labeled patterns were calculated from q value to be 36.32Å, 20.87Å and 18.16Å along y axis. The ratio between these three q values, which is $1:\sqrt{3}:2$, suggested a hexagonal superlattice structure, and further indicated that this pattern is taken for a side view of the closed packed columns. Together with (a), which is taken from another direction i.e., c axis of the column, the superlattice structure of the sample is strongly suggested to be a hexagonal superlattice. Cross-sectional TEM BF image is also taken for microtomed sample. As is shown in (c) and (d), hexagonal packed columns can be identified for the former one, while layered side-view pattern is clearly shown in the latter image. A third diffraction image can also be obtained with GIWAXS experiments, as is shown in (d). Identical d-spacing and relative positional information can be retrieved from (d) when compared to (c). This can be explained by different packing scheme of the columns on top of the silicon wafer: When packing along the direction towards closest column or that towards second closest column, the 100 (g) and 110 (h) plane will be parallel to the substrate surface for either case.
Figure 6.5 SAXS (left) and WAXS (Right) spectrum of solution precipitated samples of S-(PDI-BPOSS)$_4$, implying an amorphous phase.

Figure 6.6 GIWAXS data of S-(PDI-BPOSS)$_4$ indicating a hexagonal superlattice: pattern taken for beam direction along (a) and perpendicular (b) to c-axis, corresponding TEM-BF image of microtomed S-(PDI-BPOSS)$_4$ powder sample is presented in (e), hexagonally packed columns and (f) layered structure; (c) is the enlarged image for central part of (a), while (d) is a third typical diffraction pattern, differentiated itself from (a) by different column packing scheme on top of silicon wafer; the corresponding packing scheme is shown in (g) and (h), respectively.
6.3.3 Solution UV-Vis Absorption Analysis

UV-Vis Spectrum was taken for S-(PDI-BPOSS)$_4$ in CHCl$_3$/Methanol (v/v = 1:2) mixed solvent with different concentration. The spectrum shown in Figure 6.7 presents three peaks with wavelengths of 465nm, 495nm and 530nm are attributed to the absorption of PDI units. While with the increase of solution concentration, the low solubility of S-(PDI-BPOSS)$_4$ in the mixed solvent will render the solute to aggregate, and resulted in an appearance of multiple peaks within 330~400nm range. These peaks, with wavelength corresponds to those of absorption of typical π-π stacking of aromatic rings. Therefore, it would be reasonable to consider the appearance and strengthen of the multiple peaks located within 330~400nm range as an outcome of molecular aggregation which give rise to the π-π stacking of benzene ring and further suggests a columnar packing of the core of S-(PDI-BPOSS)$_4$ with BPOSS surrounding the column peripherally (Scheme 6.2).
Figure 6.7 UV-Vis Spectra of S-PDI-BPOSS4 in CHCl3/Methanol (1:2) Solution with different concentration; The appearance and increase in indicated absorbance as well as the slight red shift of peaks within 330-400nm wavelength range suggest the strengthen of π-π stacking with the increase of solution concentration.

Scheme 6.2 Illustration of hexagonal packing of S-(PDI-BPOSS)4 columns where the tetrahedral core are packed into columns with BPFOSS units surrounding the columns. Color code: BPOSS in blue and C-(Phenyl-PDI)4 core in red.
The pursuit of precisely control supramolecular structures by guided self-assembly via collective secondary interactions of giant molecules with designated side groups points initiated a series of studies towards the synthesis and study of giant molecules covering various families including giant surfactant, giant shape amphiphile and giant polyhedra. Following Nod-Spacer-Vertex strategy, three different giant molecules were designed and synthesized with same “nano atoms” of PDI and BPOSS. Investigations towards the structural properties of the assemblies of the samples provided crystal structural information of two molecules (triclinic and orthorhombic, for \( m \)-phenyl-(PDI-BPOSS)\(_2 \) and R-(PDI-BPOSS)\(_4 \), respectively) and hexagonal superlattice for S-(PDI-BPOSS)\(_4 \). The notion of the increase in softness of linker between PDI and BPOSS units in the two giant tetrahedra with a rigid Node resulted in a change from a crystalline material to an amorphous one (while on the other hand, a rigid 2-valence Node with a same soft linker leads to crystalline
material) give rise to the complexity and importance of the consideration of linkers as designing giant molecules.
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