DESIGN, SYNTHESIS, AND SELF-ASSEMBLY OF WELL-DEFINED HYBRID
MATERIALS INCLUDING POLYMER AMPHIPHILES AND GIANT
TETRAHEDRA MOLECULES BASED ON POSS NANOPARTICLES

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Mingjun Huang

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Mingjun Huang

Dissertation

Approved: ___________________________                Accepted: ___________________________

Advisor
Dr. Stephen Z.D. Cheng

Department Chair
Dr. Coleen Pugh

Committee Member
Dr. Toshikazu Miyoshi

Dean of the College
Dr. Eric J. Amis

Committee Member
Dr. Mesfin Tsige

Dean of the Graduate School
Dr. Chand K. Midha

Committee Member
Dr. Yu Zhu

Date

Committee Member
Dr. Chrys Wesdemiotis
“Bottom-up” techniques-based self-assembly are always attracting people’s interests since this technology provides relatively low economic cost and fast route to construct organized structures at different scales. Considering unprecedented benefits from polymer materials, self-assemblies utilizing polymer building blocks have been extensively studied to achieve diverse hierarchical structures and various attractive properties. However, precise controls of chemical primary structures and compositions and exact constructions of hierarchal ordered structures in synthetic polymers are far from being fully appreciated. In this dissertation, a novel approach has been utilized to construct diverse well-defined nano-building blocks, giant molecules, via conjugating different, and functionalized molecular nanoparticles (MNPs) which are shape- and volume-persistent nano-objects with precise molecular structure and specific symmetry. The representative examples of the three basic categories of giant molecules, “giant polyhedra”, “giant surfactants”, and “giant shape amphiphiles” were discussed in details. First, a class of precisely defined, nanosized giant tetrahedra was constructed by placing different polyhedral oligomeric silsesquioxane (POSS) molecular nanoparticles at the vertices of a rigid tetrahedral framework. Designed symmetry breaking of these giant tetrahedra introduces accurate positional interactions and results in diverse selectively assembled, highly ordered supramolecular lattices including a Frank-Kasper (FK) A15 phase. The FK and quasicrystal phases are originally identified in metal alloys and only
sporadically observed in soft matters. It remains unclear how to correlate their stability with the chemical composition and molecular topology in the self-assembling systems. We then for this purpose designed and studied the self-assembly phase transition sequences of four series of hybrid giant surfactants based on hydrophilic POSS cages tethered with one to four polystyrene (PS) tails. With increasing the number of tails, molecular topological variations not only affect phase boundaries in terms of the PS volume fraction, but also open a window to stabilize supramolecular FK and quasicrystal phases in the spherical phase region, demonstrating the critical role of molecular topology in dictating the formation of unconventional supramolecular lattices of “soft” spherical motifs. The FK A15 phase was even surprisingly observed in the giant shape amphiphile molecule, triphenylene-6BPOSS, which has a disk-like flat triphenylene core connected with six hydrophobic POSS cages by sides. Without conical molecular shape, triphenylene-6BPOSS self-assembled and stabilized into supramolecular sphere via π-π interactions through a completely different mechanism with precious two cases. These studies indicate that “bottom-up” self-assemble based on well-defined giant molecules approach can be rather powerful to fabricate usually complicated hierarchical structures and open up a wide field of supramolecular self-assembly with unexpected structure and properties.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>xi</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>xii</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I.  INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. BACKGROUND</td>
<td>7</td>
</tr>
<tr>
<td>2.1 Bottom-Up based Self-assembly</td>
<td>7</td>
</tr>
<tr>
<td>2.2 Molecular Nanoparticles and Giant Molecules as Building Blocks in Self-</td>
<td>13</td>
</tr>
<tr>
<td>Assembly</td>
<td></td>
</tr>
<tr>
<td>2.2.1 Self-Assembly of Biomacromolecules</td>
<td>13</td>
</tr>
<tr>
<td>2.2.2 Molecular Nanoparticles (MNPs)</td>
<td>17</td>
</tr>
<tr>
<td>2.2.3 Three Categories of Giant Molecules</td>
<td>21</td>
</tr>
<tr>
<td>2.2.4 POSS Nanoatom and “Click” Chemistry</td>
<td>25</td>
</tr>
<tr>
<td>2.3 Recent Developments for the Self-assemble Studies of Giant Molecules</td>
<td>27</td>
</tr>
<tr>
<td>2.4 Frank-Kasper Phases and Quasicrystal Phases in Soft Matters</td>
<td>37</td>
</tr>
<tr>
<td>2.4.1 Topological Close Packing (TCP)</td>
<td>38</td>
</tr>
<tr>
<td>2.4.2 Frank-Kasper Phases</td>
<td>47</td>
</tr>
<tr>
<td>2.4.2.1 A15 Phase</td>
<td>48</td>
</tr>
<tr>
<td>2.4.2.2 Sigma (σ) Phase</td>
<td>50</td>
</tr>
<tr>
<td>2.4.2.3 The Laves Phases</td>
<td>52</td>
</tr>
</tbody>
</table>
2.4.3 Dodecagonal Quasicrystal Phase (DQC) .......................................................... 56
2.4.4 Various Systems Exhibiting FK phases and DQC Phase .............................. 67
   2.4.4.1 Dendrimers ......................................................................................... 67
   2.4.4.2 Anionic Surfactants Templated Mesoporous Silicas (AMSs) .............. 76
   2.4.4.3 ABC Type Star Copolymers ................................................................. 83
   2.4.4.4 Linear Block Copolymers ................................................................. 88
   2.4.4.5 Nanoparticles and Colloidal Particles ............................................ 91
2.4.4.6 Aperiodic 2D Quasicrystals with Five-Fold Symmetry ....................... 96
2.4.5 Discussion and Simulation about FK and DQC Phases .............................. 99

III. EXPERIMENTAL .......................................................................................... 115
   3.1 Chemical Characterization ........................................................................ 115
      3.1.1 Chemicals and Solvents ........................................................................ 115
      3.1.2 Chemical Characterization ................................................................ 116
   3.2 Phase Identification and Morphology Confirmation in Bulk .................... 117
   3.3 Molecular Packing Simulation ................................................................... 120
   3.4 Synthesis of Three Categories of Giant Molecules .............................. 121
      3.4.1 Giant Tetrahedra .............................................................................. 121
      3.4.2 Giant Surfactants ............................................................................. 140
      3.4.3 Giant Shape Amphiphile ................................................................... 150

IV. SELECTIVE-ASSEMBLIES OF GIANT TETRAHEDRA VIA PRECISELY
    CONTROLLED POSITIONAL INTERACTIONS ............................................. 153
   4.1 Sample Preparation .................................................................................. 155
   4.2 Self-assembly Behavior of Giant Tetrahedron 1 ...................................... 158
   4.3 Self-assembly Behavior of Giant Tetrahedron 2a-2d ............................... 161
4.4 Self-assembly Behavior of Giant Tetrahedron 3a-3c ........................................168
4.5 Self-assembly behavior of giant tetrahedron 4a-4c .................................171
4.6 Summary ..................................................................................................173

V. TOPOLOGY-INDUCED EVOLUTION TOWARDS “SOFT” FRANK-KASPER AND QUASICRYSTALLINE PHASES IN GIANT SURFACTANT ...............175
5.1 Design and Synthesis of Giant Surfactants with Multi-tails ......................178
5.2 Self-assembly of DPOSS-PS_m and DPOSS-4PS_m ..................................181
5.3 Self-assembly of DPOSS-3PS_m and DPOSS-2PS_m ...............................189
5.4 Discussion of the Phase Diagram ..............................................................194

VI. GIANT SHAPE AMPHIPHILE ....................................................................200

VII. SUMMARY AND OUTLOOK ....................................................................207

REFERENCES ................................................................................................213
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Summary of various secondary interactions</td>
</tr>
<tr>
<td>2.2</td>
<td>Summary of the geometrical features in four Kasper polyhedra</td>
</tr>
<tr>
<td>4.1</td>
<td>Crystallographic parameters of the supramolecular lattice of 1</td>
</tr>
<tr>
<td>4.2</td>
<td>Superlattice analysis of all of the molecular giant tetrahedra with different symmetries</td>
</tr>
<tr>
<td>5.1</td>
<td>Summary of the characterization data of DPOSS-NPS$_m$</td>
</tr>
<tr>
<td>5.2</td>
<td>Index of the $\sigma$ phase found in DPOSS-4PS$_{13}$</td>
</tr>
<tr>
<td>5.3</td>
<td>Index of the $\sigma$ phase found in DPOSS-3PS$_{15}$</td>
</tr>
<tr>
<td>5.4</td>
<td>Summary of molecular characterizations of the DPOSS-NPS$_m$ samples</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>Representative examples of anisotropic building blocks reported recently. From the left to right shows the increase in the size of building blocks, while the different categories of anisotropic building blocks are shown in the rows. Reprinted with permission from Ref 5. Copyright 2007 Nature Publishing Group.</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>The top town and bottom up approach of creating structure with order</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Hierarchical structures of proteins and their self-assembly in nature. (a) The 3D structures at primary, secondary, tertiary and quaternary levels. (b) Scheme of tubular TMV shell helically assembled from coat proteins. Side view and end-on view of TMV are both illustrated. The basic amino acids residues (Arg90, Arg92 and Arg41 in yellow, and Asp116 in pink) shown are related to the coat protein–genomic-RNA interaction. Reproduced with permission from Ref 13. Copyright 2012 Royal Society of Chemistry. (c) Scheme of protein cages with icosahedron shape. Reproduced with permission from Ref 14. Copyright 2008 Nature Publishing Group.</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Scheme of tetrahedral protein cage design. The top models illustrate the design principle of a fusion protein bridging a dimer and trimer protein complex and a tetrahedral cage formed by self-assembly of twelve fusion proteins. The bottom shows the specific structures of natural protein oligomers and designed fusion protein with its actual crystal structure (middle). The tetrahedral geometry of the designed assembly with 5 nm porous center (illustrated by black sphere) was confirmed by the crystal structure of the cage. Reprinted with permission from Ref 15. Copyright 2012 American Association for the Advancement of Science.</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>(a) Representative MNPs are shown including [60]fullerenes, T₈-POSS, POMs, metal-ligand coordination cage and a folded globular protein. (b) The functionalization strategies for MNPs. Reproduced with permission from Ref 21. Copyright 2014 ACS.</td>
<td></td>
</tr>
<tr>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Comparison of traditional bottom up self-assembly approach (top) and MNPs based approach (bottom). Reproduced with permission from Ref 21. Copyright 2014 ACS.</td>
<td></td>
</tr>
</tbody>
</table>
2.7 Three categories of giant molecules include (A) giant surfactants, (B) giant shape amphiphiles, (C) giant polyhedra. Reproduced with permission from Ref 21. Copyright 2014 ACS .................................................................22

2.8 (a) The Scheme of T₈-POSS structure. (b) Two click reactions used for functionalization of POSS .................................................................27

2.9 Equilibrium structures formed by tethered nanoplate, nanotriangle and nanowheel building blocks. (a) Hexagonally packed columnar phase formed by tethered nanodisks and its face view in (b). (c) Hexagonally packed columnar phase formed by tethered nanotriangular nanoplates and its face view in (d). (e) Lamellar phase formed by tethered nanowheels and its face view in (f). Reproduced with permission from Ref 40. Copyright 2003 ACS .................................................................29

2.10 Phase diagram for the self-assembly in DMF/Dioxane/water solution. The bottom TEM images show the morphologies of PS₇₀−AC₆₀ with different initial molecular concentrations including (a) 0.1% wt for spheres, (b) 0.5% wt for cylinders; (c) 1.0% for mixtures of cylinders and vesicles, (d) 2.0% for vesicles. Reproduced with permission from Ref 43. Copyright 2012 ACS .................................................................31

2.11 The small angle X-ray scattering pattern (a) and bright field TEM images (b) of ordered phases (from left to right: Lam, DG, Hex, and BCC) from DPOSS-PS. The phase diagram is listed in the bottom of (b). Reproduced with permission from Ref 44. Copyright 2013 PNAS .................................................................32

2.12 (a) Chemical structure of PEO-C₆₀ and PEO-POSS; (b) schematic illustration of integral folding and half-stemmed crystals; (c) relationships between lamellar thickness, $L$, and crystallization temperature ($T_c$); and (d) relationships between melting temperature, $T_m$, and crystallization temperature ($T_c$). The insets are corresponding SAXS pattern (c) and ultrafast heating chip DSC thermograms (d). Reproduced with permission from Ref 45. Copyright 2013 ACS .................................................................34

2.13 (a) Self-assembled structure of BPOSS-C60 packing in orthorhombic crystal, with the corresponding TEM morphology in (b) and SAED pattern along [001] in (c). (d) Molecular packing in hexagonal crystal with the corresponding morphology in (e) and SAED pattern in (f) along [0001]. Reproduced with permission from Ref 50. Copyright 2011 Royal Society of Chemistry .................................................................35

2.14 (a) Chemical structure of a shape amphiphile, porphyrin-C₆₀. (b) Wide-angle X-ray diffraction pattern and electron diffraction pattern (inset) of porphyrin-C₆₀ to determine its 129₄₄ helical structure. (C) Simulated molecular packing of the 129₄₄ helix of the column and their packing into
a hexagonal columnar phase. Reproduced with permission from Ref 51. Copyright 2012 John Wiley and Sons .................................................................36

2.15 (a) The coordination environments of the central atom in polyhedra shapes of cuboctahedron in FCC, twinned cuboctahedron in HCP, and icosahedron in TCP. (b) Scheme of octahedral interstices in FCC and HCP ..........40

2.16 The four coordination polyhedra with coordination number of 12, 14, 15 and 16. The yellow and dark red spheres represent minor sites and major sites, respectively ........................................................................................................41

2.17 The different surface coordination of each atom (yellow spheres) and their accommodation with an equal sized core atom (dark red sphere) shown in the top. The bottom 2D scheme indicates the distorted angle values from equilateral triangles .........................................................................................................................43

2.18 (a) Construction of layered structure starting from ABC triangle in which all of three ligands are minor and its top view in the right. (b) Construction of layered structure starting from ABC triangle in which AB ligand is major and its top view in the right........................................................................................................46

2.19 The most representative tessellation Kagome net composed of hexagons and triangles ..........................................................................................................................47

2.20 Schematic illustration of the A15 phase. (a) In an A15 cubic unit cell, the dark red and pale red colors represent different coordination environments. (b) Schemes of CN = 12 and CN = 14 coordination environments in the A15 lattice. (c) The major skeleton connecting six A units is along three <100> row directions. Reproduced with permission from Ref 28 and 58. Copyright 2015 the American Association for the Advancement of Science and 2005 Royal Society of Chemistry ........................................................................................................49

2.21 The A15 phase structure can be dissembled into simpler layer tiling pattern. The primary layer pattern at z = 0.00 and z = 0.50 have the same feature but rotated for 90°. The secondary layer pattern at z = 0.25 and z = 0.75 have the same 4\(^4\) tiling ........................................................................................................50

2.22 The unit cell of \(\sigma\), and five sub-lattices A, B, C, D and E with their nearest-neighbour shell atoms. Reproduced with permission from Ref 64. Copyright 2011 Taylor & Francis ........................................................................................................51

2.23 The \(\sigma\) phase structure can be dissembled into simpler layer tiling pattern. The primary layer pattern at z = 0.00 and z = 0.50 have the same feature but rotated for 90°. The secondary layer pattern at z = 0.25 and z = 0.75 have the same 3\(^2\)·4·3·4 tiling ........................................................................................................52
2.24 (a) Crystal structure of unit cell of C15, C14 and C36 Laves phases. (b) Laves phase structures showing connectivity of A atom major skeletons and tetrahedral double layers. (c) Six-layer stacking of (111) planes in the Cu2Mg Laves phase structure. (d) Four-layer stacking of (00.1) planes of the MgZn2 structure. Reproduced with permission from Ref 60. Copyright 2012 Cambridge University Press.

2.25 (a) Two dimensional P3 tiling exhibiting 5-fold symmetry. (b) An equivalent Penrose tiling constructed in 3D by rhombohedra. Reproduced with permission from Ref 58. Copyright 2005 Royal Society of Chemistry. (c) A binary magnetic quasicrystal based on rare earths and cadmium, presenting icosahedron crystal morphology and corresponding five-fold sharp diffraction patterns in (d). Reproduced with permission from Ref 69. Copyright 2013 Nature Publishing Group.

2.26 2-D tilings (top), projection of the unit vectors of the polygonal reciprocal lattices in a 4-D space (middle) and simulated diffraction patterns (bottom), all along the highest symmetry zone axis for (a) octagonal, (b) decagonal, and (c) dodecagonal quasicrystals. Reproduced with permission from Ref 60. Copyright 2012 Cambridge University Press.

2.27 (a) Deterministic dodecagonal quasilattice generated by the projection method. Reproduced with permission from Ref 70. Copyright 2011 John Wiley and Sons. (b) DQC with random tiling of triangles and squares. (c) Scheme of phason flips in random tiling DQC. The top shows the creation and final annihilation of a pair of thin rhombi, both of which involve the energy state change. The bottom is the phason flip movements with energy state remaining unchanged. Reproduced with permission from Ref 72. Copyright 1993 American Physical Society.

2.28 Local configurations with atomic decoration for different FK phases. (a) Zr4Al3-36. (b) σ-32·4·3·4 (c) H-3·4·3 (d) A15-44. (e) Three basic unique decoration units with coordination number of each site included in two regular triangular prism and one cube. Reproduced with permission from Ref 70. Copyright 2011 John Wiley and Sons.

2.29 (a) Chemical structures of tapered 1 and 2, conical 3 and 4 dendrons. (b) Scheme of self-assembly process. The low generation flat tapered dendrons self-assemble into a supramolecular hexagonal cylindrical liquid crystal phase, while the high generation conical dendrons result a spherical Pm̅3n A15 phase. (c) Bright field TEM image of A15 phase. Reproduced with permission from Ref 76. Copyright 1997 American Association for the Advancement of Science.

2.30 (a) Chemical structure of a conical Dendron with the apex attached with a dipeptide. (b) TEM image (bottom) and Fourier analysis of the A15 phase.
structure (upper left for FFT and upper right for the reconstructed image after Fourier filtering). (c) Schematic of dendrons self-assembly and polyhedron space-filling view of the unit cell. (d) Simplified models of CN12 and CN14 distorted spherical assemblies. Reproduced with permission from Ref 82. Copyright 2008 American Chemical Society ................................71

2.31 (a) Chemical structure of two dendrimers exhibiting $\sigma$ phase. (b) SAXS profile of dendrimer II indexed with a tetragonal unit cell of $a = 16.74$ nm and $c = 8.80$ nm. (c) Scheme of $\sigma$ tetragonal unit cell with five different atom sites. (d) The projection of electron density map viewed from the top exhibiting the characteristic tiling pattern of $\sigma$ phase. Reproduced with permission from Ref 83. Copyright 2003 American Association for the Advancement of Science ........................................................................................................74

2.32 (a) Chemical structure of the dendrimer resulting DQC structure. (b) Three basic decorated tiles, one square and two triangular, are used to generate the model of the DQC. (c) Single-domain diffraction pattern along the 12-fold axis (on the left) and diffraction pattern shoot perpendicular to the 12-fold axis. Reproduced with permission from Ref 84. Copyright 2004 Nature Publishing Group........................................................................................................76

2.33 The synthetic strategy for the AMS materials using anionic surfactants and 3-aminopropyltrimethoxysilane (APS, left row) and N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (TMAPS, right row) as the CSDA. Reproduced with permission from Ref 86. Copyright 2012 Royal Society of Chemistry. (b) The formation mechanism of the anionic surfactants templated nanoporous silicas. Reproduced with permission from Ref 88. Copyright 2012 Nature Publishing Group........................................................................................................78

2.34 (a) Phase diagram of the C$_{14}$GluA–NaOH–TMAPS system by varying the composition ratios. (b) Scheme of C15 Laves phase unit cell ($Fd\overline{3}m$). (c) and (d) are the [111] and [110] bright field TEM images of obtained $Fd\overline{3}m$ AMS structure. (e) [001] axis of the $Pm\overline{3}n$ structure. (f) [001] axis of the $P4_2/mnm$ structure. (g) [110]axis of $Fm\overline{3}m$ structure. Reproduced with permission from Ref 86. Copyright 2012 Royal Society of Chemistry..............81

2.35 (a) Mesoporous particles with dodecagonal prism morphology under SEM. (b) TEM image taken from the central part of the sample (as indicated in the top left inset) with the tiling edges superimposed on the image. The upper right inset is the FFT of this image, exhibiting 12-fold symmetry. (c) Comparison of electron diffraction taken from the circled center part of this sample and simulated diffraction pattern from deterministic DQC tiling. Both show 12-fold symmetry and match very well. Reproduced with permission from Ref 94. Copyright 2012 Nature Publishing Group........................................................................................................83
2.36 (a) Eleven possible Archimedean tilings. The Archimedean tiling is the tessellation of regular polygons provided that all vertices are of the same type. (b) Schematic alignment of ABC star-shaped block terpolymer molecules, in which the junction points are all aligned along a perpendicular line due to the strong geometrical restriction. Reproduced with permission from Ref 99. Copyright 2005 John Wiley and Sons.................84

2.37 In the series of I_{1.0}S_{Y}P_{2.0} star-based blend samples, the tiling patterns of the samples with Y of 1.3 (a), 1.6 (b), 2.3 (c), and 2.7 (d) are analyzed by TEM images (top) and reconstructed schemes. Reproduced with permission from Ref 97. Copyright 2006 American Chemical Society. (e) (3^{2}.4.3.4) tiling manner superimposed on the I_{1.0}S_{2.3}P_{2.0} (figure 2.38c) tiling pattern and SAXS pattern of this sample exhibiting tetragonal lattice. (f) TEM image of the sample of I_{1.0}S_{2.7}P_{2.5}. The imaginary random square-triangle tiling is superimposed on this TEM image. FFT in the bottom right inset shows 12-fold symmetry. The right scheme in figure 2.38f shows the transcribed tiling obtained by transcribing the tile tessellation style using regular triangles and squares. The characteristic 3^{2}.4.3.4, 3^{3}.4^{-2} and 3^{6} can all be identified. Reproduced with permission from Ref 96. Copyright 2007 American Physical Society..............................86

2.38 (a) Chemical structures of SISO-3 tetrablock copolymers and IL-5 diblock copolymers exhibiting σ phase structure. As showed in the middle scheme, contact between I and O blocks is unfavorable, resulting the avoided I/O interface in the supramolecular sphere. (b) SAXS pattern of SISO-3 sample after annealing at 140 °C, which can be identified as a tetragonal unit cell (a = 777 Å and c = 411 Å) with P4_2/mnm space group. Reproduced with permission from Ref 106. Copyright 2010 American Association for the Advancement of Science. (c) Representative synchrotron SAXS data obtained from SISO-2. A phase transition from simple HEX to DQC phase and to σ-phase was identified. The TEM images of microtomed thin section of σ-phase and DQC phase are shown in the bottom left and right. Reproduced with permission from Ref 108. Copyright 2012 American Chemical Society .................................................................90

2.39 (a-e) TEM micrographs of superlattices isostructural with MgZn_{2} formed by 6.2 nm PbSe and 3.0 nm Pd Nanoparticles: (a) TEM overview of the (001) plane and its ED pattern in the bottom right inset. (b) but at high magnification of TEM image in (a); (c) scheme of the MgZn_{2} unit cell (P63/mmc). (d) The nanoparticle packing along the projection of (001) plane. (e) Projection along the (001) planes. Reproduced with permission from Ref 110. Copyright 2006 American Chemical Society. (f) 5.8 nm PbSe and 3.0 nm Pd nanoparticles made the C36 (MgNi_{2}) Laves phase. The bottom right inset shows the scheme of this unit cell. Reproduced with permission from Ref 111. Copyright 2006 Nature Publishing Group ..........92
DQC self-assembled from BNSL. (a) TEM image of a quasicrystalline superlattice self-assembled from 13.4-nm Fe$_2$O$_3$ and 5-nm Au nanocrystals, with the inset of SAED showing 12-fold diffraction pattern. (b) Magnified view of a local image from (a). (c) DQC superlattice self-assembled from 9-nm PbS and 3-nm Pd nanocrystals with the FFT in the bottom right inset. Reproduced with permission from Ref 109. Copyright 2009 Nature Publishing Group.

Synchrotron SAXS patterns of FCC phase (a) and the quasicrystalline phases Q12 (b) and Q18 (c). The SANS patterns have also been recorded for Q12 phase, parallel (d) and normal (d) to the 12-fold rotation axis. Reproduced with permission from Ref 113. Copyright 2011 PNAS.

(a) Chemical structure of FcCOOH. (b) Minimum-energy structure of (FcCOOH)$_5$ pentamers calculated by DFT. (c) High resolution STM images of FcCOOH monolayer and the model structure superimposed on this image, with the central pentamer surrounded by five FcCOOH dimers; (d-f) the comparison of a quasicrystal FcCOOH monolayer structure to a P1 Penrose tiling. (d) The FFT pattern of FcCOOH monolayer STM image in (e), exhibiting long-range five-fold and ten-fold symmetry. (e) The image is overlaid with pentagons to show the long range, quasicrystalline order. (f) Scheme of Penrose P1 tiling with groups of pentagons highlighted in white to match the star, boat and rhombus of the P1 tiling in experimental in (e). Reproduced with permission from Ref 114. Copyright 2014 Nature Publishing Group.

(a) ED patterns of the 10-fold template surface of the Al-Ni-Co decagonal phase and (b) of the C60 film deposited on that surface. (c) STM image of the C60 monolayer formed on the 10-fold template surface and its corresponding FFT pattern in (d). The most frequent local configurations are highlighted in yellow. (e) Part of the P1 tiling including pentagons and star with 2 nm edge length superimposed on an enlarged STM image. (f) Model of the template surface perpendicular to the 10-fold axis and the packing of C60 molecules in the monolayer. The big yellow ring figures out the 2-nm cluster with the cluster centers highlighted as yellow circles, which further form the tiles of Pentagon (P), Star (S), and Boat (B). The green circles inside the P tile at the bottom of the figure indicate additional 5-fold symmetric sites. The C60 molecules occupy both the yellow and green sites. Reproduced with permission from Ref 115. Copyright 2014 American Chemical Society.

(a) 2D illustration of the minimal-area rule. The volume is the product of interface area (dotted line) and the average separation between the cores. (b) The interfacial configurations (Wigner-Seitz cell) of FCC (rhombic dodecahedron), BCC (tetrakaidecahedron), and A15 (six Goldberg tetrakaidecahedra, and two irregular pentagonal dodecahedra).
respectively. Reproduced with permission from Ref 120. Copyright 2001 American Chemical Society .................................................................102

2.45 (a) Scheme of the diblock topologies. (b) Scheme of the AB interfaces in the BCC phase. The left figure has $\varphi = 0.222$ and the interface is almost spherical. The right figure has $\varphi = 0.45$ and the interface takes on the shape of the Voronoi cell. The insets depict the spherical interface limit (small $\varphi$) on the left and the flat interface limit (large $\varphi$) on the right. (c) The phase diagram of linear diblock copolymer melt calculated by SCFT. (d) The phase diagram of third-generation branched diblock copolymer melt calculated by SCFT. Reproduced with permission from Ref 119. Copyright 2003 American Physical Society .................................................................104

2.46 Phase diagrams of conformationally asymmetric AB diblock copolymers are shown with (a) $\epsilon = 1.5$ and (b) $\epsilon = 2.0$. The red dot line in (b) indicates the metastable A15-BCC and A15-HEX boundaries. Phase diagrams of sphere phases for miktoarm AB$_m$ branched block copolymers, with $m = 2$ and 3 are shown in (c) and (d). Reproduced with permission from Ref 116. Copyright 2014 American Chemical Society ........................................................................107

2.47 (a) The ideal average radial distribution of volume $dV/dr$ for supramolecular dendrimers in different phases, where $r = 0$ at the center of a Voronoi polyhedron. (b) The distribution of $-d\Omega/dr$, the decrease rate of the average solid angle in different phases. Reproduced with permission from Ref 83. Copyright 2003 American Association for the Advancement of Science ........................................................................110

2.48 DQC structure grown from supercooled liquids. With the same periodic seed nucleus (blue), distinguishable QC tiling arrangements could be obtained indicating that DQC growth is mainly a stochastic entropy-driven process. Reproduced with permission from Ref 129. Copyright 2007 American Physical Society ........................................................................111

2.49 (a) The MSM model: a rigid scaffolding (diameter 5.27 $\sigma$) having 42 points on the surface, and each point position is anchored with a small spherical particle (diameter $\sigma$) via harmonic springs of stiffness k. It can go through dimerization to introduce shape anisotropy. (b) Schematic of a mono-TNS building block. It can self-assemble into spherical micelles with a soft core (small blue beads) surrounded by relatively mobile hard shell nanoparticles (large white beads). The packing structures of 60 micelles and 120 micelles are shown in the upper right of (b). The asphericity analysis of shape polydispersity for the mono-TNS micelles is shown in the bottom of (b). (c) Schematic of the di-TNS building block, and the self-assembled $\sigma$ phase from polydisperse micelles. Reproduced with permission from Ref 118. Copyright 2011 PNAS ........................................................................114
Synthetic scheme of giant tetrahedra molecules. (i), (ii) CuBr, PMDETA, 70 °C, THF; (iii) thioglycolic acid (or 3-mercaptopropionic acid, 1-thioglycerol, and 2-mercaptopoethanol), Irgacure 2959, THF, \( hv \), 10 min, ~70 - 85% ..................122

Representative \(^1\)H-NMR spectra of giant tetrahedra molecules and their precursors. (A) \(^1\)H-NMR spectrum of B3; (B) \(^1\)H-NMR spectrum of C3; (C) \(^1\)H-NMR spectrum of 4a; (D) \(^1\)H-NMR spectrum of 4b; (E) \(^1\)H-NMR spectrum of 4c; (F) \(^1\)H-NMR spectrum of 2a; (G) \(^1\)H-NMR spectrum of 1 ............134

MALDI-TOF mass spectroscopy characterization of giant tetrahedra precursors. (A) MALDI-TOF mass spectra of B1-B3. Due to the facile release of \( \text{N}_2 \) from the azido groups under the experimental conditions, some fragments were also observed; (B) MALDI-TOF mass spectra of C1-C3 and 1. For C3, some fragments were observed due to the bond breakage of vinyl groups, but the strongest peak matches well with the calculated molecular weight...............................139

Synthetic scheme of VPOSS-2alkyne ...........................................140

(A) \(^1\)H NMR and (B) \(^{13}\)C NMR spectra of VPOSS-2alkyne. Resonance peaks in (A) are assigned. Asterisks indicate corresponding signals from CDCl\(_3\) solvent.................................141

Synthetic scheme of giant surfactant DPOSS-4PS\(_m\). Reagents and conditions: (i) CuBr, PMDETA, toluene, r.t., overnight, ~ 80%; (ii) 1-thioglycerol, Irgacure 2959, THF, \( hv \), 10 min, ~70 - 85%..............................142

\(^1\)H NMR spectra of (A) VPOSS-4PS\(_{10}\) and (B) DPOSS-4PS\(_{10}\) with characteristic resonance peaks assigned. Asterisks indicate corresponding protons in CDCl\(_3\) solvent.................................145

\(^{13}\)C NMR spectra of (A) VPOSS-4PS\(_{10}\) and (B) DPOSS-4PS\(_{10}\). After the thiol-ene reaction, characteristic resonance peaks from vinyl carbons disappeared. Asterisks indicate corresponding signals from CDCl3 ......146

Normalized SEC overlay of 2PS\(_{10}\)-N\(_3\) (black curve), VPOSS-4PS\(_{10}\) (red curve), and DPOSS-4PS\(_{10}\) (blue curve).................................147

FT-IR spectra of 2PS\(_{10}\)-N\(_3\) (black curve), VPOSS-4PS\(_{10}\) (red curve), and DPOSS-4PS\(_{10}\) (blue curve). Characteristic absorbance peaks from azide groups and the Si-O framework of POSS cages were assigned ...............148

MALDI–TOF mass spectrum of VPOSS-4PS\(_{10}\) with monoisotopic resolution. The inset showed the full spectrum ...............................................149

Synthetic route of Triphenylene-6BPOSS .......................................150

xx
3.13 $^1$H-NMR of triphenylene-6BPOSS

4.1 Chemical structures of the four categories of giant tetrahedra (the space-filling model also illustrated in the shadow). Four cartoons in the left corner are corresponding simplifications of these four giant tetrahedra in which the dark blue spheres represent hydrophilic POSS cages and the dark red spheres represent hydrophobic BPOSS cages.

4.2 Crystal structure determination and simulation of giant tetrahedron 1. (A) Synchrotron X-ray powder diffraction pattern of 1. (B) SAED of a single crystal of 1 along the [100] zone. (C) Simulated diffraction pattern at [100] by Cerius². (D) Side view of a column consisted of 1. (E) Simulated molecular packing model in the triclinic crystal lattice of 1 projected on the $ab$-plane, the $bc$-plane, and the $ac$-plane with 2x2x2 repeated unit cells. The BPOSS cages are shown in brown and the tetrahedral core are shown in blue and grey. The aliphatic spacers are neglected in the simulation. (F) SAED of a single crystal of 1 along the [110] zone acquired by tilting 34° along the c* axis at [100]. (G) BF TEM image of a flat crystal with an FFT image as the inset, showing the side view on columns. (H) BF TEM image of the microtomed thin slice of the crystals showing the cross section of the columns. The upper right inset is the corresponding FFT image, and the lower right inset is the Fourier filtered image.

4.3 (A) Combined SAXS and WAXD profiles of 2a evaporated from THF/MeCN mixed solvents at 25 °C. (B) BF TEM image of a microtomed thin section confirms the lamellar superlattice. The right-up inset is the corresponding FFT pattern.

4.4 (A) SAXS pattern and (B) WAXD pattern of 2a after the sample was heated to above its $T_m$ and annealed at 140 °C for 12 hours. (C) and (D) are the SAXS patterns of 2b and 2c after similar sample treatment. (E) {100} plane of an A15 superlattice was identified by the BF TEM image after the thin section sample was stained by RuO₄. The inset is the FFT pattern of this image. (F) Fourier filtering of the image shown in (E) resulted in a clear view of the 2D 4⁴ tiling along the <100> direction. (G) Inverse colored and magnified image of (F). White spherical regions represent the hydrophilic POSS spherical domains with different sizes. The red-dot circles correspond to the body center and vertex positioned domains in the A15 unit cell. The left-top inset is the simulated projection view along the <100> direction. (H) BF TEM image of thin-sectioned 2a sample showing the {210} plane of the A15 structure. (G) Schematic selective assembly mechanism and molecular packing model in the A15 superlattice.
4.5 High temperature self-assembled structures of giant tetrahedron 2d. (A) Chemical structure of 2d with seven hydroxyl groups on the hydrophilic POSS cage. (B) SAXS profile of 2d after melting and thermally annealing at 140 °C for 12 h. The bcc structure was proved by the observed q value ratio of 1:√2:√3:√4. (C) A bcc packing model showing one unit cell. (D,E) BF TEM images of thin-sectioned 2d samples (D) along the {100} plane, and (E) along the {111} plane. The inset images at the right up corner are the corresponding FFT patterns. (F) BF TEM image of occasionally found {100} plane of an A15 structure in thin-sectioned 2d samples. This indicates that spheres self-assembled from 2d reaches the upper limit of the non-deformable size of the spheres.

4.6 Characterization data of the self-assembled structures from giant tetrahedra 3a-c. (A) Combined SAXS and WAXD patterns of 3c evaporated from THF/MeCN mixed solvents at 25 °C indicating a lamellar structure of 3c. (B) SAXS pattern of 3c taken at 25 °C after thermal annealing at 130 °C and quenched in liquid nitrogen to avoid BPOSS crystallization. (C) SAXS pattern of 3a after the identical sample preparation process. (D) BF TEM image of a thin-sectioned 3a sample showing a lamellar structure at 25 °C with a thickness of 5.4 nm. (E) BF TEM image of thin sectioned 3c with the lamellar superlattice identical to that deduced by the SAXS result shown in (B). (F) BF TEM image of thin sectioned and RuO4-stained 3a with the double gyroid superlattice identical to that deduced from the SAXS result shown in (C). In (E) and (F) the insets are the FFT patterns of the TEM images. (G) Schematic assembly mechanisms and packing models of 3a-3c.

4.7 (A) SAXS pattern and (B) WAXD pattern of 4b after the sample was directly annealed at 130 °C. (C) and (D) show BF TEM images of thin sectioned 4c with the honeycomb-like hexagonal superlattice identical to that deduced by SAXS result shown in (A). (E) and (F) show the SAXS patterns of 4a and 4c after the sample was directly annealed at 130 °C. (G) Schematic assembly mechanisms and packing models of 4a-4c.

5.1 Chemical structures of the DPOSS-NPSm giant surfactants with topological variations. In each molecule, the PS tails are of the same statistical length. Cartoons in the boxes are corresponding simplifications to emphasize their molecular topology.

5.2 Self-assembly phase structures of DPOSS-4PSm giant surfactants. SAXS patterns and BF TEM images of five representative DPOSS-4PSm samples showing (A and F) HEX, (B and G) A15, (C and H) σ, (D and I) DQC, and (E and J) BCC phases. The TEM images are taken along the [0001] zone of HEX phase in (F), the <001> zone of A15 phase in (G), the [001] zone of σ phase in (H), the [00001] zone of DQC phase in (I), and the
<001> zone of BCC phase in (J). Insets of the TEM images are corresponding FFT patterns. 2D tilting patterns of (K) the A15 phase, (L) the \( \sigma \) phase, and (M) the DQC phase are abstracted from the TEM images bounded by the red-lined squares shown in (G to I), respectively. Their elements observed and tilting numbers are summarized in the boxes .................182

5.3 SAXS pattern of the \( \sigma \) phase found in DPOSS-4PS13 ........................................184

5.4 SAXS pattern of the DQC phase found in DPOSS-4PS15 ........................................186

5.5 Analysis of random tiling DQC. (A) Original BF TEM image of DQC along [00001] direction. Replacing the 2D projections of supramolecular spheres with perfect circular dots in the center creates (B), and only the position information of the supramolecular spheres is picked out in (C). (D) is the FFT pattern of (C), compared with the calculated 2D DQC tiling diffraction peaks. (E) illustrated the d-spacing in real space. (F) 2D tiling scheme described by four vectors .................................................................188

5.6 Self-assembly phase structures of DPOSS-3PS\(_m\) giant surfactants. SAXS patterns and BF TEM images of four representative DPOSS-3PS\(_m\) samples showing (A and E) A15, (B and F) \( \sigma \), (C and G) DQC, and (D and H) BCC phases. The TEM images are taken along the <001> zone of A15 phase in (E), the [001] zone of \( \sigma \) phase in (F), the [00001] zone of DQC phase in (G), and the <001> zone of BCC phase in (H). Insets of the TEM images are corresponding FFT patterns ........................................................................................................................................190

5.7 SAXS pattern of the \( \sigma \) phase found in DPOSS-3PS\(_{15}\). The peaks indicated by the red number belong to A15 phase in a small fraction.......................191

5.8 Self-assembly phase structures of DPOSS-2PS\(_m\) giant surfactants. SAXS patterns and BF TEM images of four representative DPOSS-2PS\(_m\) samples showing (A and E) LAM, (B and F) DG, (C and G) HEX, and (D and H) BCC phases. The TEM images are taken along the the <111> zone of DG phase in (F), the [0001] zone of HEX phase in (G), and the <001> zone of BCC phase in (H). Insets of the TEM images are corresponding FFT patterns ........................................................................................................................................194

5.9 Phase boundary diagrams of the four series of giant surfactants with different molecular topology. The overall phase boundary diagram with four different LAM (aqua), DG (yellow), HEX (green) and spherical (rest of the colors) phase regions is represented. Note that the phase boundary lines are tilted with respect to the number of PS tails. The window opened in the spherical phase region is opened for DPOSS-NPS\(_m\) with N = 3 and 4. The detailed phase boundaries of the A15 (blue), \( \sigma \) (red), DQC (purple) and BCC (brown) phases within the spherical phase region are shown by
different colors. The black dots represent experimentally accessed data points.

6.1 The evolution of a dendron shape from tapered to conical shapes and the correlation with the projection of the solid angle $\alpha'$. Reproduced with permission from Ref 18. Copyright 2014 Royal Society of Chemistry.

6.2 (A) Chemical structure of triphenylene-6BPOSS; (B) SAXS pattern of triphenylene-6BPOSS annealed at 160 °C and corresponding WAXD pattern in (C).

6.3 (A) {100} plane of an A15 superlattice was identified by the BF TEM image from the microtomed thin-section of triphenylene-6BPOSS. The top right inset is the FFT of this image. (B) Fourier filtering of the image shown in (A) resulted in a clear view of the 2D $4^4$ tiling along the $\langle100\rangle$ direction. (C) Inverse colored image of (B). (D) Selected area electron diffraction of triphenylene-6BPOSS.

6.4 Molecular models of the supramolecular sphere assembled from triphenylene-6BPOSS.

7.1 Flat disk-like core structures with different symmetries.
CHAPTER I

INTRODUCTION

Rapid developments of polymer materials have revolutionized many aspects of human society and now are so popularly beneficial to our everyday life. Considering the special relationship between material structures and their properties, the diverse hierarchical structure construction utilizing polymer building blocks has been extensively studied to achieve various functions which are useful in practical applications. Self-assembly method is always attracting people’s interest due to relatively low economic cost and fast route to construct certain organized structures at different scales. Specifically, in the fields of chemistry and material science, the design and development of novel self-assembling materials is a central piece in advancing our understandings of their thermodynamic driving forces, kinetic pathways and nano-structure formations as well as exploring potential applications.

The living/controlled polymerization techniques including cationic polymerization, anionic polymerization, radical polymerization and even few examples of step polymerization have greatly advanced tool box for chemists to synthesize diverse polymers with controlled molecular weight (MW), controlled tacticity, narrow MW distribution, and end group functionalization. One of the most important features is the
control of topologies, such as linear, branched, or other architectures of diblock copolymers and multi-block copolymers. These progresses help produce rich libraries of unprecedented polymeric materials to fabricate diverse ordered self-assembled structures. However, precise controls of chemical primary structures and compositions and exact constructions of hierarchal physical structures in synthetic polymers are far from being fully appreciated. Polymer properties are more associated with MW, MW distribution, tacticity, and topology, and less controlled in the critical supramolecular structures across different length scales between monomers at nanometer scale and properties at macroscopic scales.

Inspiration for further improvement in self-assembly study comes from the nature, which has presented people huge source of building blocks with precise structure, together with delicate and complicated principles for their self-assembly into hierarchical structures. For example, proteins, which consist of one or more peptide chains with specific amino acid sequence, can perform diverse functions within living organisms, such as catalysis, neural function, vision, and movement, based on complicated three-dimensional (3D) structures with primary, secondary, tertiary and quarterly structure levels which are created via self-assembly of precise amino acid sequence. The nature inspires that precise syntheses of primary chemical structures and control over higher level supramolecular structures are prerequisites to seek for related and specific material properties. One possible approach for realizing these features is to build macromolecules (a more broad coverage than polymers) using precise molecular nano-building blocks. Synthetic dendrimers with a cascade topology which are regularly-branched and monodisperse, could be one of examples. However, they are no shape-persistent. It is
necessary that nano-building blocks must possess relatively independent, well-defined 3D structure and shape so that their further assembly into variety of hierarchal structures at different length scales could be more predictable and robust.

In recent years, our research group has developed novel approaches to construct precise macromolecules utilizing functionalized molecular nanoparticles (MNPs) which are shape- and volume-persistent nano-objects with well-defined molecular structure and specific symmetry. Typical MNPs include, but are not limited to, globular proteins and some cage-like organic or inorganic compounds, such as polyhedral oligomeric silsesquioxane (POSS), [60]fullerene (C60), and polyoxometalate (POM), held together by covalent or non-covalent bonds. By covalently connecting different MNPs in a controlled manner, new macromolecules are built, named “giant molecules” to distinguish from the natural macromolecules. The combinations from diverse MNP library are essentially endless. In general, many basic categories of giant molecules can be recognized such as “giant surfactants” (conjugates of MNP and polymer tail), “giant shape amphiphiles” (conjugates of MNPs with different shapes), and “giant polyhedra” (conjugates of MNPs in polyhedral framework), etc.

The collective physical secondary interactions among the functional groups on the periphery of MNPs constitute the enthalpic driving force to assemble MNPs into hierarchal structures under the chemical and geometrical constraints imposed by the overall giant molecular affinities and shapes. Specifically, unusual Frank-Kasper phases and dodecagonal quasicrystals (DQC) phase were discovered in some categories of giant molecules. Frank-Kaser (FK) phases are topologically close-packed phases with periodic structures, originally observed in complex metal alloy structures and performed
many special properties such as high-temperature super-conducting materials. The most common FK phases include A15, σ phases, both are known as quasicrystal approximants, and others. The DQC phase is a type of two-dimensional (2D) quasicrystal phase which has long-range orientational order but no translational periodicity perpendicular to the 12-fold symmetry. Only very limited systems in soft matters exhibit FK and quasicrystal phases. The forming mechanism and deep relationship between DQC and FK approximants are still unclear. In our specific systems of giant surfactants, giant shape amphiphile and giant polyhedron, FK phases and DQC are constructed from relatively simple building block structures. These progresses may help people in achieving deeper understandings and better controls of FK and DQC phases in soft matters.

The organization of this dissertation is as following: Chapter II first provides a brief review of the “bottom-up” based self-assembly including introduction of secondary interactions as description of driving force for assembly of natural or synthetic building blocks. We then define the molecular nanoparticles and giant molecules as building blocks in self-assembly, followed by recent developments for the self-assemble studies of giant surfactants, giant shape-amphiphiles, and giant polyhedra. In the last section, a detailed introduction of topological close packing of FK and quasicrystal phases is presented, of which the A15, Laves, σ phases, and DQC are discussed, respectively. Finally, an overall review of the soft matter systems exhibiting these FK and quasicrystal phases is provided, including various systems from liquid crystals, dendrimers, small molecular surfactants, nanoparticles, colloidal particles, to block copolymers.

In chapter III, detailed synthesis procedures, synthesis characterizations, sample preparations, experimental conditions, and instruments involved in this dissertation are
presented. We will first focus on the general characterization methods for the synthesized molecules, such as $^1$H-NMR, $^{13}$C-NMR, FTIR, MALDI, and GPC. Then, the techniques for phase identifications and morphology observation including DSC, TGA, bright field TEM will be discussed, followed by the crystallographic unit cell determination and phase structure calculation utilizing WAXD, SAXS, SAED, and molecular packing simulation. In the last part, the detailed synthesis procedures and synthesis characterizations for those giant molecules involved in this dissertation will be covered, including three main categories of giant tetrahedra, giant surfactants with multi-tails and giant shape amphiphile of disk-cubic conjugate.

In chapter IV, we describe a class of precisely defined, rigid, nano-sized giant tetrahedra, which are constructed by positioning polyhedral oligomeric silsesquioxane (POSS) molecular nanoparticles with different functional groups at the vertices of a tetrahedron framework. Designed symmetry breaking of these giant tetrahedra accurately controls the positional interactions, leads to diverse selectively assembled, highly ordered supramolecular lattices. In particular, a FK A15 supramolecular lattice is obtained from a series of giant tetrahedra with three hydrophobic and one hydrophilic POSS cages, which resembles the essential structure of certain metal alloys, but with tunable feature sizes at much larger length scales. Formation of the A15 phase is due primarily to the deformability of the self-assembled spherical building blocks that allows size polydispersity from monodisperse giant tetrahedra.

It still remains unclear how to correlate FK and quasicrystal phase stability with the chemical composition and molecular topology in the self-assembling systems. In chapter V we report the self-assembly phase transition sequences of four series of hybrid giant
surfactants based on hydrophilic POSS cages tethered with one to four polystyrene (PS) tails. With increasing the number of tails, molecular topological variations not only affect phase boundaries in terms of the PS volume fraction, but also open a window to stabilize supramolecular FK and DQC phases in the spherical phase region, demonstrating the critical role of molecular topology in dictating the formation of unconventional supramolecular lattices of “soft” spherical motifs.

In chapter VI, a giant shape amphiphile constructed by the center disk-like triphenylene building block and six periphery rigid hydrophobic POSS cages is designed and synthesized through [3+2] cyclo-addition click reaction. With a completely different molecular shape from giant tetrahedra and giant surfactants, the self-assemble of this type of giant shape amphiphile surprisingly results the FK A15 phase. The molecular packing in the A15 phase is discussed in detail.

Research progresses described in this dissertation only opens the new gate to an even broader research field. Chapter VII summarizes the current work and provides the outlook that might guide further study in this direction.
2.1 Bottom-Up based Self-assembly

People are always being surprised by the highly ordered systems in this world, especially in live bacteria, plants, animals, and human beings. A direct basis for the origin of life is to create molecular orders. The molecules or atoms must arrange in the just right form to construct the original biomacromolecules (DNA, RNA, protein) spontaneously. Self-assembly process in which a disordered system of pre-existing components develops into a certain kind of organized structures resulting from specific and intrinsic interactions without external energy intervention, plays the critical role in creating such complicated structures against disorder. The ordered states reached by self-assembly are generally in thermodynamically stable states, but could also be in thermodynamically metastable states, depending on the balance of entropy and binding enthalpy to create a free energy minimum.

In material chemistry, self-assembly, as a bottom-up approach, has been extensively utilized by scientists to form various hierarchical structures to achieve diverse functions and properties. Two key factors of self-assembly are rational design of non-covalent interactions (secondary interactions) and building blocks. With respect to
traditional covalent, ionic, and metallic chemical bonds, secondary interactions exhibit weaker strength (Table 2.1)² and thus, are easier to be broken with lower bond energies. On the other hand, the weaker secondary interactions can facilitate the association and disassociation of bonds to achieve different kinetic pathways and reach a free energy minimum. The development of supramolecular chemistry has significantly advanced people’s knowledge about their formation origin, strength, and chemical structure dependence. The general aspects of secondary interactions are summarized in Table 2.1, including van der Waal forces, π-π interactions, hydrogen bonds and others.
Table 2.1. Summary of various secondary interactions.\textsuperscript{2} Reprinted with permission from Ref 2. Copyright 2015 Springer.

<table>
<thead>
<tr>
<th>Name</th>
<th>Energy</th>
<th>Directionality</th>
<th>Origin</th>
<th>Length scale</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals interaction</td>
<td>&lt; 5 kJ/mol</td>
<td>No</td>
<td>Weak electrostatic attraction in nature; Induced by electron cloud polarization</td>
<td>Several Å</td>
<td>Ubiquitous; decays rapidly with distance</td>
</tr>
<tr>
<td>Hydrogen bonding (D-H⋯A)</td>
<td>~ 1–161.5 kJ/mol</td>
<td>Yes</td>
<td>Weakly electrostatic</td>
<td>0.5 nm</td>
<td>Master key in supramolecular chemistry</td>
</tr>
<tr>
<td>Halogen bonding (D-X⋯A)</td>
<td>~ 5–180 kJ/mol</td>
<td>Yes</td>
<td>The tendency of halogen atoms to interact with atoms possessing lone electron pair</td>
<td>~ 0.2–0.5 nm</td>
<td>Effective and reliable, similar to hydrogen bonding</td>
</tr>
<tr>
<td>Ion-Dipole interactions</td>
<td>~ 40–600 kJ/mol</td>
<td>Yes</td>
<td>Electrostatic attraction between an ion and a neutral molecule that has a dipole</td>
<td>~ 0.1–10 nm</td>
<td>Medium range interactions (~1/r(^2)), important in solvation processes</td>
</tr>
<tr>
<td>Ion-Ion interactions</td>
<td>~ 100–350 kJ/mol</td>
<td>No</td>
<td>Electrostatic attraction/repulsion</td>
<td>~ 0.1–10 nm</td>
<td>Basis for the formation of ionic structures and colloids</td>
</tr>
<tr>
<td>Dipole-Dipole interactions</td>
<td>~ 5–25 kJ/mol</td>
<td>Yes</td>
<td>Type I: from a single pair of poles on adjacent molecules; Type II: from dipoles with opposing alignment</td>
<td>~ 0.1–10 nm</td>
<td>Significant in solid state; relatively weak in solution</td>
</tr>
<tr>
<td>Cation-π interactions</td>
<td>~ 5–80 kJ/mol</td>
<td>Yes</td>
<td>The face of an electron-rich π system with an adjacent cation</td>
<td>&lt; 1 nm</td>
<td>Strong in transition metals; weak in alkaline and alkaline earth metal cations</td>
</tr>
<tr>
<td>π-π interactions</td>
<td>~ 0–50 kJ/mol</td>
<td>Yes</td>
<td>Electrostatic intermolecular overlapping of p-orbitals in π-conjugated systems</td>
<td>~ 0.3–0.5 nm</td>
<td>Important in understanding organic electronic materials</td>
</tr>
<tr>
<td>Metal-Ligand coordinations</td>
<td>Varies with metal, ligand, and coordination number</td>
<td>Yes</td>
<td>Lone electron pair occupying the empty orbitals</td>
<td>Several Å</td>
<td>Important in crystal engineering, MOF, and supramolecular chemistry</td>
</tr>
<tr>
<td>Hydrophobic effect</td>
<td>&lt; 40 kJ/mol</td>
<td>No</td>
<td>Nonpolar molecules that tend to minimize unfavorable interaction with solvent</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
Another important aspect dictating the self-assembly process is the chemical and topological characteristics (size, shape, or composition) of the building blocks. Building blocks are not limited to atoms and molecules. Recent examples of novel building blocks include polyhedra, patchy particles, proteins, and DNA in the length scale for nm to µm. In the past few years great progress has been witnessed in nanoparticle/colloidal particle syntheses, leading to a variety of building blocks with different sizes, shapes, functionalities, and compositions as a consequence of advances in modern chemistry, biochemistry and nanotechnology.\textsuperscript{3,4} Figure 2.1 shows some representative examples of synthesized anisotropic particle building blocks that have been achieved.\textsuperscript{5} Each individual building block can be specifically designed and conceivably incorporated into supramolecular lattice assemblies with hierarchical structures, and further serve as advanced material for a range of technological applications. Nevertheless, there are still many challenges need to solve in terms of precision and functionality of these particles. The sizes and shapes are poly-dispersed although in a better control manner after the continuous efforts during the past decade. The functionalities of these particles are not uniform on the particle surface, creating property fluctuation and unevenness. This dissertation will only pay attention to the building blocks with precise chemical structures and mono-disperse sizes and uniform functionalities.
Figure 2.1 Representative examples of anisotropic building blocks reported recently. From the left to right shows the increase in the size of building blocks, while the different categories of anisotropic building blocks are shown in the rows. Reprinted with permission from Ref 5. Copyright 2007 Nature Publishing Group.

To create the hierarchical structures at different length scales, the traditional method is the “top-down” approach (figure 2.2). In the top-down approach such as various lithographic techniques, externally controlled tools has to be utilized in traditional workshop or by microfabrication methods to cut materials into the desired order. The representative micropatterning techniques, such as photolithography and inkjet printing transfer the pattern of certain photo-masks to the substrate, are two examples. It is widely accepted that photolithography is difficult to generate sub-10 nm feature sizes. However,
by understanding how to manipulate the building blocks, all these orders may be realized by “bottom-up” process with self-assemblies being the central process. Taking the example in Figure 2.2, small molecule nucleotides (below 1 nm) can be combined through covalent bonds catalyzed by enzyme to synthesize the DNA with special sequence. The DNA double helix (1 nm to 10 nm) acts as the template and direct the synthesis of peptide chains with specific amino acid sequence, which further fold and associate into 3D protein (1 nm to 100 nm) structures by self-assembly process. The protein can be a part component of membranes (µm) to construct different cells (µm), and participate at the activity of life (cm to m). “Bottom-up” approaches, broadly speaking, are economically more efficient and faster than the “top-down” approach, but more difficult to control when the size and complexity of assembled structure increase.

Figure 2.2. The top town and bottom up approach of creating structure with order.
2.2 Molecular Nanoparticles and Giant Molecules as Building Blocks in Self-Assembly

Molecules are supposed to be small and generally below 1 nm. The original definition of molecule comes from Latin phrase and means “a tiny mass of something”. Nevertheless, modern science has expanded the concept of molecule to macroscopic size or weight and even infinite scale (network structure). People would not be surprised when a molecule is weighted about 1 kg in weight or sized 1 m in distance. There are many kinds of molecules with scale at least one order larger than traditional small molecules, called ‘giant molecules’. Using the giant molecules to replace traditional small molecules or atoms as starting building blocks for the novel design of “bottom-up” based self-assemblies has been extensively studied in recent years.

2.2.1 Self-Assembly of Biomacromolecules

Nature has presented people huge source of giant molecules, together with delicate and complicated principles for their self-assembling into hierarchical structures. The most representative examples belong to DNA and RNA, which are intrinsically information storage macromolecules. They have special sequence and help encode the complete set of the corresponding genomes to generate specified proteins. With precise molecular chemical structure and special sequence of base pairs, DNAs are directing the replication of themselves and generation of proteins with all different functions. Learning from the DNA giant molecular structure, various studies are gradually focused on synthesizing artificial macromolecules with precise length and sequence of functionalities. Furthermore, the DNA ‘origami’ nanotechnology was developed in 2006 by Paul Rothemund at the California Institute of Technology based on Watson-Crick base pairing
principle.\textsuperscript{8} This nanotechnology can achieve folding of DNA to create non-arbitrary 2D and 3D shapes in the nanoscale through design of its base sequences.\textsuperscript{8-11}

Another example of natural giant molecule is protein. Proteins consist of one or more peptide chains with specific amino acid sequence and perform diverse functions within living organisms, such as catalysis, neural function, vision, and movement. Different from 1D DNA or RNA, proteins commonly fold into complicated 3D structures with four levels (Figure 2.3a). The primary structures are the amino acid sequences, and the secondary structures including the alpha helix, beta sheet and turns are local structures stabilized by hydrogen bonds. Tertiary structure is the overall folding shape of a single protein, generally stabilized by nonlocal interactions such as hydrogen bonds, salt bridges, hydrophobic interaction, disulfide bonds, and metal-ion coordination. The tertiary structure is already an integrated function unit and controls the basic function of the protein. In some cases several protein molecules with tertiary structure (called subunit proteins) can form a complex to create quaternary structure, which can act as a new single function unit. Self-assembly of proteins are commonly found in nature, such as viruses, bacteria. Tobacco mosaic virus (TMV) has a rod-like appearance, consist of coat protein and one 6400 bases long molecule of genomic single strand RNA. Over 2000 copies of the same proteins wrap around this RNA to construct the helical coat architecture (Figure 2.3b).\textsuperscript{12,13} Three complete turns contain 49 subunits and the helical rise per subunit is 0.1408 nm. Another common protein self-assembly structure is in the spherical-like protein cages, among which are mostly icosahedron structures (Figure 2.3c).\textsuperscript{14} Icosahedrons contain 20 triangle faces composed of hexagonal “hexon” units and 12 vertices formed by curved “penton” units with pentameric symmetry.
Figure 2.3. Hierarchical structures of proteins and their self-assembly in nature. (a) The 3D structures at primary, secondary, tertiary and quaternary levels. (b) Scheme of tubular TMV shell helically assembled from coat proteins.\textsuperscript{12,13} Side view and end-on view of TMV are both illustrated. The basic amino acids residues (Arg90, Arg92 and Arg41 in yellow, and Asp116 in pink) shown are related to the coat protein–genomic-RNA interaction. Reproduced with permission from Ref 13. Copyright 2012 Royal Society of Chemistry. (c) Scheme of protein cages with icosahedron shape.\textsuperscript{14} Reproduced with permission from Ref 14. Copyright 2008 Nature Publishing Group.

The naturally occurring protein assemblies can serve as inspiration for protein engineering to build artificial networks or 3D structures from monomeric proteins. Yeates’s group pioneered in this area of rationally design self-assembled protein structures.\textsuperscript{15} The association of proteins in nature could produce oligomers such as dimers, trimmers, etc., which belong to the quaternary structures of proteins. By carefully designing the amino acid sequence, a single larger fusion protein which contains two connected distinct protein domains, can be created by genetic manipulation (Figure 2.4). This fusion protein carries two parts connected by a helical linker, each with a strong tendency to associate with other copies of themselves. The connecting angle value between these two distinct parts is 109.5°, a basic angle of tetrahedral cage. As a consequence of this design, homogeneous 12-subunit cage assemblies were obtained in
solution with 16 nm in size. Precise x-ray single crystal structure was also determined and confirmed the tetrahedral cage structure.

Figure 2.4. Scheme of tetrahedral protein cage design. The top models illustrate the design principle of a fusion protein bridging a dimer and trimer protein complex and a tetrahedral cage formed by self-assembly of twelve fusion proteins. The bottom shows the specific structures of natural protein oligomers and designed fusion protein with its actual crystal structure (middle). The tetrahedral geometry of the designed assembly with 5 nm porous center (illustrated by black sphere) was confirmed by the crystal structure of the cage.\textsuperscript{15} Reprinted with permission from Ref 15. Copyright 2012 American Association for the Advancement of Science.

In great contrast to diverse biomacromolecules, man-made giant molecules are mostly synthetic polymers and still face grand challenges in terms of precise syntheses of
primary chemical structures and control over hierarchical structures across multi-length scales. Nevertheless, we should be encouraged by the fast development of polymerization methods, especially the living/controlled polymerizations of all kinds of monomers, including cationic polymerization, anionic polymerization, radical polymerization and even few examples of step polymerization. This largely advanced tool box for chemists to synthesize diverse polymers may control MW, tacticity, narrow MW distribution, and end group functionalization. Among the most important features is the control of topologies, such as linear, branched, or other architectures of diblock copolymers and multi-block copolymers. These progresses help produce a rich library of unprecedented polymeric materials to fabricate diverse ordered self-assembled structures and facilitate the study of the corresponding structure-property relationships. Still, grand efforts are needed to truly mimic the complexity of biomacromolecules to precisely control the sequences of monomers with different chemical structure into a desired length and a specific topology.

2.2.2 Molecular Nanoparticles (MNPs)

Due to the tedious reaction and purification steps, precision polymer synthesis mimicking the process of biomacromolecules synthesized in living organisms remains an enormous challenge. However, dendrimers is an almost perfect and unique example among all the synthetic polymers.\textsuperscript{16} They have controlled exterior functionality and core composition. With regularly branched topology and monodisperse molecular weight, they can be treated as precise macromolecules. Although dendrimers are often used as
building blocks in self-assembly, they only have limited shapes such as cones, fans, or spheres in the solution.\textsuperscript{17} Besides, they usually adopt collapsed pancake-like conformations in the solid state upon evaporation of solvents.\textsuperscript{18,19} The flexible feature of dendrimers makes them difficult to sustain 3D structure as in the case of proteins.

In a brief summary, to mimic the hierarchical structure construction of biomacromolecules, nano-building blocks with precise molecular weight, controlled topologies and shape persistent ability are required. We have designed and utilized molecular nanoparticles (MNPs) as functional building blocks to be included into precision polymer synthesis. MNPs are nano-objects which have precise molecular structure and shape- and volume-persistent with specific symmetry.\textsuperscript{20} Typical MNPs include, but are not limited to, some cage-like organic or inorganic compounds and globular proteins (Figure 2.5a). The cage-like molecular compounds, such as POSS, [60]fullerene (C\textsubscript{60}), and polyoxometalate (POM), are held together by covalent bonds. They can be organic, inorganic or organic-inorganic hybrid molecular structures. Globular proteins are the folded proteins with spherical tertiary structures as we mentioned above, stabilized by hydrogen bonds and other related bonds. Recently, a type of novel cages self-assembled through metal-ligand coordination non-covalent interactions were also reported, which can be classified in the family of MNPs.\textsuperscript{21} These cages carry positive charges, balanced by the counter ions.
An important feature of MNPs is that the periphery of nanoparticles can be introduced to link with different functional groups, which would facilitate tuning the physical and functional properties of MNPs. With precisely defined surface functional sites in one MNP, collective secondary interactions can be created to form greater bonding strengths and stronger driving forces to assemble MNPs into hierarchical structures. To make use of MNPs as tunable nano-building blocks and form conjugates with other building blocks, the surface functional groups must be introduced in controllable manner. As schemed in Figure 2.5b, the MNPs can be functionalized in several controlled ways, such as site-selective mono-functionalization, regio-selective multiple-functionalization, or simultaneous multiple-functionalization.

Inspired from the self-assembly of biomacromolecules, our research group has developed a novel “bottom-up” methodology based self-assembly approach starting from
nanoatoms (functionalized MNPs) in recent years. The precise MNPs, named as “nanoatoms” which are atom analogs in nanoscale, are connected together by covalent bonds to form conjugates. As this method is quite similar to the way atoms form the traditional molecules through chemical bonds, the conjugates with precise structures can be called giant molecules. In this dissertation, the phrase of “giant molecules” specially means the conjugates synthesized in this approach, distinct from the macromolecules such as DNA and proteins. Giant molecules are able to form supramolecular assemblies through collective secondary interactions, and finally associate into macroscopic materials with different functions and properties, as shown in the scheme of Figure 2.6. This self-assembly approach starting from MNPs provides another new pathway for how to transfer the microscopic functions into macroscopic properties by constructing proper hierarchical structures.

Figure 2.6. Comparison of traditional bottom up self-assembly approach (top) and MNPs based approach (bottom). Reproduced with permission from Ref 21. Copyright 2014 ACS.
2.2.3 Three Categories of Giant Molecules

According to the scheme of Figure 2.6, a large number of diverse giant molecules can be designed by covalently connecting different MNPs, selected from the library of “nanoatoms”, in a controlled manner. The ideal giant molecules should have monodisperse size and precise chemical structures (sequence, composition, and topology), similar to natural biomacromolecules. The combinations from even partial “nanoatoms” libraries are essentially endless, and may achieve undiscovered properties or beyond those found in nature’s products. But considering the special importance of polymers including endless possibilities for structural variation and property diversity, we will also add the polymers with relatively narrow polydispersity into the tool box of nanoatoms. In this sense, three basic categories of giant molecules are proposed, namely, “giant surfactants”, “giant shape amphiphiles”, and “giant polyhedra” (Figure 2.7).
Figure 2.7. Three categories of giant molecules include (A) giant surfactants, (B) giant shape amphiphiles, (C) giant polyhedra.\textsuperscript{21} Reproduced with permission from Ref 21. Copyright 2014 ACS.

Giant surfactants are constructed by connecting compact and incompressible MNP heads and flexible polymer or lipid tails together. Lots of parameters can be adjusted to tune the intrinsic properties of giant surfactants. Among them, the parameters include topologies (the number of MNP heads and polymer tails, connecting manners), chemical compositions (the species of MNPs and polymers) and functionalities (functional groups on MNP surface). When the MNPs are functionalized with hydrophilic groups and the polymer or lipid tails are hydrophobic, these giant surfactants would be the sized and
amplified analogs of small surfactant molecules. This feature makes the origin of the words “giant surfactants”\textsuperscript{,22} As a new class of size amplified surfactants, giant surfactants sit in between small molecule surfactants and block copolymers, and bridge the gap of both of them. Thus the self-assembly of giant surfactants would share some similar features with each of them, and of course would exhibit some special behaviors due to the intermediate length scale. A very important part of this dissertation is going to focus on the self-assembly structures of giant surfactants with different architectures. Detailed descriptions and discussions will be presented in the following chapters.

As shown in Figure 2.7, giant shape amphiphiles are built upon covalently linking different MNPs of distinct shapes and competing interactions. The concept of shape amphiphiles was first used to describe a disc-rod liquid crystal dyad system\textsuperscript{.23} In this giant molecule system, giant shape amphiphiles generally are composed of the MNPs having specific 3D shapes with certain geometry, symmetry, and preferred packing scheme. The structure engineering ability also comes from these parameters of MNPs. Representative examples of giant shape amphiphiles include sphere-cube, sphere-triangle, cube-disk, sphere-disk, and sphere-rod dyads. This construction method for giant shape amphiphiles provides numerous combination possibilities and enormous potential to engineer diverse ordered structures.

The third category in giant molecules is “giant polyhedra”. Two different types of giant polyhedra exist. The first type of giant polyhedra is closed framework structures, which have straight edges and sharp corners or vertices but without flat faces\textsuperscript{.20} They often come from the intrinsic feature of MNPs themselves. The best example can be found from Figure 2.5, the negative charged polyhedral cage resulting from metal-ligand
coordination non-covalent interactions.\textsuperscript{21} By careful design of the metal-ligand ratio, the chemical structure of ligand or other parameters, people can produce the cages in different sizes and different polyhedral shapes. Another good example is the nanometer sized tetrahedral protein cages, which were already discussed in Figure 2.4.\textsuperscript{15} The second type of giant polyhedra possesses polyhedral symmetry, with only sharp corners or vertices connected together to center position. The small molecule structure of “CH\textsubscript{4}” makes a good structure analog for this type of tetrahedron. The colloidal nano-tetrapods\textsuperscript{24} or nano-octapods are also belongs to this type.\textsuperscript{25-27} Starting from MNPs, this type of polyhedra can be constructed easily. If MNPs are placed on the apexes of a rigid core structure with polyhedral symmetry to form larger faceted giant molecules, such molecules would amplify the symmetry of the cores and can be treated as giant polyhedra molecules, reminiscent of the classic small molecule valence shell electron pair repulsion structures. In these giant polyhedra, the MNPs may possess different surface functionalities to establish the driving force for assembly. Due to the complexity and rareness of polyhedron core structures, very limited examples of this type of polyhedra are reported.\textsuperscript{28} Among all the polyhedra, tetrahedron is the simplest one to start with. Another important part of this dissertation is about the self-assembly behaviors of this type of tetrahedra in the bulk state. Diverse self-assemblies are created by breaking the symmetry of tetrahedra and introducing different positional interactions. Details descriptions would also be discussed in the following chapters.

Note that a clear distinction is difficult and there would be certain overlaps between these three categories. Nevertheless, categorization in this way captures the
essential molecular features of the corresponding giant molecules, and provides the direction to molecular design and establishing structure–property relationships.

2.2.4 POSS Nanoatom and “Click” Chemistry

Due to the length of background, we can’t fully introduce all the MNPs. There are a number of reviews and perspectives discussing MNPs’ chemical structures and function properties (e.g. POSS, C_{60}, and POM). In this dissertation, we will only deal with POSS nanoatom and its role in self-assembly of giant molecules.

The family of POSS molecules are a series of cage nanostructures with the empirical formula (RSiO_{1.5})_n, where R can be any organic functional groups, e.g., hydroxyl, carboxylic acid, alkyl, vinyl or acrylate ligands. Depending on the value of n (e.g. 8, 10, 12), this series of cage compounds have a variety of sizes and symmetries (T_8, T_{10}, T_{12}). The T_8 cage with cubic symmetry is the most studied one (Figure 2.8a). POSS can be viewed as a silica nanoparticle composed of a silica cage core having silicon-oxygen backbones with diameter less than 1 nm, as well as shell structure of attached organic functional groups at the periphery of the cores. Modification of the shell functional groups has been recognized as a highly efficient method to tune the physical and chemical properties of POSS cages. The unique structures and properties of POSS cages have motivated extensive studies in POSS-polymer hybrid materials, by chemically bonding POSS cages with polymers or physically blending them with polymers. Especially, the nanocomposites composed of POSS cages and polymers have been
proved to largely enhance the mechanical strength, thermal stability, and hydrophobicity.\textsuperscript{29}

In the self-assembly approach based on giant molecules, the POSS should be first mono-site functionalized as we mentioned in Section 2.2.2, followed by the multi-functionalization for the remaining sites. In order to avoid tedious separation and purification, the reactions chosen for functionalizing multi-sites are required to be highly efficient and specific, resulting in no byproducts. The rapid development of “click” chemistry has provided powerful tools to achieve these requirements, including [3+2] cycloaddition, Diels-Alder reaction, [4+1] cycloadditions between isonitriles (isocyanides) and tetrazines, and addition reactions to carbon-carbon double bonds such as the thiol-ene reaction. Among them, two ideal reactions are chosen to provide mild, modular, stoichiometric and stable functionalization of POSS cages (Figure 2.8b). One is Huisgen [3+2] cycloaddition reaction between azido and alkyne group, in which a five member ring of triazole is created catalyzed by Copper (I).\textsuperscript{35,36} Another one is thiol-ene addition reaction between mercapto group and carbon-carbon double bond initiated by photo-initiation.\textsuperscript{36,37} Note that the ideal spatial distribution of the multi-functional groups is dictated by the molecular symmetry of the MNP, although the real conformation may be less symmetric due to the flexibility of linkers.
2.3 Recent Developments for the Self-assemble Studies of Giant Molecules

The idea to make use of MNPs as nano-building blocks has gradually achieved promising progress in recent years, initiated from the conjugates between a variety of MNPs and diverse polymers. Now we can classify these conjugates into the giant surfactant category in giant molecules. In 2002 Nolte et al. described the first synthesis of a precisely defined, nearly monodisperse enzyme–polymer hybrid derived from a lipase and polystyrene. They further studied its self-assembling properties in water and found the formation of fibers consisting of bundles of rod-like micelles in which the proteins are distributed at the surface, surrounding the hydrophobic PS tails. Due to the limitation of precise chemical functionalization of MNPs, few studies of this kind of giant molecule self-assembly were carried out, till Glotzer et al. pioneered performing molecular
simulations to study the self-assembly of oligomer tethered nanoparticles.\textsuperscript{39-41} They use a coarse-grained model to construct diverse tethered nano-building blocks. The representative examples are tethered nanospheres, tethered nanoplate, tethered nanowheel or nanocube, and triblock nano building blocks created by joining two nano-objects with a polymer tether.\textsuperscript{40} Their simulation results predicted that by tethering oligomers to specific locations on nanoparticle surfaces, the self-assembly of nanoparticles into specific ordered structures can be achieved driven by the thermodynamically immiscibility between tethers and nanoparticles. This method provides a possible way to construct hierarchical structures that are potentially far richer than conventional block copolymer, small molecule surfactant, and liquid-crystal systems. Figures 2.9a and 2.9b, show equilibrium columnar structures formed by tethered nanodisks in which six tethers are attached along the disk edge in selective good solvent for tethers. Similar hexagonal columnar structure can be found for the tethered nanotriangles in similar condition. However, when tethers are attached on opposite faces of the wheels instead of edge, layered sheet-like structures would be obtained in poor solvent for wheels due to the hindrance of face-to-face stacking.
Figure 2.9. Equilibrium structures formed by tethered nanoplate, nanotriangle and nanowheel building blocks. (a) Hexagonally packed columnar phase formed by tethered nanodisks and its face view in (b). (c) Hexagonally packed columnar phase formed by tethered nanotriangular nanoplates and its face view in (d). (e) Lamellar phase formed by tethered nanowheels and its face view in (f). Reproduced with permission from Ref 40. Copyright 2003 ACS.

Later on, the rapid development on living polymerization and MNPs functionalization has emerged the diverse self-assembly ordered structures and interesting properties. The representative progress in this area especially in our research group, will be introduced in the following section.

Yu et al. reported the first self-assembly example of a giant surfactant (PS-APOSS) composed of hydrophobic PS tail and hydrophilic POSS head with seven carboxylic acid
groups (APOSS) in solution. Different morphologies including spheres, cylinders, and vesicles can be observed via tuning APOSS-APOSS and APOSS-solvent interactions of this giant surfactant. Interestingly, the PS tails in these micellar cores were found to be highly stretched, exhibiting a similar feature as in small molecular surfactants. Later, other giant surfactant systems of hydrophilic C\textsubscript{60} (AC\textsubscript{60}) tethered with one or two PS chain(s) (PS\textsubscript{n}−AC\textsubscript{60} and 2PS\textsubscript{n}−AC\textsubscript{60}) were also designed and synthesized. Various parameters, such as molecular topology, polymer tail length, and initial molecular concentration were investigated carefully for the effects on the self-assembled micellar morphologies. For example, the series of PS\textsubscript{n}−AC\textsubscript{60} exhibited the micellar morphological formation of spheres, cylinders, and vesicles upon increasing the initial molecular concentration (Figure 2.10a-d). A systematic morphological phase diagram for the self-assembly in DMF/Dioxane/water solution was illustrated in Figure 2.10 for the series of PS\textsubscript{n}−AC\textsubscript{60}. 
Figure 2.10. Phase diagram for the self-assembly in DMF/Dioxane/water solution. The bottom TEM images show the morphologies of PS$_{70}$–AC$_{60}$ with different initial molecular concentrations including (a) 0.1% wt for spheres, (b) 0.5% wt for cylinders; (c) 1.0% for mixtures of cylinders and vesicles, (d) 2.0% for vesicles. Reproduced with permission from Ref 43. Copyright 2012 ACS.

In the bulk state, the diverse phase behaviors of these giant surfactants can be clearly elucidated by a representative giant surfactant with polystyrene (PS) tails and hydrophilic hydroxyl-functionalized POSS (DPOSS) (DPOSS-PS). With increasing the volume fraction of PS tail, the traditional phases observed in block-copolymers including lamellae (LAM), bicontinuous double gyroids (DG), hexagonal packed cylinders (HEX), and body-centered cubic packed spheres (BCC), were obtained, as deduced by SAXS results (Figure 2.11a) and TEM images on microtomed bulk samples (Figure 2.11b). The collective hydrogen bonding interaction among the DPOSS heads drives the phase
separation and largely enhances the interaction parameters $\chi$, therefore, provides a probability of acquiring these phases in low MW of PS and creating very small feature sizes. Note that all the phase structures have sub-10-nm feature sizes, which are very difficult to achieve in traditional block copolymers. These findings have critical potential applications in relevant technologies such as in nanopatterning technology and microelectronics.

Figure 2.11. The small angle X-ray scattering pattern (a) and bright field TEM images (b) of ordered phases (from left to right: Lam, DG, Hex, and BCC) from DPOSS-PS. The phase diagram is listed in the bottom of (b).\textsuperscript{44} Reproduced with permission from Ref 44. Copyright 2013 PNAS.

In the MNP-polymer conjugates, the specific molecular shape and rigid conformation of MNPs can impose packing constraints on the polymer tails, leads to intriguing unconventional structures that are inaccessible for free polymers. A very intriguing example can be found in the crystalized poly(ethylene oxide) (PEO) polymer
system. The giant surfactants having a PEO tail and alky chain POSS or C$_{60}$ heads (PEO-POSS and PEO-C$_{60}$) (Figure 2.12a) were observed to fold into exactly defined half-stemmed polymer lamellar crystals with polymer chain-ends remain trapped in the middle of the lamellar crystal core as defects. In these lamellar crystals, PEO tails are sandwiched between two layers of MNPs. To balance the cross-sectional areas of the MNPs and the PEO stems, the half-stemmed crystals with precisely controlled defects are observed, as evidenced by lamellar thickness and melting temperature (Figures 2.11c and d). Note that the half-stemmed crystals are thermodynamically much less stable and will be further reorganized into integral folded crystals. With the geometric restrictions imposed by MNPs, these half-stemmed PEO crystals are now settled in free-energy minima and experimentally accessible.

A lot of other giant surfactant systems, such as fluorinated POSS-PS conjugate (FPOSS-PS)$^{46}$, FPOSS-PS-PEO$^{47}$, BPOSS-PS-DPOSS$^{48}$, PS-AC$_{60}$$^{43}$, and PEO-PS-AC$_{60}$$^{49}$ were studied to present more different phase behaviors.
Figure 2.12. (a) Chemical structure of PEO-C₆₀ and PEO-POSS; (b) schematic illustration of integral folding and half-stemmed crystals; (c) relationships between lamellar thickness, $L$, and crystallization temperature ($T_x$); and (d) relationships between melting temperature, $T_m$, and crystallization temperature ($T_x$). The insets are corresponding SAXS pattern (c) and ultrafast heating chip DSC thermograms (d). Reproduced with permission from Ref 45. Copyright 2013 ACS.

Our research group has also carried out the self-assembly studies of giant shape amphiphiles based on MNPs. The simplest example is isobutylPOSS (BPOSS)-C₆₀ conjugates, a giant cube-sphere shape amphiphile, also treated as molecular Janus nanoparticle. The immiscible nature of BPOSS and C₆₀ could drive BPOSS-C₆₀ into a double-layered lamellar structure. Crystals of the shape amphiphile exhibited polymorphism with two different crystal structures: an orthorhombic unit cell when BPOSS cages initiate the crystallization process (Figures 2.13a-c) and a more thermodynamically stable hexagonal unit cell when C₆₀ packed into the first layer to
dominate the supramolecular structure formation (Figures 2.13d-e). Considering the bilayer feature with alternating conductive fullerene and insulating BPOSS layers, this type of shape amphiphile is of great interest for potential application in nano-capacitors.

Figure 2.13. (a) Self-assembled structure of BPOSS-C\textsubscript{60} packing in orthorhombic crystal, with the corresponding TEM morphology in (b) and SAED pattern along [001] in (c). (d) Molecular packing in hexagonal crystal with the corresponding morphology in (e) and SAED pattern in (f) along [0001].\textsuperscript{50} Reproduced with permission from Ref 50. Copyright 2011 Royal Society of Chemistry.

Wang et al. reported another series of giant shape amphiphile with more asymmetric shape difference, porphyrin-C\textsubscript{60} conjugates (Figure 2.14a), in which flat disk-like porphyrins tend to pack into columns through $\pi$-$\pi$ interaction while spherical fullerenes prefer to crystalized into FCC lattice.\textsuperscript{51} Droving by the cooperative intermolecular Por–Por and C\textsubscript{60}–C\textsubscript{60} interactions, a stable phase was obtained possessing a supramolecular “double-cable” structure with one p-type porphyrin core columnar channel and three helical n-type C\textsubscript{60} peripheral channels, confirmed by the structural
analysis utilizing X-ray and TEM (Figure 2.14b). The columns pack together into hexagonal lattice, within each column is determined to possess a unique $129_{44}$ helix (Figure 2.14c). This type of giant shape amphiphile was shown to be a promising candidate as a new electron acceptor in high performance BHJ polymer solar cells.

![Figure 2.14](image-url)

Figure 2.14. (a) Chemical structure of a shape amphiphile, porphyrin-$C_{60}$. (b) Wide-angle X-ray diffraction pattern and electron diffraction pattern (inset) of porphyrin-$C_{60}$ to determine its $129_{44}$ helical structure. (C) Simulated molecular packing of the $129_{44}$ helix of the column and their packing into a hexagonal columnar phase. Reproduced with permission from Ref 51. Copyright 2012 John Wiley and Sons.

Other intriguing giant shape amphiphile systems, including $C_{60}$-2BPOSS, BPOSS-PDI-BPOSS, Poryrin-2$C_{60}$, BPOSS-APOSS, $C_{60}$-AC$C_{60}$ and BPOSS-
POM\textsuperscript{57} were investigated in recent years and found to exhibit distinct self-assembly behaviors.

2.4 Frank-Kasper Phases and Quasicrystal Phases in Soft Matters

Self-assembled ordered nano- or meso-structures in soft matters including small surfactant molecules, liquid crystals, dendrimers and some amphiphilic molecular systems have drawn people’s interests for a long time. They have been found to pack into increasingly new phases with complex 2D and 3D geometries, and are expected many potential applications in the field of molecular electronics, nanoporous catalysts, porous materials, drug delivery, and bio-mimetic biological systems.\textsuperscript{58} Another focused attention of studying ordered nanostructures in soft matter is on the self-assembly of block copolymers. The phase diagrams of block copolymers has been clearly estimated as from BCC, HEX, DG, Lam to inversed DG, HEX, and BCC phase structures as increasing the volume fraction of one block. In past few years, several new complicated phases constructed from block copolymers were identified since the development of polymer chemistry push the steps forward of the controlled synthesis of novel polymers with low molecular weight, narrow polydispersity, and reserved end functional groups. These progresses lead people reexamine the traditional phase diagrams and try to build the full-scale diagram for block copolymers self-assembly. Great efforts are being put on theory and computer simulation works, especially about the new FK phases. As we introduced in Section 2.2 and 2.3, the giant molecules based on MNPs serve as a bridge between traditional block copolymers and small surfactants or liquid crystals, it is possible that
this class of materials will shine new light to study possible new phases and their relationship with the well-studied phase structures in soft matter. Especially, diverse ordered structures appear most frequently in the spherical packing phases, due to the complicated 3D close packing and the different types of frustration arisen from the flexibility and compressibility of motifs which are formed by giant molecules. In the following section we will introduce the different packing methods of spheres and resulted ordered structures, and special attention will be focused on FK phases resulted from topological close packing.

2.4.1 Topological Close Packing (TCP)

Taking metal as typical example, imagined hard spheres (atoms in this case) will fill space and make the most efficient and close packing, creating high symmetry and high coordination number. In a general accepted analysis, the domain of an atom can be defined as space in which all points are nearer to this atom than any other. This domain of an atom is equivalent to Wigner-Seitz cell and Voronoi polyhedron, in which each face is the plane equidistant between this atom and its neighbor. The number of the neighbors is called coordination number, and all the neighbors construct the coordination shell, which is in a shape of polyhedron called coordination polyhedron. It has been generally accepted that 12 is the largest coordination number of hard spheres with an equal size which can be put in contact with the central one. The 12 coordination with hard spheres allow three distinct possibilities: face-centered cubic (FCC), hexagonal close packing (HCP), and icosahedral coordination that is in TCP (Figure 2.15). The coordination
environments of the central atom are in polyhedra shapes of cuboctahedron in FCC, twinned cuboctahedron in HCP, and icosahedron in TCP (Figure 2.15a). Sir Charles Frank had demonstrated that icosahedral coordination yields minimum free energy in the local close packing of 13 metal atoms, comparing with FCC and HCP.\(^5^9\) This stability makes icosahedral coordination prevail the densely packing of liquid amorphous metals, and accounts for the local packing order. The stability of icosahedral coordination is rational considering the fact that spheres of the coordination shell are not in contact with each other, and the distance from the central atom to the vertex atom is 5%-10% shorter than that between neighboring atoms in coordination shell.\(^6^0\) As a consequence, the icosahedral coordination can create a range of structures with 12 equidistant spheres surrounding central one allowing a freedom of slight deformation to comply with the simultaneous coordination requirements of atoms on the coordination shell.
Distinct difference between FCC, HCP and TCP exists in terms of the interstice type produced in close packing. The icosahedral coordination in TCP has exclusively tetrahedral interstices, while in FCC and HCP the ratio of tetrahedral interstices and octahedral interstices is 2:1 (Figure 2.15b). Apparently, the region around tetrahedral interstice leads to denser packing than octahedral interstice since the center in octahedral interstice is much further to the surrounding coordination shell. Unfortunately, regular tetrahedra with equal size can’t fill the space without gap, making FCC and HCP the better two choices of close packing of hard spheres. In order to fit the gap between tetrahedra, we have two different approaches. One is to stretch the tetrahedra, which has been used in our construction of icosahedral coordination polyhedra. We have mentioned
that the distance from the central atom to the shell atoms is 5%-10% shorter than that between the neighboring atoms in the shell. The second solution is introducing two or more atom types with different sizes, which can explain the common icosahedral coordination environments in metal alloys. The packing method in the structures having exclusively tetrahedral interstices is called “topological close packing” (TCP). Note that the tetrahedra in TCP are mostly stretched or distorted. In TCP the tetrahedral interstices share triangle faces with other tetrahedral interstices.

![Figure 2.16. The four coordination polyhedra with coordination number of 12, 14, 15 and 16. The yellow and dark red spheres represent minor sites and major sites, respectively.](image)

Even with the unique icosahedra alone they can’t fill the entire space due to the special 5-fold symmetry contained in icosahedra. This problem is similar with the inability of full 2D tiling using regular pentagons. Frank and Kasper demonstrated the distorted icosahedra can be accommodated with other polyhedra that possess larger coordination numbers in the crystal packing. These coordination polyhedra are required to have all triangular faces and there are total three other possible polyhedra derived with coordination number of 14, 15, 16 (Figure 2.16).
To a specific atom which lies in the coordination shell surface, the number of neighbors on the same surface is termed as surface coordination number ($S_q$). This term is very important to apply for the surface coordination distinction between FCC, HCP and TCP. In FCC and HCP the surface coordination number of any atom is 4 (Figure 2.15a), while in the icosahedra this value is 5 and can be up to 6 in CN 14, 15, 16 polyhedra (Figure 2.16). The surface coordination number term is also useful to distinct the four different TCP polyhedra. But first we can do simple analysis to understand why only surface coordination of 5 and 6 exist in TCP polyhedra. A tetrahedron is formed by a triangle and an outside apex. In a coordination polyhedron, all the tetrahedra have a common apex, which is the core atom. The surface coordination of each atom can be allowed with 3, 4, 5, or 6. If all the neighboring spheres around a surface atom on the coordination shell are identical and in touch with each other, then equilateral triangle faces will form and the accommodated core atom will have different radius dependent on the surface coordination number. To accommodate the core atom having nearly equal size with the surface atom, some distortion from equilateral triangle faces should be allowed. If we considered the equal spheres placed at the vertex of bipyramids with 3, 4, 5 and 6 fold symmetries (Figure 2.17), all the triangles are equivalent but with different distorted angle values from $60^\circ$. The surface coordination number of 5 ($S_5$) is well suited for coordination of atoms with slightly different sizes. Among $S_3$, $S_4$, and $S_6$, $S_6$ need least distortion from equilateral triangles, and thus also favored in the TCP with only tetrahedral interstices. Although the distortion of $S_4$ doesn’t vary too much comparing with $S_6$, $S_4$ is not considered in TCP because they often give rise to octahedral interstices.
Figure 2.17. The different surface coordination of each atom (yellow spheres) and their accommodation with an equal sized core atom (dark red sphere) shown in the top. The bottom 2D scheme indicates the distorted angle values from equilateral triangles.\textsuperscript{61}

After derivation by Frank and Kasper, four coordination polyhedra are proved to satisfy the requirements of TCP (Figure 2.16). The four different polyhedra have 12 $S_5$, and 0, 2, 3 and 4 $S_6$, respectively (Table 2.2). Note that there is no $CN=13$ coordination shell. Their geometrical features including ideal point group symmetry, edge number and face number of polyhedra are summarized in Table 2.2.
Table 2.2. Summary of the geometrical features in four Kasper polyhedra. Reproduced with permission from Ref 60. Copyright 2012 Cambridge University Press.

<table>
<thead>
<tr>
<th>Item</th>
<th>CN12</th>
<th>CN14</th>
<th>CN15</th>
<th>CN16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal point group symmetry</td>
<td>m\text{3}5 (I\text{h})</td>
<td>\text{12}2m (D_6d)</td>
<td>\text{6}m2 (D_3\text{h})</td>
<td>\text{4}3m (T_d)</td>
</tr>
<tr>
<td># S_q = five vertices</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td># S_q = six vertices</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td># Edges</td>
<td>30</td>
<td>36</td>
<td>39</td>
<td>42</td>
</tr>
<tr>
<td># Faces</td>
<td>20</td>
<td>24</td>
<td>26</td>
<td>28</td>
</tr>
</tbody>
</table>

To better understand the connectivity between Kasper polyhedra, the concepts of major skeleton and layering in structures deserve further discussion. The line connecting a pair of atoms which share 6 neighbors in common is called a major ligand, and these two atoms are called major sites. In this sense, this pair of atoms both belong to S_6 on coordination shell and have coordination number larger than 12. The networks in one structure formed by the major ligands are called major skeleton. The geometry of the major skeleton provides a simpler way to analyze TCP structures. Taking the Kasper polyhedra as simple example, the central atoms are the meeting sites of 2, 3, or 4 major ligands. They are in the geometry of line, 120° apart on a plane or tetrahedral vertex (the red spheres on the shell in Figure 2.16), respectively. These nodes serve as similar roles of di-valent, tri-valent, or tetra-valent elements in organic chemistry. CN15 can be the polyhedron units to construct infinite network of major skeleton, while the CN16 naturally would result in 3D networks such as diamond network.

Another principle emerged from the normal coordination of Kasper polyhedra is the existence of nearly planar layers of atoms arranged in certain patterns. Start from a triangle face ABC on the plane, and all the coordinations are in normal direction. AB, BC
and AC can’t be all major ligands at the same time. In the first case in which all of three ligands are minor, we can easily deduce the atom array to complete the tetrahedra (Figure 2.18a for both the side view and top view). A 3-fold symmetry can be expected for the array because of the equilateral triangle nature. If there is one major ligand, such as AB, the atom array deduced for the tetrahedron interstices would achieve 2-fold symmetry (Figure 2.18b for the side view and top view). The continuance of the tetrahedron construction in either case would result in infinite tessellation network of nearly coplanar continuous atoms, with the angles between ligands either 60° or 120°. The tessellation is composed of hexagons and triangles but not unique defined, since the case in Figure 2.18a and 2.18b can appear alternatively, together with the appearance of pentagon due to some distortions.
Figure 2.18. (a) Construction of layered structure starting from ABC triangle in which all of three ligands are minor and its top view in the right. (b) Construction of layered structure starting from ABC triangle in which AB ligand is major and its top view in the right.\textsuperscript{61}

The most representative tessellation composed of hexagons and triangles is Kagome net (Figure 2.19). It has a symbol of 3\cdot6\cdot3\cdot6, specifying the number, sequence and shape around each vertex. Further examination of Figures 2.18a and 2.18b indicates the layer structures with infinite coplanar atom array. The main layer containing tessellation arrays of hexagons, triangles and pentagons is called primary layer, in which the connections correspond to interatomic distances. The planes schemed in Figures 2.18a, 2.18b and the Kagome net in Figure 2.19 belongs to primary layer. Meanwhile, the atoms below and above the primary layer are also arranged into layer with certain array, and this layer is called secondary layer. In secondary layer, the nearest atoms do not
correspond to the neighbor atoms in coordination shell. In the following section, we will use the major skeleton and layer structure to illustrate the specific examples of Frank-Kasper phases.

![Tessellation Kagome net composed of hexagons and triangles.](image)

**Figure 2.19.** The most representative tessellation Kagome net composed of hexagons and triangles.\(^{61}\)

**2.4.2 Frank-Kasper Phases**

Based all the background knowledge introduced above, we can now give a clear definition of FK phases. These phases are topologically close-packed phases with periodic structures\(^{61}\), originally observed in complex metal alloy structures. The atoms all take the coordination environment of Frank icosahedron with CN12 or Kasper polyhedra with CN14, CN15 and CN16. FK phases have only tetrahedral interstice in slightly distorted shape. The most common FK phases include A15, Laves phases, \(\sigma\), \(\mu\), M, P, and R phases. The most representative A15, Laves and \(\sigma\) phases would be discussed in details in this section.
2.4.2.1 A15 Phase

The most widely occurring FK phase is A15 phase with a typical cubic unit cell as shown in Figure 2.20a by a space-filling model. Actually the name with “A” title is a mistake as “A” family structures represented by single element. The original found A15 prototype was thought to be β-tungsten with single element W, and later was corrected to and oxide with W₃O stoichiometry. A15 has an A₃B stoichiometry with B unit in the body center and eight corners sheared with its four neighboring unit cells constructing a BCC frame and six A units sit on the face sheared with one neighboring unit cell. The total atom number in one unit cell is thus eight. The unit positions are (0, 0, 0), (½, ½, ½), (½, 0, ¾), (½, 0, ¼), (0, ¾, ½), (0, ¼, ½), (¼, ½, 0), and (¾, ½, 0), respectively. Figure 2.20b scheme out six A units (larger pale-red spheres) in CN14 polyhedron and two B units (smaller dark-red spheres) in CN12 icosahedron with a space group of \( Pm\bar{3}n \) \( (O^3_h) \). Generally speaking A and B have slightly different unit size, resulting distorted tetrahedra interstices. The major skeleton connecting six A units is along three \( <100> \) row directions (figure 2.20c).
If we utilize the concept of layered structure introduced in section 2.4.1, the A15 phase structure can be disassembled into simpler layer tiling pattern. Figure 2.21 illustrate the four-layer packing of A15 structure along the <001>. The primary layer at \( z = 0.00 \) has two kinds of vertex (tiling numbers), \( 3\cdot6\cdot3\cdot6 \) and \( 3^2\cdot6^2 \), in which the hexagons are stretched to make a square cell (dashed square). This net is rotated 90° about the 2-fold axis to yield the primary layer at \( z = 0.50 \). In between the primary layers the second layer with \( 4^4 \) tiling sit at the position \( z = 0.25 \) and \( z = 0.75 \), centering the hexagons. The alternative stacking of these four layers would create the A15 structure in three dimensions. The primary layer is sometimes called dense layer due to the contact of neighboring units and the secondary layer called sparse layer. In a given structure, only one kind of tiling pattern in secondary layer would exist. This could be a simple feature to distinct FK phases with different structures. In this sense, A15 phase is represented by \( 4^4 \) tiling.
The A15 phase can be disassembled into simpler layer tiling patterns. The primary layer pattern at $z = 0.00$ and $z = 0.50$ have the same feature but rotated for 90°. The secondary layer pattern at $z = 0.25$ and $z = 0.75$ have the same 4\(^4\) tiling.\(^{60,62}\)

A15 phases include many important metal alloy superconductors, e.g. Nb\(_3\)Sn, Nb\(_3\)Zr due to the influence of topological close packing on the Fermi level of the alloy electric structures.\(^{60}\)

### 2.4.2.2 Sigma (\(\sigma\)) Phase

Another common FK phase is the \(\sigma\) phase with AB stoichiometry and similar sizes of A and B.\(^{63}\) This phase is more complicated with 30 spheres in one tetragonal unit cell (space group of \(P4_2/mnm\)). Figure 2.22 is a single unit cell of the \(\sigma\) phase and its five different sub-lattices A, B, C, D and E with their nearest-neighbors shell atoms, that is, Kasper polyhedra.\(^{64}\) The five sites A, B, C, D and E have the occupation numbers of 2, 4, 8, 8, 8, and coordination numbers of 12, 15, 14, 12, and 14 respectively. The precise
position and symmetry of each site can be found in the reference.\textsuperscript{60} All the sites have different nearest-neighbour-distances and thus different volume available around each site (within Wigner-Seitz cells) in the order: $V_A \approx V_D < V_C \approx V_E < V_B$, which follows the same order of coordination numbers.

![Diagram](image)

Figure 2.22. The unit cell of $\sigma$, and five sub-lattices A, B, C, D and E with their nearest-neighbour shell atoms.\textsuperscript{64} Reproduced with permission from Ref 64. Copyright 2011 Taylor & Francis.

Using the layered structure to dissemble the $\sigma$ phase could largely facilitate the analysis of this complicated tetragonal structure (Figure 2.23).\textsuperscript{59,61} At $z = 0.00$ position, a Kagome-tiling pattern including four hexagons and six triangles construct the primary layer. After $90^\circ$ rotation along the 2-fold axis, a similar primary layer is put at the position $z = 0.50$. In between these two layers, the secondary layers center the hexagons.
The alternative stacking of these four layers would produce the $\sigma$ phase structure. The featured $3^2\cdot 4\cdot 3\cdot 4$ tilting of secondary layer can be used to identify sigma phase structure.

![Figure 2.23](image)

**Figure 2.23.** The $\sigma$ phase structure can be dissembled into simpler layer tiling pattern. The primary layer pattern at $z = 0.00$ and $z = 0.50$ have the same feature but rotated for 90°. The secondary layer pattern at $z = 0.25$ and $z = 0.75$ have the same $3^2\cdot 4\cdot 3\cdot 4$ tiling.$^{60,62}$

### 2.4.2.3 The Laves Phases

Both A15 and $\sigma$ phases only involve the coordination polyhedra of CN12, CN14 and CN15. Here, we introduce another family of famous FK phases involving CN16, the Laves phases. Laves phase have a common stoichiometry of $AB_2$, in which every two of four smaller B atoms in close packed array are replaced by a larger A atom. This requires A atom having nearly doubled volume of atom B, resulting the atom size ration between A and B being around 1.26.$^{60}$ Laves phases apparently accommodate two kind of atom
specifies with larger size difference than in A15 and σ phases. The prototype structures of Laves phases include the cubic Cu$_2$Mg (C15), hexagonal MgZn$_2$ (C14), and Mg$_2$Ni (C36) phases. Their space-filling unit cell structures are schemed out in Figure 2.24a. All the smaller B atoms have icosahedral CN12 and the larger A atoms have CN16. In this simple case, the connectivity of all the major sites A would present the major skeleton of these Laves phases. Their corresponding major skeletons are schemed in figure 2.24b. With only CN16 major sites, the interpenetrating tetrahedral connectivity of CN16 results in three dimensional networks. For C15, the major skeleton is a diamond cubic lattice. The stacking of double layered structure in C15 can also be described by X, Y, Z, in analogy to A, B, C layers in close packing array. Thus, the stacking for C15 is XYZXYZ. Similarly, the stacking of the Wurtzite major skeleton network can be represented by XYXY in C14. The major skeleton of C36 is a mixture of diamond cubic and Wurtzite structure, represented by XYXZXYXZ.

Figure 2.24c is the disassembled layered structure of C15 Laves structure, which illustrates six-layer stacking along (111) plane. The primary layer is a Kagome net with a tiling of 3·6·3·6, and the secondary layer is a triangular net have a tiling of 3$^6$ constructed by mixed A and B atoms. The atoms in this secondary layer would center all the hexagons and triangles in the corresponding primary layer. There are also anther two primary layers at the positions of z = 0.5 and z = 0.833, but different orientations from the first one at z = 0.167. Of course, the corresponding secondary layers would follow the orientations of primary layers.

C14 Laves structure has a similar layered structure although along the (001) direction and total four layers (Figure 2.24d). Kept the primary layer Kagome net array,
the secondary layer has a different tiling of 6\(^3\), a mixture of A and B atoms. Alternative stacking of the four layers assemble into the C14 Laves phase structure. C36 Lave structure can be understood as eight layer stacking with intermediate mixed planes between C15 and C14.
Figure 2.24. (a) Crystal structure of unit cell of C15, C14 and C36 Laves phases. (b) Laves phase structures showing connectivity of A atom major skeletons and tetrahedral double layers. (c) Six-layer stacking of (111) planes in the Cu$_2$Mg Laves phase structure. (d) Four-layer stacking of (00.1) planes of the MgZn$_2$ structure.$^{60}$ Reproduced with permission from Ref 60. Copyright 2012 Cambridge University Press.
Due to the length limitation of the background, we won’t introduce all the 24 FK phases in details.

2.4.3 Dodecagonal Quasicrystal Phase (DQC)

In crystals, atoms repeat periodically, analogous to a tessellation in a two dimensional plane with only a single type of tile. Therefore, it has been a long-standing belief that crystals can only exhibit rotational symmetries with 2-, 3-, 4-, and 6-fold, and other kinds of rotation symmetries were considered “forbidden” in crystallography. However, this was broken by the discovery of quasicrystals with icosahedral symmetry by Daniel Shechtman et al. in a beautiful study of an alloy of Al and Mn.\(^{65}\) The discrete diffraction peaks exhibit striking 10-fold symmetry. After then, theory works have been carried out to prove the existence of quasicrystal, and numerous quasicrystals of alloys have been reported with different forbidden symmetries.\(^{66}\) Discovery of quasicrystals has led the International Union of Crystallographers to redefine the term crystal as any solid having an essentially discrete diffraction pattern.

Quasicrystals have long-range orientational order but no three dimensional translational periodicity. As a consequence, sharp diffraction spots can occur, but unable to be described by 280 space groups in both real and reciprocal spaces. There are two types of quasicrystals, 2D quasicrystals and 3D quasicrystal.\(^{67}\) In 2D quasicrystals, the direction perpendicular to the quasiperiodic layers is periodic, resulting in a true layer structure within which no any transitional order exists. Typical 2D quasicrystals include octagonal, decagonal, and dodecagonal polygonal quasicrystals with 8-fold, 10-fold, and
12-fold respectively. The 3D quasicrystals have no any periodic direction, represented by icosahedral quasicrystals. The icosahedral symmetry extends along three dimensions.\textsuperscript{66}

Three independent vectors in traditional crystallography are not enough to index the diffraction peaks in quasicrystals, instead, at least 5 linearly independent vectors are necessary. The necessary n vectors span independently in n dimensional space. In other words, the quasicrystals in 3D space can be constructed as periodic crystal in n dimensional space. The real structures of quasicrystals in 3D-physical space can be obtained by appropriate projection/section techniques preserving the symmetries from n dimensional space.\textsuperscript{68} In fact 5 indices are needed for 2D polygonal quasicrystals and 6 indices for 3D icosahedral quasicrystals.
Before the discovery of alloy quasicrystals, Roger Penrose created a set of prototiles to tile a plane quasi-periodically according to certain marching rule while preserving 5-fold rotational symmetry, which became a starting motivation of much work on theory of quasicrystals. This famous third type of Penrose tiling (P3) is composed of two types of rhombi tiles with different angles (Figure 2.25a). An equivalent Penrose tiling can also be constructed in 3D, resulting in icosahedral symmetry (Figure 2.25b). This so-called 3D-Penrose Tiling is made up of rhombohedra instead of the rhombi.
Figure 2.25c shows a family of beautiful binary magnetic quasicrystals based on rare earths and cadmium, presenting icosahedron crystal morphology and five-fold sharp diffraction patterns. The example of icosahedral quasicrystals certainly contains this kind of 3D tiling method. Besides 5-fold Penrose tiling, it is also possible to construct 2D tiling with other rotational symmetries including 8-fold, 10-fold, or 12-fold, illustrated in Figure 2.26a-c for some examples. Their corresponding reciprocal space lattice vectors can be obtained through projection from higher dimensional spaces and showed in Figure 2.26 middle array. We can see that 4 vectors are projected on the plane to describe related rotational symmetry. Their simulated diffractions exhibit 8-fold, 10-fold, and 12-fold symmetries respectively. The fifth vector projected is perpendicular to the plan.
A distinct feature of these 2D or 3D tiling is scaling “self-similarity”, which means any feature of the tiling occurs again within a larger length scale. People have developed methods to construct quasiperiodic tilings, which include the inflation–deflation method, the dual grid method, high-dimensional embedding (projection) method, and the section method. We will not talk about these in details, instead focus on a very special type of 2D quasicrystal, the dodecagonal quasicrystals.
Dodecagonal quasicrystals (DQC) phase structures frequently appear in soft matters, such as dendrimers, block copolymers, multi-component surfactant systems, or even nanoparticle blends. These examples will be introduced in the following sections. Surprisingly, nearly all the quasicrystal phases in soft matter only show 12-fold symmetry, no any example of 8-fold or 10-fold. Unfortunately, the development of dodecagonal quasicrystal studies seems slow, although remarkable progress in icosahedral quasicrystals has been achieved.

In most cases, either the crystals of DQC are too small or DQC coexist with other quasicrystal approximants results the big difficulty in determining the atoms packing in the DQC structure. At this moment, the physic model in 2D quasicrystals is treated as combination of a framework and the decoration with atoms. The framework is just the tiling pattern on 2D plane which has been discussed in Figure 2.26. The dodecagonal tiling pattern proposed in Figure 2.26c is mainly composed of rhombus with the same edge length. The rhombus structure is relatively rare in real quasicrystals, and triangles and squares occupy the most space. The ideally quasiperiodic DQC structure is still not constructed yet, but many methods have been developed to create tiling pattern with 12-fold using only triangles and squares. The deterministic DQC with triangle-square tiling is presented in Figure 2.27a generated by the projection method. The 12-fold symmetry of the tiles results from the long range orientations of the edges restricted in 12 directions with intervals of 30° and equal frequency. Three various tiling methods of $3^2\cdot4\cdot3\cdot4$, $3^3\cdot4^2$, and $3^6$ can be identified, among which the $3^6$ has two different orientations rotated by 30° and causes also two orientations for dodecagons consisting of 12 triangles and 6 squares. According to the self-similarity principle, second generation of dodecagons in larger
scale can be constructed by connecting centers of the smallest dodecagons, illustrated by red lines in Figure 2.27a.\textsuperscript{70} They have $2 + \sqrt{3}$ times larger edge length than that of original ones. Continuing this process can obtain higher generations. The ratio of triangles to squares would have significant influence on the properties of a tiling composed of triangles and squares. It has been discussed and proved by experiments that the number ratio of equilateral triangles to squares is $4/\sqrt{3}$ in this DQC. Considering the corresponding areas of equilateral triangle and square, it is amazing to note, squares and triangles each occupy exactly half of the total area.\textsuperscript{72,73}
Figure 2.27. (a) Deterministic dodecagonal quasilattice generated by the projection method.\textsuperscript{71} Reproduced with permission from Ref 70. Copyright 2011 John Wiley and Sons. (b) DQC with random tiling of triangles and squares. (c) Scheme of phason flips in random tiling DQC. The top shows the creation and final annihilation of a pair of thin rhombi, both of which involve the energy state change. The bottom is the phason flip movements with energy state remaining unchanged.\textsuperscript{72} Reproduced with permission from Ref 72. Copyright 1993 American Physical Society.

Besides the deterministic quasicrystal tiling, various random tilings can be constructed using the same number of triangles and squares, Figure 2.27b as one example. In details, a square-triangle tiling contains exclusively equilateral squares and triangles.
The random tilings belong to an ensemble of tilings satisfies certain boundary conditions, which require long-range bond orientational order but exhibiting 12-fold diffraction symmetry. This ensemble thus has many probabilities for random tilings.\textsuperscript{72} With respect to the local tiling types, another basic tiling of $4^4$ is added, constructing random tilings together with the same types of $3^2\cdot 4\cdot 3\cdot 4$, $3^3\cdot 4^2$, and $3^6$. A proposed mechanism of random tiling formation is the special local atom sites relocation, phason flips, which are related with phase strain (Figure 2.27c).\textsuperscript{72} A pair of rhombi shapes can be created accompany with the change of energy states in the local sites. Each rhombus then follows A-type, B-type or bounce phason flips through the square-triangle tiling, in a way analogous to the operation of a zip fastener. This pair of two rhombi would sooner or later annihilate back into a square and triangle, acting the role as a zipper of squares and triangles in their whole life and creating randomness. Why do the quasicrystals always have random tilings? A reasonable answer is the minimized free energy in random tiling caused by the maximized density of entropy. This entropy arises from coordinated atomic relocations, where each such relocation is equivalent to a rearrangement of tiles. In the condition of either infinite temperature or zero Hamiltonian the maximally random tiling would occur and the phason strain vanishes.\textsuperscript{72,73}

The analysis method we treat DQC is nearly the same as we have done on FK phases which are also called “quasicrystal approximants”. A quasicrystal approximant is a tiling that tiles a periodic unit cell. Although both with the periodicity perpendicular to the layers, the tilings in FK phases tile periodic unit cells within the layers, while the tilings in quasicrystals tile rotational symmetries without periodicity. These FK phases are regarded as crystal approximants of the dodecagonal quasicrystal, e.g. A15 phase,
Zr₄Al₃-type, σ, F, K, H, and J phases. Generally speaking, the larger for the unit cell size, the better approximants to the quasicrystals. In Section 2.4.2, tessellations composed of squares and triangles were introduced to disassemble FK phases into layered structures. Figure 2.28 illustrates the typical layered structures of DQC approximants Zr₄Al₃-type (a), σ phase (b), H phase (c), and A15 phase (d) along the z-direction, with four layers at positions z = 0.00, 0.25, 0.50, and 0.75 stacking alternatively. The atoms at z = 0.00 (open circles), z = 0.50 (closed circles), z = 0.25 and 0.75 (double circles) planes are represented in figure 2.28a-d, respectively. Note that the layers at z = 0.00 and 0.50 belongs to primary layers with different orientations, while the layers at z = 0.25 and 0.75 have same atom arrangements and belong to secondary layers. The characteristic tiling types in these phases are 3⁶ (Zr₄Al₃), 3²·4·3·4 (σ), 3³·4² (H), and 4⁴ (A15). Immediately we will recall that all the four tiling types are included in the random tiling of DQC. This relationship would be used to help us build the physical models of DQC.
In most of FK structures such as the examples illustrated in Figure 2.28a-d, there are three basic unique decoration units, the square, and two types for the triangles (Figure 2.28e). These two triangles have relatively ½ shift along the z-direction. The coordination numbers of each individual atom sites in these three decoration units are figured out in Figure 2.28e. Only CN12 and CN14 appear in the square, and CN 15 site is located in the center of triangle. The coordination number of each site included in these decoration units will not be affected by local configurations or conformations. Learning from the decoration method in FK phases, these three decoration units are also introduced to the DQC physical models construction. That means, the real space structures of DQC are built from the combination of the random tiling and the decoration units introduced above. Each square-triangle tilings are replaced by the corresponding decoration units,
resulting in layered structure with 12-fold symmetry along perpendicular direction. This is a good substitution method for analyzing DQC structures, considering the facts that real dodecagonal quasicrystals exhibit in limited size and often coexistence with structurally related approximants. No evidence has been provided so far that a quasicrystal with ideal quasiperiodicity can be realized.

2.4.4 Various Systems Exhibiting FK phases and DQC Phase

The FK phases are discovered in metal alloys more than half a century ago. Numerous examples of FK packing structures with different metal atoms are reported. The DQC is rather rare in the material world, but has been observed since 1980s. Till recent years the complicated FK phases and DQC phase were surprisingly observed in soft matter systems, and opened the gate to various systems from liquid crystals, dendrimers, and surfactants to block copolymers. In this section we review through these systems and hope to contribute to the full knowledge of FK and DQC phases.

2.4.4.1 Dendrimers

The A15 phase structure with $Pm\bar{3}n$ symmetry has a symbol of $Q^{223}$ (cubic unit cell with #223 space group) and was found in early 1990s to be existed as direct micellar lyotropic phase of the dodecyltrimethylammonium chloride-water and palmitoyllysophosphatidy choline-water systems.\textsuperscript{75} Percec et al. first reported the thermotropic A15 phase in the systems of wedge-shaped dendrimer in 1997,\textsuperscript{76,77} followed
by semifluorinated pentaerythritol tetrabenzoate liquid crystal system. Percec type dendrimers are composed of an aromatic dendritic core from 1→2 or 1→3 branched benzyl ether connections, and terminated alkyl, fluoroalkyl tails. The parameters that can be rationally designed to change the dendrimer properties include generations, branching types, length and structure of tails, and substituents at the apex of the molecules. Compounds 1-4 in Figure 2.29 represent some of those examples. These Percec dendrimers are ready to self-assemble into supramolecular ordered structures. The main driving force could be the weak segregation between the aromatic core and aliphatic tails. The weak interactions such as hydrogen-bonding or ionic electrostatic interactions among the substituents at the apex of the molecule help stabilize the self-assembled structure. Percec type dendrimers show many distinct ordered structures of cubic thermotropic phases. Molecules 1 and 2 with low generations have flat tapered and self-assemble into hexagonal columnar phase with P6mm symmetry (schemed in Figure 2.29b). Dendrimers 3 and 4 are third generation with conical shapes readily self-assemble into cubic phase of Pm3n symmetry, that is, A15 phase, determined by XRD analysis of single domain and powder samples. This characteristic <100> projection pattern of this structure was also obtained under TEM (figure xx). The 4^4 tiling pattern is exactly the feature of A15 structure.
Figure 2.29. (a) Chemical structures of tapered 1 and 2 and conical 3 and 4 dendrons. (b) Scheme of self-assembly process. The low generation flat tapered dendrons self-assemble into a supramolecular hexagonal cylindrical liquid crystal phase, while the high generation conical dendrons result a spherical $Pm3n$ A15 phase. (c) Bright field TEM image of A15 phase. Reproduced with permission from Ref 76. Copyright 1997 American Association for the Advancement of Science.

After the discovery of A15 phase in this kind of dendrimers, continuous works has been done to make more clear view and understanding of A15 phase in soft materials, by a combination of experiments with XRD/TEM/isomorphous replacement/NMR methods, molecular simulations, and theoretical calculation. This in turn facilitates their elaboration of design principles for functional hierarchical structures constructed from spherical supramolecular micelles. Among them tuning the chemical structure plays the
most critical role. An interesting example is to attach a dipeptide to the apex of the conical (4-3,4-3,4)12G2-CH2-X dendrimer. The resulted (4-3,4-3,4)12G2-CH2-Boc-L-Tyr-L-Ala-OMe dendrimer (figure 2.30a) could maintain the shape of the supramolecular spheres resulting from the parent dendrimer. However, the dipeptide attached to the apex parent dendrimer induced A15 phase with porous structure, which contained hollow supramolecular spheres. This hollow spherical A15 phase was identified by reconstruction of the XRD data especially in higher-order peaks, and calculation of the dimensions of the hollow cores. The TEM image and its Fourier analysis (Figure 2.30b) beautifully showed small light portion in the center of the circles on the secondary layer projection indicating the hollow center of supramolecular spheres. The scheme in three dimensional model of this self-assemble process from these dendrimers is figured out in Figure 2.30c.
Figure 2.30. (a) Chemical structure of a conical Dendron with the apex attached with a dipeptide. (b) TEM image (bottom) and Fourier analysis of the A15 phase structure (upper left for FFT and upper right for the reconstructed image after Fourier filtering). (c) Schematic of dendrons self-assembly and polyhedron space-filling view of the unit cell. (d) Simplified models of CN12 and CN14 distorted spherical assemblies. Reproduced with permission from Ref 82. Copyright 2008 American Chemical Society.

A15 phase remains the most widely occurred in libraries of spherical supramolecular dendrimers reported. Although difference exists in the sphere size, inner/shell functionality, aggregation number and hollow properties, all of these A15
structures constructed from dendrimers share some general features unprecedented in metal alloys. As most of these features can be extended to other soft matter systems, it deserves a particular summary:

1) Each supramolecular sphere constructing the cubic A15 phase is consist of many subunits, which are dendrimer molecules. As illustrated in Figure 2.30c, the dendrimers have cone shape and can be divided into several parts, which include the apex (functionality), inner part (aromatic region) and shell part (aliphatic region). The segregation between these parts creates distinct domains of themselves. The aggregation number of dendrimers in each supramolecular sphere can vary from single to hundred, depending on the cone angles determined by generation and tail numbers;

2) The average size of the supramolecular spheres is between 5-10 nm, one order of magnitude larger than the metal atoms. This makes the observation of spheres arrangements in real space much easier. Besides, much large scale of the ordered structure make it possible for potential applications including molecular electronics, photonics, and precursors for nanoporous catalysts;

3) Spheres with different sizes are required to construct FK phases, as in metal alloys. This is realized by the existence of two different types of supramolecular assemblies, type I and II as schemed in Figures 2.30c and 2.30d. Type I has CN12 icosahedron coordination with high symmetry, while type II has CN14 polyhedron coordination with lower symmetry. In the example of Figure 2.30a, the simulation of the XRD profile shows best fit of experimental results when type I and II assemblies have average radii ratio of 0.878. More parameters such
as the degree of deviation from spheres if considered would help fit better. It is amusing to note that two types of supramolecular assemblies with different sizes and coordination environments can be obtained from the self-assembly of uniform molecules with precise chemical structure;

4) The A15 phase formed by dendrimers belongs to one of thermotropic phases. In many cases, the dendrimer would exhibit diverse phases in different temperature and A15 may not be the stable one at room temperature. A typical phase sequence following the temperature increasing is glass → hexagonal columnar LC → cubic A15 → isotropic.\(^8^2\)

By tuning the architecture of dendrimers, it has been discovered that conical dendrons self-assemble into thermotropic liquid crystals having a complicated tetragonal unit cell with P4\(\text{2}/\text{mnm}\) symmetry (Figure 2.31).\(^8^3\) Dendrimer II (Figure 2.31a) shows rather complicated phase sequence: glass < 110 °C < Col\(h\) < 140 °C < Cub\(p_{m\text{3}n}\) < 153 °C < Tet\(p_{42}/\text{mnm}\) < 163 °C < isotropic, spanning from hexagonal columnar to cubic A15 to tetragonal \(\sigma\) phase. The SAXS pattern shows a series of more than 20 closely spaced sharp diffraction peaks (Figure 2.31b), which can be indexed in a large tetragonal unit cell with \(a = 16.74\) nm and \(c = 8.80\) nm. Combing with the XRD of single domains in different directions, the \(\sigma\) phase structure with \(P4_2/mnm\) symmetry was determined (Figure 2.31c), together with the electron density map along \(z\) direction. Figure 2.31 d shows the projection of electron density map viewed from the top, exhibiting the characteristic tiling pattern of \(\sigma\) phase as we discussed in previous section. The fact need
further discussion in following sections that in the same structure “micelles” of a pure compound can adopt five different environments, and hence shapes.

Figure 2.31. (a) Chemical structure of two dendrimers exhibiting σ phase. (b) SAXS profile of dendrimer II indexed with a tetragonal unit cell of a = 16.74 nm and c = 8.80 nm. (c) Scheme of σ tetragonal unit cell with five different atom sites. (d) The projection of electron density map viewed from the top exhibiting the characteristic tiling pattern of σ phase. Reproduced with permission from Ref 83. Copyright 2003 American Association for the Advancement of Science.

After the discovery of these two DQC approximants, A15 and σ phase, it would not be too surprising for people to find the existence of DQC structure in this dendrimer system. By delicately tuning the chemical structure of the dendrimers described above, Zeng et al. reported a much more complicated phase structure exhibiting 12-fold symmetry, which were proved to be DQC structure. Dendrimer in Figure 2.32a shows the phase sequence: 25 °C < DQC < 71 °C < Tet_{P4_{2}/mnm} < 72 °C < isotropic. The single domain grown of this dendrimer revealed the distinctive 12-fold symmetry SAXS pattern (Figure 2.32c). When the sample is shoot by the incident beam perpendicular to the 12-fold axis, a different pattern was acquired with periodicity along one direction and this pattern can be repeated every 30° rotation along the 12-fold axis. To index this DQC pattern, five independent vectors are required as we discussed in Section 2.4.3, among
which four are projected onto the plane, showed as $q_1$, $q_2$, $q_3$, $q_4$ and the fifth perpendicular to the plane (Figure 2.32 c). After generating quasiperiodic tiling using the method we described in Section 2.4.3, the full quasicrystal structure is constructed by decoration with three basic tiling units, the square and two triangles (Figure 2.32b). The simulated diffraction pattern of DQC marked by open circles matched rather well with the experimental one. Note that this quasi-periodic structure exists in the scaled-up micellar phases, representing an unprecedented mode of organization in soft matter.
2.4.4.2 Anionic Surfactants Templated Mesoporous Silicas (AMSs)

The micelles of surfactants have already been found to possess diverse lyotropic self-assembled ordered structures for nearly one century. Over the past two decades, many investigations on preparing highly ordered mesoporous silicas (MSs) using surfactant micelles as templates have been conducted due to potential applications in porous materials. So far MSs with various mesostructures/nanostructures have been successfully achieved, utilizing both cationic surfactants and non-ionic surfactants. Later
Che et al. developed a novel co-structure directing method using organosilanes as the co-
structure directing agent (CSDA) cooperating with anionic surfactants to help direct the
formation of templates with highly ordered structures. In this mixed system, there are
three main components: amphiphilic anionic surfactants, CSDA, and silica source, e.g.,
tetraethyl orthosilicate (TEOS). A CSDA molecular structure contains two parts, an
alkoxysilane site capable of being co-condensed with TEOS and an organic site capable
of interacting with the head groups of anionic surfactants through electrostatic or
hydrogen bonding or interactions. In short, the CSDA acts the role of bridging the
surfactant template and inorganic silica species to facilitate their self-assembly into
highly ordered structures. The most studied chemical structures of surfactants and
CSDA are listed in Figure 2.33a. The fabrication of anionic surfactants templated
mesoporous silicas (AMSs) porous materials relies on this cooperative self-assembly
process which is schemed in Figure 2.33b. Ordered structures are first formed in which
the surface of the spherical or cylindrical organic domains is connected with CSDA and
the TEOS are dispersed between CSDA or in the matrix. Condensation at elevated
temperature results a covalent inorganic network. The mesoporous silicas reserving the
highly ordered structures survive the thermal degradation of the organic template.
Notably, the organic groups in the CSDA will be uniformly distributed in the pore
surface, and enable the pore surface functionalization of the AMS materials.
Figure 2.33. The synthetic strategy for the AMS materials using anionic surfactants and 3-aminopropyltrimethoxysilane (APS, left row) and N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (TMAPS, right row) as the CSDA. Reproduced with permission from Ref 86. Copyright 2012 Royal Society of Chemistry.

(b) The formation mechanism of the anionic surfactants templated nanoporous silicas. Reproduced with permission from Ref 88. Copyright 2012 Nature Publishing Group.

The liquid crystal phases formed by the surfactant–silica complex are determined by a key factor describing the surfactant geometry, that is, surfactant packing parameter,

\[ g = \frac{V}{a_0 l} \]

where \( V \) is the hydrophobic chain volume, \( a_0 \) is the effective interfacial area.
between hydrophobic/hydrophilic domains, and \( l \) is the dynamic chain length.\(^{87}\) With \( g \) values of 1, 2/3, 1/2 and 1/3, micelles having lamellar, bicontinuous minimal surfaces, cylindrical, and cage-type meso-structures can be formed, respectively.\(^{86,87}\) The mesostructures of these different liquid crystal phases are highly dependent on the geometry of the surfactant, which can be easily tuned by changing inherent geometry of surfactants (e.g. the head group type and chain length) and ionization of anionic surfactants (e.g. pH value and ratio between surfactant and CSDA).

If the \( g \) values are tuned carefully smaller than 1/3, diverse cage-type mesostructures would appear. A beautiful example of controlling the diverse cage-type mesostructures via carefully tuning the synthetic parameters of the AMS is illustrated in Figure 2.34.\(^{86,89}\) A full-scale synthesis-field diagram was obtained by varying the composition ratios between \( \text{C}_{14}\text{GluA–NaOH–TMAPS} \) (Figure 2.34a).\(^{89}\) Except for the common hard sphere close packing FCC (\( Fm\overline{3}m \)), unusual liquid crystal phases of \( Fd\overline{3}m \) (AMS-8)\(^{90}\), \( Pm\overline{3}n \) (SBA-1, SBA-6)\(^{91}\), and \( P4_2/mnm \) (AMS-9)\(^{92}\) also were obtained and they actually correspond to the discussed FK C15, A15 and \( \sigma \) phases, respectively. They all consist of topologically closed-packed multimodal cages with different sizes and coordination environments. It is worth noting that the very few example of C15 Laves phase has been reported in other system\(^{93}\), considering the big size ratio between CN12 cage and CN16 cage. Here, C15 Laves phase structure has been obtained (Figure 2.34b for the unit cell scheme, and Figure 2.34c and 2.34d for TEM images along [111] and [110] directions)\(^{90}\). According to the diagram, a rough phase sequence can be identified from \( Fd\overline{3}m \) to \( Pm\overline{3}n \), \( P4_2/mnm \), and to \( Fm\overline{3}m \) as the alkaline is increasing. Thus we can deduce that the formation of diverse cage-type mesostructures depended not only on the
g parameter but also on the cage-cage electrostatic interactions. The cage surface charging is controlled by the ionisation state of the surfactant, increased with the larger alkaline. Soft sphere packing mesostructures of $Fd\bar{3}m$, $Pm\bar{3}n$, and tetragonal $P4_2/mnm$ exist in similar but weaker electrostatic repulsion environments; in contrast, hard sphere packing mesostructures of $Fm\bar{3}m$ were obtained in high alkaline zones with strong electrostatic repulsion between cages.\textsuperscript{86}
Figure 2.34. (a) Phase diagram of the C\textsubscript{14}GluA–NaOH–TMAPS system by varying the composition ratios. (b) Scheme of C15 Laves phase unit cell (Fd\textbar3m). (c) and (d) are the [111] and [110] bright field TEM images of obtained Fd\textbar3m AMS structure. (e) [001] axis of the \textit{Pm\textbar3m} structure. (f) [001] axis of the \textit{P4\textbar2/mnm} structure. (g) [110] axis of Fm\textbar3m structure.\textsuperscript{89,90} Reproduced with permission from Ref 86. Copyright 2012 Royal Society of Chemistry.

Recently, a striking progress of AMS DQC materials in the C\textsubscript{14}GluA–NaOH–TMAPS system was reported by Xiao et al.\textsuperscript{94} This new class of MSs (Figure 2.35a) exhibits 12-fold symmetry in both electron diffraction and morphology as dodecagonal prisms. The random tiling characteristics within the whole cross-sectional area of the
dodecagonal prism were analyzed by TEM carefully, and $3^2.4.3.4$, $3^3.4^2$, $4^4$ and $3^6$ all could be observed (Figure 2.35b). The triangle/square ratio turns out to be reasonably close to that of ideal DQT (~2.31). The FFT of this image presents almost perfect dodecagonal symmetry. Besides, the electron diffraction matches well with a simulated pattern calculated for a DQT (Figure 2.35c). This DQC structure was appeared via the fine control of the intermediate alkalinity between $Pm\bar{3}n$ and $P4_2/mnm$ structures. With the decrease of the alkalinity and electrostatic repulsion, a structure sequence of $P4_2/mnm \rightarrow Cmmm \rightarrow DQC \rightarrow Pm\bar{3}n$ can be observed, in which the DQC phase often coexists with the other three phases. The growth of DQC was proposed as a non-equilibrium growth process, where the competition between the different micellar configurations plays a critical role.
Figure 2.35. (a) Mesoporous particles with dodecagonal prism morphology under SEM. (b) TEM image taken from the central part of the sample (as indicated in the top left inset) with the tiling edges superimposed on the image. The upper right inset is the FFT of this image, exhibiting 12-fold symmetry. (c) Comparison of electron diffraction taken from the circled center part of this sample and simulated diffraction pattern from deterministic DQC tiling. Both show 12-fold symmetry and match very well. Reproduced with permission from Ref 94. Copyright 2012 Nature Publishing Group.

2.4.4.3 ABC Type Star Copolymers

Block copolymers containing incompatible blocks are well known to form classical structures like BCC-packed spheres, hexagonally packed cylinders, double gyroid bicontinuous network and lamellar structures. However, people discovered many complicated tiling pattern among ABC star-branched three-component polymer copolymer systems. In ABC star-shaped block terpolymer systems, three polymer chains are totally incompatible and have enough length. The strong segregation between three distinct polymers would drive the junction points aligned into one-dimensional length, resulting self-organized two-dimensional tilings (Figure 2.36b). If the tiling type for each vertex is the same, which occurs most frequently, then a kind of Archimedean tiling on 2D would be obtained. There are total 11 Archimedean tiling patterns
constructed by regular polygons (Figure 2.36a). Most of them have been experimentally observed in different ABC systems. Among them the best example is the polyisoprene-polystyrene-poly(2-vinylpyridine) (I-S-P) system.  

Figure 2.36. (a) Eleven possible Archimedean tilings. The Archimedean tiling is the tessellation of regular polygons provided that all vertices are of the same type. (b) Schematic alignment of ABC star-shaped block terpolymer molecules, in which the junction points are all aligned along a perpendicular line due to the strong geometrical restriction. Reproduced with permission from Ref 99. Copyright 2005 John Wiley and Sons.

The star polymers with different volume fraction ratios were obtained by blending I–S–P star polymers with different MW, or blending with homopolymer PS and PI. In this blend sample series, macro-phase separation are not observed due to the low MWs of the homopolymers added. The sample film from solution cast was then annealed,
resulting various tiling pattern dependent on the volume ratio of these three domains. In
the series of I_{1.0}S_YP_{2.0} star-based blend samples, the tiling patterns of the samples with Y
of 1.3, 1.6, 2.3, and 2.7 are analyzed in Figures 2.37a-d, together with their corresponding
schematic tiling patterns.\textsuperscript{97} The tiling patterns of I_{1.0}S_{1.3}P_{2.0} (Figure 2.37a), I_{1.0}S_{1.6}P_{2.0}
(Figure 2.37b) and I_{1.0}S_{2.7}P_{2.0} (Figure 2.37d) can be simply classified as the Archimedean
tiling patterns (4.6.12), (5.5.10) and (4.8.8). In the tiling pattern for I_{1.0}S_{2.3}P_{2.0}, component
I has two types of 4-coordinated domains and component S consists of 6- and 8-
coordinated domains, which can be described as [4, 6.7, 10] using the Archimedean tiles
(Figure 2.37c). However, this pattern could be assigned as another Archimedean tiling
pattern (3^2.4.3.4) after applying the imaginary tiling scheme (Figure 2.37e). In the SAXS
pattern, the reflections showed clearly observed square lattice with P4gm 2D space group.
This tiling pattern is very close to the layer tiling in FK \sigma phase.\textsuperscript{97} Furthermore, a
nonperiodic random tiling DQC pattern was found from the I_{1.0}S_{2.7}P_{2.5} (Figure 2.37f),
which was acquired by blending I_{1.0}S_{1.8}P_{2.5} parent copolymer and PS homopolymer
having a MW of 3k.\textsuperscript{96} The right scheme in Figure 2.37f is the transcribed tiling obtained
by transcribing the tile using regular triangles and squares. The triangle/square number
ratio was estimated as 2.3, and dodecagonal symmetry was also observed from
microbeam x-ray diffraction pattern.
Figure 2.37. In the series of I$_{1.0}$S$_Y$P$_{2.0}$ star-based blend samples, the tiling patterns of the samples with Y of 1.3 (a), 1.6 (b), 2.3 (c), and 2.7 (d) are analyzed by TEM images (top) and reconstructed schemes. Reproduced with permission from Ref 97. Copyright 2006 American Chemical Society. (e) (3$_2$.4.3.4) tiling manner superimposed on the I$_{1.0}$S$_{2.3}$P$_{2.0}$ (figure 2.38c) tiling pattern and SAXS pattern of this sample exhibiting tetragonal lattice. (f) TEM image of the sample of I$_{1.0}$S$_{2.7}$P$_{2.5}$. The imaginary random square-triangle tiling is superimposed on this TEM image. FFT in the bottom right inset shows 12-fold symmetry. The right scheme in figure 2.38f shows the transcribed tiling obtained by transcribing the tile tesselation style using regular triangles and squares. The characteristic 3$_2$.4.3.4, 3$_3$.4$_2$ and 3$_6$ can all be identified. Reproduced with permission from Ref 96. Copyright 2007 American Physical Society.
Note that the DQC structure constructed from ABC type star polymers is distinct from the DQC we discussed in metal alloys, dendrimers, and surfactants systems, since it’s purely 2D tiling by columnar phase domains as schemed in Figure 2.37b. Thus, no any spherical building blocks are involved in these 2D tiling. These results are similarly reported in another class of thermotropic columnar liquid crystal phases, which often have the T-shaped bolaamphiphiles and facial amphiphiles.\textsuperscript{58,102-104} Generally, the aromatic rod-like mesogen cores lie perpendicular to the column axis, constructing the cells of columns which are composed of flexible side groups. The aromatic rod walls take a polygonal tiling in 2D. Various 2D polygonal tilings were obtained in this system depending on the relative volume of the side group, the number of side groups, and the additional end-groups. Surprisingly, a series of facial amphiphiles were observed to exhibit a phase with a square 2D unit cell of $p4gm$ symmetry with $3^2.4.3.4$ tiling and square $p4mm$ column phase with $4^4$ tiling at higher temperature.\textsuperscript{104} The tiling patterns in these two phases are known to be identical to the tilings of the secondary layers in the 3D $\sigma$ tetragonal phase and A15 cubic phase.

In addition, the square 2D unit cell of $p4gm$ symmetry tiling pattern was even reported in the monolayer on the cerium-directed assembly of linear polyphenyl molecular linkers with terminal carbonitrile groups on a Ag(111) metal surface.\textsuperscript{105} The spontaneous formation of planar and flexible fivefold Ce–ligand coordination motifs favors the Archimedean tiling of triangles and squares with $p4gm$ symmetry and $3^2.4.3.4$ tiling.
2.4.4.4 Linear Block Copolymers

To achieving large enough Flory-Huggins interaction parameter to facilitate phase separation between different blocks, most studies of block copolymers are focused on large MW region with a relatively large polydispersity. This has neglected the discovery of some complicated phase structure, especially in the spherical phase regions. In 2010 Bates et al. reported the formation of the spherical FK σ phase in two different single-component block copolymer melts near the order-disorder transition temperature (TODT). Poly(styrene-b-isoprene-b-styrene-b-ethylene oxide) (PS-PI-PS-PEO, simplified as SISO-3) tetrablock copolymer with \( M_n = 23 \text{ kg/mol} \) has 46% PI and only 8% volume of PEO domain (Figure 2.38a). Except for composition and overall MW, the thermodynamic driving force for block segregation mainly depends on the segment–segment interaction parameters, \( \chi_{\text{IO}}, \chi_{\text{SI}}, \text{ and } \chi_{\text{SO}} \). In this case \( \chi_{\text{IO}} > \chi_{\text{SI}} \approx \chi_{\text{SO}} \), contact between I and O blocks is unfavorable, resulting the schemed packing method in figure 2.38a in which the I/O interface is avoided in sphere-forming region. After annealing at 140 °C for 1 day, this SISO-3 sample exhibited a rather complicated SAXS pattern, which can be identified as a tetragonal unit cell (\( a = 77.7 \text{ nm} \) and \( c = 41.1 \text{ nm} \)) with \( P4_{2}mnm \) space group symmetry. The similar σ structure was also found in poly(isoprene-b-lactide) (PI-b-PLA, simplified as IL-5) diblock copolymers, which has MW of 3.89 k and 22% L block. This σ structure was confirmed by microtomed TEM in Figure 2.38c left TEM image. Note that both IL-15 and SISO-3 have relatively narrow and low molecular weights. Besides, a phase transition from BCC phase at higher temperature to σ phase is identified in IL-5 sample. This indicates the higher stability of BCC phase at higher temperature. Surprising analogies can be deduced between the
symmetry breaking of BCC to \( \sigma \)-phase transition in diblock copolymers and the symmetry breaking in certain metals and alloys (e.g. the elements Mn and U).\textsuperscript{107} As in metals or alloys the symmetry breaking of structure evolution is mediated by exchange of charge, this transition with symmetry breaking in diblock copolymers is found to be mediated by exchange of mass (diblock copolymer chains). Thus, there would be a redistribution process of mass during this transition. In details, supramolecular particle with uniform sizes, shapes and coordination environments in BCC phase could evolve into five discrete Wigner–Seitz cells with different coordination environments.\textsuperscript{107} Another analogy is made between sphericity change of Wigner–Seitz polyhedra in polymer systems, and the sphericity change of free-electron-like Fermi surface metallic systems. Assuming the perfect sphere has sphericity of 1.0, the average sphericity of \( \sigma \) phase is 0.7624, larger than the 0.7534 of BCC structure. Decreasing the temperature drives the block copolymer system into phase structure having average better approximate spherical symmetry.\textsuperscript{107} These analogies serve as direct linkage between hard metallic materials and soft materials both exhibiting complicated structures.
Figure 2.38. (a) Chemical structures of SISO-3 tetrablock copolymers and IL-5 diblock copolymers exhibiting σ phase structure. As showed in the middle scheme, contact between I and O blocks is unfavorable, resulting the avoided I/O interface in the supramolecular sphere. (b) SAXS pattern of SISO-3 sample after annealing at 140 °C, which can be identified as a tetragonal unit cell (a = 777 Å and c = 411 Å) with $P4_2/mnm$ space group. Reproduced with permission from Ref 106. Copyright 2010 American Association for the Advancement of Science. (c) Representative synchrotron SAXS data obtained from SISO-2. A phase transition from simple hexagonal order (HEX) to DQC phase and to σ-phase was identified. The TEM images of microtomed thin section of σ-phase and DQC phase are shown in the bottom left and right. Reproduced with permission from Ref 108. Copyright 2012 American Chemical Society.

In the same SISO system with different volume fraction of each block (SISO-2, S-35%, I-56%, and O-9%), a DQC like structure is claimed to occur at intermediate temperature between simple hexagonal order (HEX) and the σ-phase, $T_{\text{HEX}} < T_{\text{DQC}} < T_{\sigma} < T_{\text{ODT}}$, corresponded SAXS profiles illustrated in figure 2.38c. The distinct difference
was recorded from 120 °C to 175 °C and from 175 °C to 200 °C in SAXS. Dynamic mechanical spectroscopy (DMS) measurements also observed the G’ change upon heating at about 165 °C and 200 °C. Quenched sample of this SISO-2 from 175 °C was analyzed by microtomed TEM images, showing some feature of DQC in both tiling pattern and FFT pattern.

2.4.4.5 Nanoparticles and Colloidal Particles

Although our discussion is mainly focused on soft matter, we also need to mention the assemblies of nanoparticles and colloidal particles due to the rational design and structure diversity in binary nanoparticle superlattices.\textsuperscript{109-112} The binary nanoparticle superlattices (BNSL) are generally assembled from two different kinds of nanoparticles in mixed solution. On the surface of nanoparticles are dispersed with many organic ligands which help stabilize the nanoparticles in solution. Many complicated factors such as entropic, van der Waals, steric and dipolar forces, and electrical charges control the BNSL formation together. Recently very rich phase diagrams with multiple close-packed and non-close-packed phases were reported in a variety of BNSLs including metallic-metallic, semiconductor-semiconductor, semiconductor-magnetic, or metallic-semiconductor nanocrystal combinations.

Figure 2.39 shows beautiful examples of FK Laves structure under TEM in a system of PbSe and Pd binary nanoparticles.\textsuperscript{110,111} The PbSe and Pd nanoparticles were capped with oleic acid and dodecanethiol ligands, respectively. These ligand molecules have long hydrocarbon chains and help avoid uncontrolled aggregation formation during
the concentration process, *via* short range steric repulsion counterbalancing the van der Waals forces. After slow evaporation of the mixed colloidal solution, binary 6.2 nm PbSe and 3 nm Pd nanoparticles resulted the C14 (MgZn$_2$) Laves phase (Figure 2.39a-e), while 5.8 nm PbSe and 3.0 nm Pd nanoparticles made the C36 (MgNi$_2$) Laves phase (Figure 2.39f).

Figure 2.39. (a-e) TEM micrographs of superlattices isostructural with MgZn$_2$ formed by 6.2 nm PbSe and 3.0 nm Pd Nanoparticles: (a) TEM overview of the (001) plane and its ED pattern in the bottom right inset. (b) but at high magnification of TEM image in (a); (c) scheme of the MgZn$_2$ unit cell (P63/mmc). (d) The nanoparticle packing along the projection of (001) plane. (e) Projection along the (001) planes. Reproduced with permission from Ref 110. Copyright 2006 American Chemical Society. (f) 5.8 nm PbSe and 3.0 nm Pd nanoparticles made the C36 (MgNi$_2$) Laves phase. The bottom right inset shows the scheme of this unit cell. Reproduced with permission from Ref 111. Copyright 2006 Nature Publishing Group.
Another intriguing result of BNSL is in the exploring structure formation with intermediate 13.4 nm Fe$_2$O$_3$ to 5 nm Au nanoparticle concentration ratios.\textsuperscript{109} Several periodic structures with different nanoparticle ratios were observed to have two dimensional (3$^6$), (4$^4$), (3$^2$.4.3.4), and (3$^3$.4$^2$) Archimedean tiling pattern composed of equilateral squares and triangles, respectively. Further, in proximity to the (3$^2$.4.3.4) phase, a DQC random tiling pattern was observed (Figures 2.40a and 2.40b), exhibiting sharp electron diffraction patterns corresponding to 12-fold rotational symmetry. This DQC structure was also observed in 12.6 nm Fe$_3$O$_4$ and 4.7 nm Au nanocrystals, and 9 nm PbS and 3 nm Pd nanocrystals (Figure 2.40c). The formation of DQC in such compositional flexibility indicates that a unique combination of interparticle interactions is not necessary.
Besides in the metallic or inorganic nanoparticle systems, colloid micelle particles self-assembled from amphiphilic molecules provide another route to construct rich spherical structures. Various lyotropic phases with ordered periodic structures are discovered in aqueous solution, most common are $Fm\bar{3}m$ (FCC) or $Im\bar{3}m$ (BCC). Recently Förster et al. reported quasicrystalline phases of PI$_{30}$-b-PEO$_{120}$ micelles self-assembled in concentrated aqueous solution.$^{113}$ A phase transition sequence with increasing concentration was observed at room temperature: disordered $< 13\% < 12$-fold quasicrystal (Q12) $< 18\% <$ Cubic (FCC). In the concentration region between 13\% and 18\%, another intriguing phase sequence occurred with decreasing temperature: Q18 $< 15\degree C <$ Q12 $< 25\degree C <$ FCC. Their corresponding SAXS patterns are showed in Figures
2.41a-c. The Q12 phase was also studied by SANS parallel (Figure 2.41d) and normal (Figure 2.41e) to the 12-fold rotation axis. The characteristic 12-fold diffraction symmetry was recorded in figure 2.41d, while 6 fold and 18 fold diffraction symmetry occurred in FCC and Q18 structure. Note that quasicrystal phases are spontaneously formed from single component block copolymer micelles via self-assembly in concentrated solutions, which is relatively physically and chemically simple system. This lyotropic block copolymer colloidal system provides the only example of quasicrystal with 18 fold symmetry.

Figure 2.41. Synchrotron SAXS patterns of FCC phase (a) and the quasicrystalline phases Q12 (b) and Q18 (c). The SANS patterns have also been recorded for Q12 phase, parallel (d) and normal (d) to the 12-fold rotation axis. Reproduced with permission from Ref 113. Copyright 2011 PNAS.
2.4.4.6 Aperiodic Two-Dimensional Quasicrystals with Five-Fold Symmetry

The majority of known quasicrystals in soft matters are dodecagonal quasicrystals with 12-fold symmetry constructed by spherical motifs. The 2D quasicrystals with other fold symmetries such as 5-fold, 10-fold are only reported in metal alloys. Wario et al. represented an entirely new class of molecular self-assembly resulting in 2D quasicrystal with five-fold symmetry. Scanning tunnelling microscopy (STM) was used to study self-assembled mono-layers of ferrocenecarboxylic acid (FcCOOH, chemical structure in Figure 2.42a). Very unusual cyclic hydrogen-bonded pentamers were directly observed for FcCOOH, instead of dimeric or linear structures typical of carboxylic acids. The hydrogen-bonded pentamers (illustrated in Figure 2.42b) were calculated to be stabilized by the additional CH---O bonding, which is favorable interaction between the carbonyl group and the hydrogen atom on the second position of the cyclopentadienyl. The packing of pentamers which are simultaneously surrounded by five dimers (Figure 2.42c) produced a quasicrystalline structure in mono-layer (Figure 2.42e). The 2D quasicrystal structure has aperiodic tiling pattern, in which the pentagons and their interstitial spaces (pentagon, rhombus, boat and star) well match the first Penrose tiling (P1, illustrated in Figure 2.42f). The FFT of Figure 2.42e exhibits local five-fold and ten-fold symmetry (Figure 2.42d), the same as the 2D spatial correlation function. The discovery of quasicrystal with five-fold symmetry in self-assembled mono-layer could potentially indicate some novel supramolecular assemblies based on building blocks with special symmetries.
As we have described, the 2D quasicrystals with 5-fold or 10-fold symmetries are frequently reported in metal alloys. A very intriguing question can be proposed immediately is: can the quasicrystals in metal alloys serve as the template for the growth of molecular quasicrystal phases in soft matter? The direct interaction and size match between the metal alloy surfaces and related molecules should be built up. A representative example was reported by Fournee at al. recently that self-organized molecular C_{60} films with long-range quasiperiodic order and 5-fold symmetry have been
grown via using Al-based QCs such as Al-Cu-Co or Al-Cu-Fe quasicrystalline surfaces as templates. For Al-based QCs, they can commonly be described as 2D dense packing of partially overlapping columnar clusters, which have 2 nm diameters and extend along the 10-fold axis. The atomic arrangement within the 2 nm clusters has 5-fold symmetry, which is illustrated in Figure 2.43f. The electron diffraction pattern of the surface of the decagonal QC before deposition exhibits a 10-fold symmetry as shown in Figure 2.43a. After deposition of C$_{60}$ monolayer, a new diffraction was obtained (Figure 2.43b), with the same 10-fold symmetry but more bright spots. Figure 2.43c shows the real space image of monolayer C$_{60}$ packing, and its corresponding FFT pattern in Figure 2.43d indicates characteristic 10-fold symmetry. The C$_{60}$ molecules surprisingly adsorb at 5-fold symmetric sites, as shown in the model proposed in Figure 2.43f. In addition, the dimensions of the pentagonal packing of C$_{60}$ molecules exactly match the dimensions of the underlying QC template, resulting in the deviation from HCP in the C$_{60}$ bulk structure. The characteristic tiling units including pentagon, boat, and star in P1 tiling of QC template are all found in the C$_{60}$ monolayer packing (Figure 2.43e for the pentagon and star marked out). It is proposed that the most favorable adsorption configurations at these sites for C$_{60}$ are pentagonal face down to contact the substrate.
2.4.5 Discussion and Simulation about FK and DQC Phases

Considerable amounts of experimental progress for complicated DQC and DQC approximants formation collected in various soft matter systems and colloidal systems have stimulated lots of corresponding theory calculation and computer simulation studies.\textsuperscript{116-121} The question appears first is why the non-close packed FK phase, most frequently A15 phase, can occur instead of close packed FCC, HCP or less closed packed BCC? Among all the systems showing these complicated phase structures, dendrimers are reported earliest and seem to be relatively simple both physically and chemically.
Thus, structure models similar to dendrimer self-assembly systems are built by Kamien et al. to acquire theoretical understanding of the stability of various phase structures.\textsuperscript{120,122}

An ideal colloidal particle with a relatively dense core and a fluffy corona was established, similar with dendrimer supramolecular spherical particles having dense branched benzyl ether core and flexible alkyl chains. If these colloidal particles are hard sphere, then FCC lattice would be favored due to the maximization of entire system positional entropy. However, not only the hard-core repulsion between cores determines the structure stability, but also the short ranged interactions between flexible coronas. The more overlap between the coronas of alkyl chains, the more constrained conformations of alkyl chains and thus the smaller orientational entropy.\textsuperscript{120} In the model of bilayers as schemed in figure 2.44a, the product of the total interfacial area ($A$) and average bilayer thickness or inter-particle distance ($d$) is a constant assuming in a constant volume with uniform density.\textsuperscript{122} The soft repulsion interaction between corona chains would favor larger inter-particle distance $d$, resulting in the minimum interfacial area $A$ and maximized orientational entropy of corona. If the corona entropy factor dominates over the overall frustration caused by the non-close packing, then a packing method with minimum interfacial area $A$ to maximize the entire corona entropy would be favored for self-assembly of these colloidal particles. This becomes the same task with the famous Kelvin’s problem: What space-filling arrangement of cells of equal volume has minimal surface area to present the ideal configuration of soap froth?\textsuperscript{123} After long history of the study in this problem, three possible solutions were reported successively. Figure 2.44b shows the interfacial configurations (Wigner-Seitz cell) of FCC (rhombic dodecahedron), BCC (tetrakaidecahedron), and A15 (six Goldberg tetrakaidecahedra, and two irregular
pentagonal dodecahedra), respectively. Weaire and Phelan discovered that A15 lattice creates an area smaller than BCC lattice by 0.3%, while BCC has interfacial area 0.7% smaller than FCC lattice.\textsuperscript{124} The calculations of the interfacial area in other FK phases do not exceed the result of A15 lattice. Therefore, the A15 seems to stand out to be the best solution to Kevin’s problem so far, which could probably be replaced by other better solution in the future. Analyses of bulk free energy regarding close packing show that the bulk free energy increase per micelle due to loose packing in A15 is roughly 1 $k_B T$ and 2 $k_B T$ comparing with BCC and FCC lattices, corresponding to entropy of about 0.5 $k_B$ and 1.5 $k_B$ per chain ($K_B$ is a Boltzmann constant!) (assuming about 160 dodecyl chains in one micelle).\textsuperscript{120} However, in the less unrestricted environment of A15 lattice, each chain has a few more orientational and conformational degrees of freedom. Calculation of the kind of surface entropy indicates that it is rather physically reasonable that the increase of orientational entropy of a chain due to less interdigitation in A15 lattice can reach 0.5 $k_B$ and 1.5 $k_B$ and make up the difference of the bulk free energy. In conclusion, the favored surface term results in the minimum free energy of A15 lattice \textit{via} minimizing interfacial area and maximizing entropy.
Kamien et al. later extended the similar calculation into large MW diblock copolymer melt using self-consistent field theory (SCFT).\textsuperscript{119} Linear and third generation branched diblock copolymers were both studied (Figure 2.45a). When the diblock copolymer containing A and B blocks self-assembled into ordered spherical phases, the incompressibility of the melt would deform the spheres into the Wigner-Seitz cells with polyhedron shape in the corresponding lattice. In the strong segregation limit, the polyhedra are composed of A block in the center and B block in the shell. The total free energy in the entire system arises from two terms: the AB interface tension and the stretching energy of the polymer blocks.

The AB interface tension is proportional to its AB interface area. As illustrated in the Figure 2.45b of a BCC Wigner-Seitz cell, the interface area between A and B will increase with the volume fraction \( \phi \).\textsuperscript{119} Assuming the AB interface adopts the same polyhedron shape with the overall Wigner-Seitz cell instead of a spherical shape (this assumption will be more accurate at large \( \phi \)), the calculation of AB interface tension
would become a similar case in dendrimer system discussed above, considering A15 lattice of equal volume cells minimizes the interfacial area. In the limit of φ close to 1 where central A blocks are surrounded by vanishingly thin B blocks, the AB interface area is the same with the interfacial area between particles. The second important contribution to the overall free energy comes from the conformation change of AB blocks. Because of incompressibility, polymer chains distributed in the whole polyhedra would have very different stretching conformation within each wedge of solid angle and distance to the boundary.

The calculation of these two items indicates a geometric frustration between interfacial tension and the stretching: the BCC lattice minimizes the free energy and A15 lattice minimizes the interface tension.\textsuperscript{119} In the low φ region, the center region and the interface shrink, resulting increased curvature. The interface becomes more close to spherical shape, and the effect of decreasing the stretching energy in BCC lattice dominates over the interface tension decrease in A15, making BCC being the equilibrium phase. In the contrary, A15 is favored as the more stable phase at high φ region. The phase diagrams of linear and branched diblock copolymers are calculated using SCFT in more details, and the results are in Figure 2.45c for linear copolymer and Figure 2.45d, for branched one. The A15 lattice is the most stable one among spherical phases as φ is close to unity, however, non-spherical columnar or gyroid phases were the ground states in the symmetric linear diblock copolymer. Considering branched architecture favors the curved interface and helps stabilize spherical phases, the A15 is calculated via SCFT being stable phase in branched third generation block copolymers at values of φ in between those of which BCC spherical phase and columnar hexagonal phase are stable.
The stability of A15 is confirmed in some condition by the calculation in both dendrimer and branched diblock copolymer systems. Very recently Shi et al. presented SCFT calculations for more complicated σ phase in asymmetric AB diblock copolymers and ABₐ miktoarm block systems. A key conformational parameter, \( \varepsilon^2 = m^2(\rho_A b_A^2/\rho_B b_B^2) \) is used to merge conformation asymmetry characterized by the segment length \( b \) and density \( \rho \), and architecture asymmetry \( m \). The relatively larger \( \varepsilon \) value favors spherical
phase formation with higher A/B interface curvature since the total stretching energy can be reduced in this case. It can be expected that creating large $\varepsilon$ value can largely expand the spherical phase region into high volume fraction $f$ of A block and make other spherical phases possible. Again, the competition between interface tension and stretching energy determines the stable spherical phase at different $\varepsilon$ and $f$ region.

The $\sigma$ phase has 30 spheres in one unit cell and five different Wigner-Seitz cells of irregular polyhedra. Both belongs to topological close packing phase, $\sigma$ phase and A15 phase have very close weighted average numbers of faces, 13.467 and 13.5, respectively. They are expected to have similar free energy items and occur at high $f$ region. Figures 2.46a and 2.46b show the calculation result for the phase diagrams of conformationally asymmetric AB diblock copolymers with different conformational parameter, $\varepsilon = 1.5$ and 2.0. The $\sigma$ phase appears as stable in a narrow region between BCC and HEX phases in the left side of phase diagram with $\varepsilon = 1.5$. This $\sigma$ phase region is largely expanded toward both directions in the phase diagram with $\varepsilon = 2.0$. This calculation of appearance of $\sigma$ phase matches well with the experiment results of Bates et al in the Polyisoprene-b-polylactide (IL-5) system discussed in section 2.4.4.4. In addition, there is a narrow region of FCC stable phase in the board of order-disorder transition. Note that A15 phase is not a stable phase in the whole diagram of linear AB diblock copolymers.

The phase diagrams of $\text{AB}_m$ with $m = 2$ and 3 are illustrated in Figures 2.46c and 2.46d. The $\sigma$ phase occurs as the major spherical phase, and compresses more bcc region as $m$ increases. The A15 phase can’t exist until $m$ value reaches 3 and further expands as $m$ increases to 4. A phase sequence of HEX $\rightarrow$ A15 $\rightarrow$ $\sigma$ $\rightarrow$ BCC $\rightarrow$ FCC can be expected at strong segregation $\chi N$ region toward the increasing of volume fraction of A.
In this calculation, the spherical domain volumes of A15 and σ phases are not kept equal, but optimized by SCFT. The A15 phase seems have larger spherical domain than σ, more favorable interfacial tension although with larger stretching energy in the region of high $\chi N$ and large $f$. 
Figure 2.46. Phase diagrams of conformationally asymmetric AB diblock copolymers are shown with (a) $\varepsilon = 1.5$ and (b) $\varepsilon = 2.0$. The red dot line in (b) indicates the metastable A15-BCC and A15-HEX boundaries. Phase diagrams of sphere phases for miktoarm AB$_m$ branched block copolymers, with $m = 2$ and 3 are shown in (c) and (d). Reproduced with permission from Ref 116. Copyright 2014 American Chemical Society.

It should be noticed that all of the theoretical calculations are assumed that the chain lengths are infinitely long to apply mean-field theory. However, in reality of block copolymers, their molecular lengths of each block in most of the cases are relatively short. Although theoretical calculations provide qualitative way to understand the pathway of achieving minimum free energy for these stable phases, the perfect theoretical and experimental matches are still long distance away from each other.

The predicted phase sequence of HEX $\rightarrow$ A15 $\rightarrow$ $\sigma$ $\rightarrow$ BCC has been verified in the dendrimer system during the heating process as discussed in Section 2.4.4.1. Ungar et
al. analyzed the relationship of A15, σ, BCC and FCC from the view of close contact between alkyl chain coronas. The ideal average radial distribution of volume dV/dr for supramolecular dendrimers in different phases were calculated, where V is the mean volume of all the polyhedra in each unit cell (Figure 2.47a). dV/dr is proportional to r^2 until a sphere of radius r = r_0 first touches the Voronoi cell, then gradually decrease to 0 when the r = 1 reaches the vertex having largest distance to the center of Voronoi cell. This dV/dr parameter can be related to molecular shape of the conical dendrimer into a parabolic (r^2) fan (r = 0 of dV/dr curve is the vertex of dendrimer), illustrated in the inset of Figure 2.47a. The dV/dr diagram shown in Figure 2.47a for limited region (0.4 < r <0.8) shows very similar trends for the four different phases. However, dV/dr spatial distribution of BCC exhibits a slightly higher peak and shorter tail, comparing with A15 and σ phases. This means the polyhedra in BCC lattice have denser mass distribution and contract quickly nearly the r_0 position. Considering the fact that dendrimer molecules often get lateral thermal expansion and longitudinal contraction during heating process, the BCC lattice fits best for the molecular envelope change and becomes a stable phase at high temperature. It is also easy to understand why FCC phase seldom be observed in dendrimer or block copolymer systems since the dV/dr spatial distribution of FCC shows the highest peak and longest tail, which is incompatible with dendrimer shape.

Both A15 and σ phases have nearly indistinguishable dV/dr distributions in Figure 2.48a. They introduced another more sensitive parameter: 

$$\frac{d\Omega}{dr} = \frac{d}{dr} \left( \frac{1}{r^2} \frac{dV}{dr} \right)$$
\( \Omega \) is the average solid angle of all the polyhedra subtended by the non-truncated part of the sphere. The value of \( \Omega \) is \( 4\pi \) before the sphere of radius \( r \) first touches the Voronoi cell \( (r < r_0) \), and reduce to 0 after \( r \) completely outgrown the Voronoi cell. Figure 2.47b shows the distribution of \( -d\Omega /dr \), the decrease rate of the average solid angle. For A15 lattice, the decrease of \( \Omega \) appears first as a step at \( r = 0.5 \). This indicates the start of close contact between CN14 polyhedra, along the three principal \(<100>\) directions. In \( \sigma \) phase, the close contacts begin near \( r = 0.5 \) position but only along one direction \([001]\) and involve 27\% spheres (8 out of 30 in tetragonal cell), comparing with the 75\% value (6 out of 8 in cubic cell) in A15 phase. These close contacts don’t occur at this position in BCC and FCC. The close contacts near \( r_0 \) position indicate the high repulsion potential between spherical coronas, which are unflavored and can be reduced if the alkyl chains can be moved aside. Close contacts are more tolerable at lower temperatures or in dendrimers with fewer tethered chains, since more lateral space can be available to decrease the entropy penalty. The close contact number near the position of \( r_0 \) is HEX > A15 > \( \sigma \) > BCC, which is consist with the phase sequence observed in the heating process.
Due to the complicated and undetermined aperiodic structure of quasicrystal, the theoretical analysis of quasicrystal phase in soft matter is hardly achieved. However, the fast development of algorithm and computer performance makes the computer simulation analysis of these complicated structures possible.\textsuperscript{118,125-129} Glotzer et al. utilized molecular simulation to study the DQC growth process in supercooled liquid. Their results show that the DQC growth does not simply copy the seed, but rather attaches nearby atoms into the seed surface illustrated in Figure 2.48.\textsuperscript{129} We have discussed previously that the icosahedron is the local free energy minimum state in supercooled melts or liquids. The growth mechanism of retaining the configurations of icosahedron clusters rather than copying the nucleus surface template needs less expensive rearrangement process, and is thus kinetically favored and more rapid to finally create DQC structure. In this sense, the DQC structure incorporating high degree of icosahedron and related CN13 polyhedron is more or less a kinetically trapped metastable “structural compromise” state. This is
demonstrated in the simulation that the system consistently forms a DQC structure initiated from all different seed nucleuses with various sizes or periodic approximant structures (A15, H, σ and Z lattice structures). Besides, DQC with different random tiling arrangements were produced initially from the same seed structure, indicating that DQC growth is mainly a stochastic entropy-driven process. The appearance of many phasons discussed previously (here is tiling discrepancies showed in Figure 2.48) demonstrates the existence of energetically constrained elements. This growth mechanism of DQC can explain why quasicrystals often preferentially form in rapidly quenched metallic alloys.

Figure 2.48. DQC structure grown from supercooled liquids. With the same periodic seed nucleus (blue), distinguishable QC tiling arrangements could be obtained indicating that DQC growth is mainly a stochastic entropy-driven process. Reproduced with permission from Ref 129. Copyright 2007 American Physical Society.

Note that in all the experimental results of soft matters or even in most simulations quasicrystals mostly occur as aperiodic only in two dimensions but periodic along the 12-fold symmetry or occasionally other fold symmetry. The three dimensional icosahedral quasicrystals (IQC) so far have only been observed in complicated metal alloys via the cooperation of several different atomic elements. A very recent intriguing molecular
dynamics simulation result by Glotzer et al. show that an IQC can be obtained from one-component system of uniform particles interacting via a tunable, isotropic pair.\(^\text{125}\) This forming dynamics and structure assembly process of IQC in this finding may help direct the right design in soft matters or nanoparticle systems to achieve three dimensional IQC structures.

The two examples discussed only deal with simple spherical particles and would be too simplified comparing with the complicated entropic and enthalpic interactions in soft matters. Glotzer et al. further built other effective models as the spherical micelle analogs including one simplified model of spherical micelle (MSM) and two tethered nano-sphere (TNS) based micelle forming systems to investigate the critical factors directing the formation of quasicrystals and approximants.\(^\text{118}\) Figure 2.49a shows the MSM model: a rigid scaffolding (diameter 5.27 ζ) having 42 points on the surface, and each point position is anchored with a small spherical particle (diameter ζ) via harmonic springs of stiffness k. The k value controls surface particle mobility as low k value makes large mobility, creating a “squishier” outer corona as in dendrimer spherical micelle. In the simulation with uniform MSM particles, BCC structures appeared when k ≤ 5 while FCC or HCP were obtained when k > 5. However, finite-size DQCs and DQC approximant ζ phase were obtained consistently at k ≤ 5 when different volume fractions of dimers were introduced (Figure 2.49a). In the free energy calculation of more simplified models, it’s observed that DQC and A15 become increasingly stable comparing with FCC/HCP, and even non-close packed BCC following the increase of dimer fraction. These results were further tested in the TNS models which are more similar to the naturally occurred self-assembled spherical micelles without precise control of surface particle mobility and
shape polydispersity. Figure 2.49b shows the mono-TNS model, which can phase separated into micelles having an outer shell of mobile nanospheres that mimic the dendrimer corona. DQCs with the characteristic tiling pattern shown in figure 2.49b occurred consistently from the mono-TNS model. It is not surprising that micelles constructed from mono-TNS naturally exhibit shape polydispersity with various aspect ratios (Figure 2.49b). Figure 2.49c shows the di-TNS model, the corresponding simulated σ phase structure, and shape polydispersity of assembled micelles. This clearly indicates non-close packing structures with lower surface contact area such as DQCs and approximants would be favored at increasing surface particle mobility and shape polydispersity.
Figure 2.49. (a) The MSM model: a rigid scaffolding (diameter 5.27 σ) having 42 points on the surface, and each point position is anchored with a small spherical particle (diameter σ) via harmonic springs of stiffness k. It can go through dimerization to introduce shape anisotropy. (b) Schematic of a mono-TNS building block. It can self-assemble into spherical micelles with a soft core (small blue beads) surrounded by relatively mobile hard shell nanoparticles (large white beads). The packing structures of 60 micelles and 120 micelles are shown in the upper right of (b). The asphericity analysis of shape polydispersity for the mono-TNS micelles is shown in the bottom of (b). (c) Schematic of the di-TNS building block, and the self-assembled σ phase from polydispersed micelles. Reproduced with permission from Ref 118. Copyright 2011 PNAS.
CHAPTER III

EXPERIMENTAL

3.1 Chemical Characterization

This part includes the necessary introduction of the chemicals and solvents. The full characterization is carried out such as $^1$H-NMR, $^{13}$CNMR, FT-IR, MALDI-TOF, and GPC.

3.1.1 Chemicals and Solvents

Tetrahydrofuran (THF, Fisher Scientific) was refluxed over sodium and distilled. Dichloromethane (DCM, Fisher Scientific), chloroform (Fisher Scientific, Certified ACS), ethyl acetate (Fisher Scientific), methanol (MeOH, Fisher Scientific, reagent grade), acetonitrile (CH$_3$CN, 99.8%, Aldrich), 1,2-dichloroethane (99.0%, Aldrich), benzene (99.8%, Aldrich), hexanes (Fisher Scientific, Certified ACS), Toluene (ACS grade, EMD), and styrene (99%, Sigma-Aldrich), propiolic acid (98%, Acros Organics), 4-Pentynoic acid (98%, Acros Organics), $p$-toluenesulfonic acid monohydrate ($p$-TsOH, 98.5%, Aldrich), $N,N'$-diisopropylcarbodiimide (DIPC, 99%, Aldrich), 1-hydroxybenzotriazole (HOBT, 95+, Aldrich), copper(I) bromide (98%, Acros Organics), $N,N,N',N''$-pentamethyldiethylenetriamine (PMDETA, 99%, Sigma-
Aldrich), 2-mercaptoethanol (99+%, Aldrich), thioglycolic acid (98+%, Aldrich), 3-mercaptopropionic acid (99+%, Aldrich), 1-thioglycerol (98+%, Fluka), 2-hydroxy-4'- (2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959, 98%, Sigma-Aldrich), aminopropylisobutyl POSS (BPOSS-NH₂, Hybrid Plastics) were used as received. VPOSS-OH was prepared from OctaVinyl POSS (Hybrid Plastics) according to the reported procedure (35). Tetrakis(4-azidophenyl)methane was prepared according to the reported procedure (36). Mono-hydroxyl heptavinyl substituted POSS (VPOSS-OH), azide-end-capped PS (PS-N3), middle-chain-functionalized PS (m-PS-N3), VPOSS-alkyne, VPOSS-S-2OH and VPOSS-PS were synthesized as reported.

3.1.2 Chemical Characterization

Nuclear Magnetic Resonance (NMR) Spectroscopy. ¹H and ¹³C NMR spectra of the samples were obtained in CDCl₃ (Sigma-Aldrich, 99.8% D) or CD₃OD (v/v = 1/1, whenever stated) solvents utilizing Varian Mercury 300 MHz NMR or 500 MHz NMR spectrometer. ¹H NMR spectra were referenced to the residual proton impurities in CDCl₃ at δ 7.27 ppm and ¹³C NMR spectra were referenced to ¹³CDCl₃ at δ 77.00 ppm.

Fourier-Transform Infrared (FTIR) Spectroscopy. Infrared spectra of the chemicals were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting sample films on KBr plates at room temperature. The data were processed using the Win-IR software.

Size Exclusion Chromatography (SEC). SEC analyses for the synthesized hybrid polymers were performed on a Waters 150-C Plus instrument equipped with three HR-
Styragel columns [100 Å, mixed bed (50/500/103/104 Å), mixed bed (103,104,106 Å)], and a triple detector system. The three detectors included a differential viscometer (Viscotek 100), a laser light scattering detector (Wyatt Technology, DAWN EOS, $\lambda = 670$ nm), and a differential refractometer (Waters 410). THF was used as the eluent with a flow rate of 1.0 mL/min at room temperature. Data processing was accomplished using the software on a workstation equipped with this system.

Matrix-assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) Mass Spectrometry. MALDI-TOF mass spectra of the samples were recorded on a Bruker Ultraflex III TOF/TOF mass spectrometer (Bruker Daltonics, Billerica, MA), equipped with a Nd:YAG laser which emits at a wavelength of 355 nm. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich, >98%) served as the matrix, which was dissolved in THF at a concentration of 20.0 mg/mL. The cationizing agent (sodium trifluoroacetate or silver trifluoroacetate) was dissolved in THF at a concentration of 10 mg/mL. The matrix and cationizing agent solutions were mixed in the ratio of 10/1 (v/v). Samples were dissolved in THF at a concentration of 5 mg/mL. The sample preparation procedure involved depositing 0.5 μL of matrix and salt mixture on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 μL of each sample on a spot of dry matrix, and adding another 0.5 μL of matrix and salt mixture on top of the dry sample. After the solvent was evaporated, the plate was inserted into the MALDI mass spectrometer for analysis in reflection mode. The mass scale was calibrated with standards of polystyrene or PMMA at the molecular weight region under consideration. Data analyses were conducted with Bruker’s flexAnalysis software.
3.2 Phase Identification and Morphology Confirmation in Bulk

The general procedure for a sample analysis is as the following sequence: TGA, DSC, SAXS/WAXD, and BF-TEM/SAED. These characterization methods are introduced in the following part.

Thermogravimetric Analysis (TGA). The nonisothermal decomposition experiments were carried out in a thermogravimetric analysis instrument (Model Q500, TA Instruments) protected by a nitrogen atmosphere. For each run of the experiments, initial mass of the samples used was about 3 mg, scanned within the temperature range of 30 to 650 °C with a heating rate of 10 °C/min.

Differential Scanning Calorimetry (DSC). Thermal properties of all the samples were characterized utilizing a PerkinElmer PYRIS Diamond DSC with an Intracooler 2P apparatus. The temperature and heat flow scales were calibrated at different heating and cooling rates (1−40 °C/min) using a series of standard materials. For each run of the experiments, initial mass of the samples used was about 3-5 mg under nitrogen flow.

Small-Angle X-ray Scattering (SAXS). SAXS experiments were performed on a Rigaku MicroMax 002+ instrument equipped with a two-dimensional (2D) multiwire area detector and a microfocus sealed copper tube. The working voltage and current used were 45 kV and 0.88 mA, with the wavelength of the X-ray is 0.154 nm. The scattering vector (q) was calibrated using standard of silver behenate with the primary reflection peak at (q = 1.067 nm⁻¹). The recording time for each sample was 10−20 min, depending on the scattering intensity. The data analysis was done with SAXSgui software.

Synchrotron SAXS experiments were performed at 12-ID-B station with X-ray energy of 12 KeV at the Advanced Photon Source of the Argonne National Laboratory.
The sample-to-detector distance was such as to provide a detecting range for scattering vector $q = 4\pi (\sin \theta)/\lambda$ of $0.01 < q < 0.30 \text{ Å}^{-1}$. The typical exposure time was 0.1 for each sample. A CCD area detector was used to receive scatter radiation. The scattering vector was calibrated using a silver behenate standard.

Wide Angle X-ray Diffraction (WAXD). WAXD experiments were conducted on the instrument equipped with a Rigaku 18 kW rotating anode generator and an image plate as the detector. The working voltage and current used were 200 kV and 50 mA, with the wavelength of the X-ray is 0.154 nm. The instrument was calibrated using silicon powders with 2θ value of 28.4° under Cu Kα radiation in the high angle region and silver behenate in the low angle region. The air scattering was subtracted. The 1D WAXD curve was integrated from the 2D image.

Bright Field Transmission Electron Microscopy (BF-TEM). A JEOL-1230 TEM with an accelerating voltage of 120 kV was utilized to record the bright field images of thin sections of different samples. Bright Field TEM images were collected on a digital CCD camera for different record time and processed with the accessory digital imaging system.

Selected Area Electron Diffraction (SAED). For the SAED experiments, they were carried out on TEM (Philips Tecnai 12) at an accelerating voltage of 120 kV. The tilting experiments were specifically conducted on the Philips TEM to provide the ED patterns of different crystallographic zones. The tilting axis is almost parallel to the beam stop. Samples were first adjusted to the eucentric height prior to the tilting. Camera length was chosen between 1.35 m to 4.2 m depending on the unit cell size range of diffraction samples. The d-spacing of each diffraction spot was calibrated by the standard thallous
chloride (TlCl) with the first diffraction ring of 0.384 nm. The collection time for the electron diffraction lasts from 1 second to 10 seconds.

3.3 Molecular Packing Simulation

After the unit cell determination by diffraction experiments including SAXS, WAXD and SAED, the final step for the structure determination is to solve the molecular packing in each unit cell. The molecular number in one unit cell can first be calculated knowing the MW, unit cell size, and the density. Note that the measured density was compared with the calculated density determined by the unit cell parameters to check if the determination of unit cell is correct. Then the molecular packing was simulated based on the diffraction intensity on different zones and overall powder diffraction pattern to generate the conformation and arrangement of molecules in the unit cell with minimized overall energy. The repeat corrections for the simulated diffraction intensity comparing with experiment diffraction intensity have to be performed to achieve best fitted simulated molecular packing.

Density Measurements. The sample was first placed in a vial with water followed by ultrasonication to remove the air bubbles embedded within the sample. Saturated potassium iodide aqueous solution was then added drop-wise into the vial to gradually increase the solution density at the interval of more than 20 min. The density of solution is identical with sample when the sample started to suspend in the middle of the solution.

Structure Simulation. Molecular modelling and diffraction pattern analyses of crystal structures were conducted on the Accelrys Cerius² software package. Basic unit
cell parameters determined by crystallographic experimental data from 1D WAXD and SAED experiments were used to build the unit cell. The positions of atoms in this unit cell were judged by comparing the calculated ED patterns with the experimentally observed patterns.

3.4 Synthesis of Three Categories of Giant Molecules

The synthesis procedures for three categories of giant molecules, giant tetrahedra, giant surfactants with multi-PS tails, and giant shape amphiphile of flat disk-like triphenylene-BPOSS conjugates would be covered separately. The synthesis design and their self-assemble behavior will be discussed in chapter IV, V, and VI, separately.

3.4.1 Giant Tetrahedra

BPOSS-Yne (X). To a 100 mL round-bottomed flask equipped with a magnetic stirring bar were added BPOSS-NH₂ (2.00 g, 2.33 mmol), propiolic acid (0.179 g, 2.56 mmol), HOBt (0.346 g, 2.56 mmol), and 25 mL freshly distilled THF. The flask was capped by a rubber septum. The mixture was cooled to 0 °C. With stirring, DIPC (0.381 g, 3.03 mmol) in 1 mL dried THF was added via a syringe. The solution was further stirred at room temperature for 24 h, and then evaporated by *in vacuo* to remove the solvent. The residue was purified by flash chromatography on silica gel with CH₂Cl₂/hexanes (v/v = 2/1) as the eluent to afford the product as a white solid (1.85 g, 87%). ¹H NMR (300 MHz, CDCl₃, ppm, δ): 5.95 (s, 1H, CH₂CH₂NH₂CO), 3.31 (q, 2H, SiCH₂C₂H₅NHCO), 2.77 (s, 1H, -C≡CH), 2.0-1.75 (m, 7H, SiCH₂C₂H₅H₆), 1.66 (m, 2H, SiCH₂C₂H₅CH₂NHCO), 0.96 (d, 42H, SiCH₂CH₂H₆), 0.67-0.55 (m, 16H, 121
Figure 3.1. Synthetic scheme of giant tetrahedra molecules. (i), (ii) CuBr, PMDETA, 70 °C, THF; (iii) thioglycolic acid (or 3-mercaptopropionic acid, 1-thioglycerol, and 2-mercaptoethanol), Irgacure 2959, THF, hv, 10 min, ~70 - 85%.

\[
\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCO} + \text{SiCH}_2\text{CHC}_2\text{H}_6.
\]
\[\text{\textsuperscript{13}C NMR (75 MHz, CDCl}_3, \text{ppm, } \delta: \text{151.98, 77.45, 72.82, 42.01, 25.67, 23.85, 22.67, 22.44, 9.35. MS (MALDI-TOF, m/z): Calc. for C}_{34}\text{H}_{71}\text{NO}_{13}\text{Si}_8: 925.31. Found: 948.55 (M+Na)^+.}\]

VPOSS-Yne (Y). VPOSS-OH (1.50 g, 2.30 mmol), propiolic acid (0.323 g, 4.60 mmol), \(p\)-TsOH (0.437 g, 2.30 mmol), 50 mL of benzene were added in a 100 mL round
flask fitted with a Dean-Stark trap and a reflux condenser. Activated 4 Å molecular sieves were placed in the Dean-Stark trap, which was wrapped with cotton and aluminum foil to prevent heat loss. The mixture was stirred in an oil bath and refluxed for 24 h. Then the solution was cooled to room temperature, and concentrated by rotary evaporator. The residual was directly applied to the top of the silica gel column. The final product was separated with CH₂Cl₂/hexanes (v/v = 1/1) as the eluent to afford a white solid (1.33 g, 82 %). ¹H NMR (300 MHz, CDCl₃, ppm, δ): 6.25-5.85 (m, 21H, CH=CH₂), 4.35 (t, 2H, CH≡CCOOCH₂), 2.84 (s, 1H, -C≡CH), 1.28 (t, 2H, SiCH₂). ¹³C NMR (75 MHz, CDCl₃, ppm, δ): 152.64, 137.15, 128.45, 74.78, 74.41, 62.76, 13.01. MS (MALDI-TOF, m/z): Calc. for C₁₉H₂₆O₁₄Si₈: 701.95. Found: 725.05 (M+Na)⁺.

General Procedure for Step i. Tetrakis(4-azidophenyl)methane (0.290 g, 0.599 mmol), X (1.50 g, 1.62 mmol) were added to a 100 mL Schlenk flask equipped with a magnetic stirring bar and dissolved in 20 mL dried THF. CuBr (0.010 g, 0.070 mmol) was suspended in the solution. The resulting solution was degassed by three freeze-pump-thaw cycles before adding PMDETA (30 mg, 0.173 mmol) via pipette. The mixture was further degassed by one more cycle and was then stirred at 70 °C for 24 h. After cooled to room temperature, the solvent was removed by rotary evaporator. The residue was applied to the top of the silica gel column. The different products (1 and B1-B3) were separated by using a mixture of EA/hexane as the gradient eluent (v/v = 1/8 to 1/4).

Compound 1. Appearance: White solid (120 mg, 10%). ¹H NMR (500 MHz, CDCl₃, ppm, δ): 8.50 (s, 4H, triazole-H), 7.82 (d, 8H, triazole-Arₘ-H), 7.50 (d, 8H, 123
triazole-Ar-H), 7.15 (t, 4H, -CH$_2$NHCO), 3.49 (q, 8H, SiCH$_2$CH$_2$NHCO), 1.93-1.82 (m, 28H, SiCH$_2$CH$_2$H$_6$), 1.80-1.73 (m, 8H, SiCH$_2$CH$_2$NHCO), 0.96 (d, 168H, SiCH$_2$CH$_2$H$_6$), 0.71 (t, 8H, SiCH$_2$CH$_2$NHCO), 0.62 (t, 56H, SiCH$_2$CH$_2$H$_6$). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm, δ): 159.50, 146.20, 144.26, 135.28, 132.15, 123.09, 120.52, 64.31, 41.57, 30.34, 25.67, 23.88, 23.10, 22.49, 9.50. MS (MALDI-TOF, m/z): Calc. for C$_{161}$H$_{300}$N$_{16}$O$_{52}$Si$_{32}$: 4185.39. Found: 4208.79 (M+Na)$^+$. Compound B1. Appearance: Pale yellow solid (0.30 g, 17%). $^1$H NMR (300 MHz, CDCl$_3$, ppm, δ): 8.52 (s, 3H, triazole-H), 7.73 (d, 6H, triazole-Ar$_m$-H), 7.44 (d, 6H, triazole-Ar$_o$-H), 7.26 (t, 3H, -CH$_2$NHCO), 7.24 (d, 2H, azido-Ar$_m$-H), 7.00 (d, 2H, azido-Ar$_o$-H), 3.48 (q, 6H, SiCH$_2$CH$_2$H$_6$), 1.96-1.70 (m, 27H, SiCH$_2$CH$_2$H$_6$ + SiCH$_2$H$_5$CH$_2$NHCO), 1.00-0.95 (m, 126H, SiCH$_2$CH$_2$H$_6$), 0.71 (t, 6H, SiCH$_2$H$_5$CH$_2$NHCO), 0.68-0.55 (m, 42H, SiCH$_2$CH$_2$H$_6$). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm, δ): 159.50, 146.62, 144.13, 141.29, 139.03, 135.02, 132.06, 131.93, 123.10, 120.25, 118.90, 63.99, 41.47, 29.58, 25.62, 23.80, 22.44, 21.70, 9.42. MS (MALDI-TOF, m/z): Calc. for C$_{127}$H$_{229}$N$_{15}$O$_{39}$Si$_{24}$: 3260.04. Found: 3283.24 (M+Na)$^+$. Compound B2. Appearance: Pale yellow solid (0.25 g, 14%). $^1$H NMR (300 MHz, CDCl$_3$, ppm, δ): 8.47 (s, 2H, triazole-H), 7.70 (d, 4H, triazole-Ar$_m$-H), 7.41 (d, 4H, triazole-Ar$_o$-H), 7.26 (t, 2H, -CH$_2$NHCO), 7.21 (d, 4H, azido-Ar$_m$-H), 7.00 (d, 4H, azido-Ar$_o$-H), 3.49 (t, 4H, SiCH$_2$CH$_2$H$_5$NHCO), 1.99-1.75 (m, 18H, SiCH$_2$CH$_2$H$_6$ + SiCH$_2$H$_5$CH$_2$NHCO), 1.05-0.90 (m, 84H, SiCH$_2$CH$_2$H$_6$), 0.71 (t, 4H, SiCH$_2$H$_5$CH$_2$NHCO), 0.65-0.55 (m, 28H, SiCH$_2$CH$_2$H$_6$). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm, δ): 159.58, 147.22, 144.12, 141.85, 138.80, 134.87, 132.15, 132.02, 123.10, 120.16,
118.79, 63.80, 41.55, 25.67, 23.85, 23.09, 22.47, 9.49. MS (MALDI-TOF, m/z): Calc. for C_{93}H_{158}N_{14}O_{26}Si_{16}: 2334.78. Found: 2352.97 (M+Na)^+.

Compound B3. Appearance: Pale yellow solid (0.26 g, 11%). ^{1}H NMR (300 MHz, CDCl_{3}, ppm, δ): 8.46 (s, 1H, triazole-H), 7.67 (d, 2H, triazole-Ar_m-H), 7.38 (d, 2H, triazole-Ar_o-H), 7.22 (t, 1H, -CH_{2}NHCO), 7.19-7.13 (m, 6H, azido-Ar_m-H), 6.98-6.93 (m, 6H, azido-Ar_o-H), 3.49 (t, 2H, SiCH_{2}CH_{2}CH_{2}NHCO), 1.96-1.70 (m, 9H, SiCH_{2}HC_{2}H_{6} + SiCH_{2}CH_{2}CH_{2}NHCO), 1.05-0.95 (m, 42H, SiCH_{2}HC_{2}H_{6}), 0.71 (t, 2H, SiCH_{2}CH_{2}CH_{2}NHCO), 0.65-0.61 (m, 14H, SiCH_{2}CH_{2}H_{6}). ^{13}C NMR (75 MHz, CDCl_{3}, ppm, δ): 159.61, 147.65, 144.00, 142.83, 142.32, 138.44, 138.16, 134.64, 132.09, 131.98, 123.11, 119.92, 118.54, 118.35, 63.49, 41.50, 30.28, 25.63, 23.82, 23.05, 22.43, 9.44. MS (MALDI-TOF, m/z): Calc. for C_{59}H_{87}N_{13}O_{13}Si_{8}: 1409.47. Found: 1432.56 (M+Na)^+.

General Procedure for Step ii. To a 100 mL Schlenk flask equipped with a magnetic stirring bar were added the intermediate compounds B (B1, B2, or B3) and Y (at different molar ratios), CuBr, and 15 mL dried THF. The resulting solution was degassed by three freeze-pump-thaw cycles before adding PMDETA via pipette. The mixture was further degassed by one more cycle and was then stirred at 70 °C for 12 h. After cooled to room temperature, the solvent was removed by rotary evaporator. The residue was purified by flash chromatography on silica gel with EA/hexanes mixtures as the eluent to afford the product.

Compound C1. Compound B1 (280 mg, 0.0857 mmol), Y (66.3 mg, 0.0943 mmol), CuBr (5.0 mg, 0.035 mmol), and PMDETA (32 mg, 0.184 mmol) were reacted following the general procedure for step ii. Product: White solid (140 mg, 41%). ^{1}H NMR (300
MHz, CDCl₃, ppm, δ): 8.52 (s, 3H, triazole-H), 8.48 (s, 1H, triazole-H), 7.80-7.76 (m, 8H, triazole-Arᵣ-H), 7.51-7.47 (m, 8H, triazole-Arᵣ-CH₂), 7.24 (t, 3H, -CH₂NHC), 6.15-5.85 (m, 21H, CH=CH₂), 4.57 (t, 2H, SiCH₂CH₂OCO), 3.49 (q, 6H, SiCH₂CH₂CH₂NHCO), 1.95-1.70 (m, 27H, SiCH₂CH₂NHCO), 1.04-0.89 (m, 126H, SiCH₂CH₂H₆), 0.70 (t, 6H, SiCH₂CH₂CH₂NHCO), 0.65-0.55 (m, 42H, SiCH₂CH₂H₆) ³¹C NMR (75 MHz, CDCl₃, ppm, δ): 160.28, 159.50, 146.32, 146.16, 144.22, 140.95, 137.15, 137.04, 135.26, 135.06, 132.11, 132.07, 128.49, 125.18, 125.12, 120.71, 120.50, 67.92, 64.29, 61.97, 41.54, 25.66, 23.85, 23.08, 22.47, 13.31, 9.47. MS (MALDI-TOF, m/z): Calc. for C₁₄₆H₂₅₅N₁₅O₅₃Si₃₂: 3962.03. Found: 3985.30 (M+Na)⁺.

Compound C2. Compound B2 (150 mg, 0.0649 mmol), Y (95.9 mg, 0.136 mmol), CuBr (5.0 mg, 0.035 mmol), and PMDETA (35 mg, 0.201 mmol) were reacted following the general procedure for step ii. Product: White solid (143 mg, 58%). ¹H NMR (300 MHz, CDCl₃, ppm, δ): 8.53 (s, 2H, triazole-H), 8.48 (s, 2H, triazole-H), 7.79-7.75 (m, 8H, triazole-Arᵣ-H), 7.56-7.45 (m, 8H, triazole-Arᵣ-CH₂), 7.24 (t, 3H, -CH₂NHC), 6.20-5.83 (m, 42H, CH=CH₂), 4.56 (t, 4H, SiCH₂CH₂OCO), 3.49 (q, 4H, SiCH₂CH₂CH₂NHCO), 1.95-1.70 (m, 18H, SiCH₂CH₂CH₂H₆ + SiCH₂CH₂CH₂NHCO), 1.41 (t, 4H, SiCH₂CH₂OCO), 1.05-0.90 (m, 84H, SiCH₂CH₂CH₂H₆), 0.70 (t, 4H, SiCH₂CH₂CH₂NHCO), 0.65-0.55 (m, 28H, SiCH₂CH₂H₆). ¹³C NMR (75 MHz, CDCl₃, ppm, δ): 160.21, 159.46, 146.26, 146.10, 144.18, 140.89, 137.12, 137.01, 135.24, 135.03, 132.05, 128.44, 125.15, 123.10, 120.68, 120.47, 64.27, 61.91, 41.50, 25.63, 23.08, 23.04, 22.43, 13.25, 9.43. MS (MALDI-TOF, m/z): Calc. for C₁₃₁H₂₁₀N₁₄O₅₄Si₃₂: 3738.67. Found: 3762.08 (M+Na)⁺.
Compound C3. Compound B3 (70.0 mg, 0.0496 mmol), Y (115 mg, 0.164 mmol), CuBr (5.0 mg, 0.035 mmol), and PMDETA (32 mg, 0.184 mmol) were reacted following the general procedure for step ii. Product: White solid (110 mg, 63%). $^1$H NMR (300 MHz, CDCl$_3$, ppm, δ): 8.43 (s, 1H, triazole-$H$), 8.40 (s, 3H, triazole-$H$), 7.69 (d, 8H, triazole-$Ar_m$-$H$), 7.40 (d, 8H, triazole-$Ar_o$-$H$), 7.15 (t, 1H, $CH_2NHCO$), 6.10-5.75 (m, 63H, $CH=CH_2$), 4.49 (t, 6H, SiCH$_2CH_2OCO$), 3.41 (q, 2H, SiCH$_2CH_2CH_2NHCO$), 1.90-1.60 (m, 9H, SiCH$_2CHC_2H_6$ + SiCH$_2CH_2CH_2NHCO$), 0.93-0.85 (m, 42H, SiCH$_2CHC_2H_6$), 0.65 (t, 2H, SiCH$_2CH_2CH_2NHCO$), 0.59-0.50 (m, 14H, SiCH$_2CHC_2H_6$). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm, δ): 160.25, 159.45, 146.25, 146.08, 144.23, 140.95, 137.16, 137.06, 135.26, 135.06, 132.02, 128.44, 125.17, 123.09, 120.75, 120.66, 120.50, 64.29, 61.97, 29.65, 25.65, 23.84, 23.07, 22.45, 13.30, 9.46. MS (MALDI-TOF, m/z): Calc. for C$_{116}$H$_{167}$N$_{15}$O$_5$Si$_{32}$: 3513.35. Found: 3536.80 (M+Na)$^+$. 

General procedure for step iii. To an open vial were added reactants C with vinyl groups (C1, C2 or C3), thiol ligands (thioglycolic acid, 3-mercaptopropionic acid, 1-thioglycerol, or 2-mercaptoethanol), the photo-initiator Irgacure 2959, and 2 mL THF. After irradiation under a 365 nm UV lamp at room temperature for 10 minutes, the mixture was purified by precipitation from the concentrated THF solution in water three times. The product was collected by filtering and then dried in vacuo.

Compound 2a. C1 (43.1 mg, 0.0108 mmol), thioglycolic acid (34.8 mg, 0.38 mmol), and the photo-initiator Irgacure 2959 (1 mg, 0.0045 mmol) were reacted following the general procedure for step iii. Product: white solid (33.9 mg, 68%). $^1$H NMR (500 MHz, CDCl$_3$, ppm, δ): 8.76 (br, 7H, -COOH), 8.71 (s, 3H, triazole-$H$), 8.61 (s,
1H, triazole-\( \text{-H} \), 7.80 (d, 8H, triazole-Ar\textsubscript{n}-\( \text{-H} \)), 7.51 (d, 8H, triazole-Ar\textsubscript{o}-\( \text{-H} \)), 7.37 (t, 3H, -CH\textsubscript{2}NHCO), 4.55 (t, 2H, SiCH\textsubscript{2}CH\textsubscript{2}OO), 3.50 (q, 6H, SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NHCO), 3.27 (d, 14H, CH\textsubscript{2}SCH\textsubscript{2}COOH), 2.72 (m, 14H, CH\textsubscript{2}SCH\textsubscript{2}COOH), 1.93-1.80 (m, 21H, SiCH\textsubscript{2}CH(C\textsubscript{2}H\textsubscript{5})\textsubscript{2}H\textsubscript{6}), 1.80-1.72 (m, 6H, SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NHCO), 1.36 (t, 2H, SiCH\textsubscript{2}CH\textsubscript{2}OO), 1.04 (m, 14H, SiCH\textsubscript{2}CH\textsubscript{2}S), 1.00-0.90 (m, 126H, SiCH\textsubscript{2}CHC\textsubscript{2}H\textsubscript{6}), 0.71 (t, 6H, SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NHCO), 0.65-0.56 (m, 42H, SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NHCO).

\(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}, ppm, δ): 175.34, 175.19, 174.80, 160.41, 160.04, 151.50, 146.63, 146.20, 143.72, 140.60, 137.16, 135.80, 135.21, 134.88, 132.15, 128.24, 125.44, 123.74, 120.72, 120.57, 67.95, 64.33, 41.74, 34.22, 33.42, 30.33, 29.68, 25.68, 23.87, 22.97, 22.47, 22.05, 12.15, 9.49.

Compound 2b. C1 (40.5 mg, 0.0102 mmol), 3-mercaptopropionic acid (45.5 mg, 0.43 mmol), and the photo-initiator Irgacure 2959 (1 mg, 0.0045 mmol) were reacted following the general procedure for step iii. Product: white solid (28.3 mg, 59%).

\(^{1}\)H NMR (300 MHz, CDCl\textsubscript{3}, ppm, δ): 9.67 (br, 7H, -COOH), 8.78 (s, 3H, triazole-\( \text{-H} \)), 8.60 (s, 1H, triazole-\( \text{-H} \)), 7.80 (d, 8H, triazole-Ar\textsubscript{n}-\( \text{-H} \)), 7.50 (d, 8H, triazole-Ar\textsubscript{o}-\( \text{-H} \)), 7.38 (t, 3H, -CH\textsubscript{2}NHCO), 4.56 (t, 2H, SiCH\textsubscript{2}CH\textsubscript{2}OO), 3.49 (q, 6H, SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NHCO), 2.9-2.6 (m, 42H, CH\textsubscript{2}SCH\textsubscript{2}CH\textsubscript{2}COOH), 1.93-1.80 (m, 21H, SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}H\textsubscript{6}), 1.80-1.70 (m, 6H, SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NHCO), 1.36 (t, 2H, SiCH\textsubscript{2}CH\textsubscript{2}OO), 1.02 (m, 14H, SiCH\textsubscript{2}CH\textsubscript{2}S), 1.00-0.90 (m, 126H, SiCH\textsubscript{2}CHC\textsubscript{2}H\textsubscript{6}), 0.71 (t, 6H, SiCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NHCO), 0.65-0.56 (m, 42H, SiCH\textsubscript{2}CHC\textsubscript{2}H\textsubscript{6}).

\(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}, ppm, δ): 177.02, 176.85, 176.75, 160.41, 160.04, 151.50, 146.19, 143.75, 140.71, 135.80, 135.20, 134.94, 132.14, 128.24, 125.49, 123.81, 120.69, 120.49, 105.00, 64.33, 41.74, 34.94, 34.22, 30.32, 29.68, 26.68, 26.12, 25.67, 23.88, 22.98, 22.47, 12.82, 9.49.
Compound 2c. C1 (45.0 mg, 0.0114 mmol), 1-thioglycerol (25.9 mg, 0.239 mmol), and the photo-initiator Irgacure 2959 (1 mg, 0.0045 mmol) were reacted following the general procedure for step iii. Product: white solid (39.8 mg, 74%). $^1$H NMR (500 MHz, CDCl$_3$, ppm, δ): 8.62 (s, 1H, triazole-$H$), 8.57 (s, 3H, triazole-$H$), 7.79 (m, 8H, triazole-$Ar_m-H$), 7.49 (d, 8H, triazole-$Ar_o-H$), 7.27 (t, 3H, -CH$_2$NHCO), 4.55 (t, 2H, SiCH$_2$CH$_2$OCO), 3.9-3.42 (m, 27H, SCH$_2$CH$_2$(OH)CH$_2$OH + SiCH$_2$CH$_2$H$_2$NHCO), 2.78-2.55 (m, 28H, CH$_2$SCH$_2$CH(OH)CH$_2$OH), 1.96-1.72 (m, 27H, SiCH$_2$CH$_2$H$_6$ + SiCH$_2$H$_3$CH$_2$NHCO), 1.04 (m, 14H, SiCH$_2$CH$_2$S), 1.00-0.90 (m, 126H, SiCH$_2$CH$_2$H$_6$), 0.70 (t, 6H, SiCH$_2$CH$_2$CH$_2$NHCO), 0.65-0.56 (m, 42H, SiCH$_2$CH$_2$H$_6$). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm, δ): 159.67, 146.15, 144.04, 135.79, 135.22, 132.12, 125.79, 125.47, 123.30, 120.53, 71.09, 70.95, 65.38, 64.66, 41.60, 35.40, 34.20, 30.31, 26.67, 25.65, 23.86, 23.03, 22.45, 21.15, 12.90, 9.48.

Compound 2d. C1 (45.1 mg, 0.0114 mmol), 2-mercaptoethanol (21.8 mg, 0.279 mmol), and the photo-initiator Irgacure 2959 (1 mg, 0.0045 mmol) were reacted following the general procedure for step iii. Product: white solid (39.1 mg, 76%). $^1$H NMR (500 MHz, CDCl$_3$, ppm, δ): 8.60 (s, 1H, triazole-$H$), 8.55 (s, 3H, triazole-$H$), 7.78 (d, 8H, triazole-$Ar_m-H$), 7.49 (d, 8H, triazole-$Ar_o-H$), 7.27 (t, 3H, -CH$_2$NHCO), 7.25 (t, 3H, -CH$_2$NHCO), 4.56 (t, 2H, SiCH$_2$CH$_3$OCO), 3.74 (m, 14H, SCH$_2$CH$_3$OH), 3.47 (t, 6H, SiCH$_2$CH$_2$H$_3$NHCO), 2.78-2.65 (m, 28H, CH$_2$SCH$_2$CH$_2$OH), 1.95-1.80 (m, 27H, SiCH$_2$CH$_3$CH$_3$H, + SiCH$_2$CH$_2$CH$_2$OCO), 1.37 (t, 2H, SiCH$_3$CH$_2$OCO), 1.03 (t, 14H, SiCH$_2$CH$_3$S), 0.95 (m, 126H, SiCH$_2$CH$_2$H$_6$), 0.73 (t, 6H, SiCH$_2$CH$_2$CH$_2$OCO), 0.61 (t, 42H, SiCH$_2$CH$_2$H$_6$). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm, δ): 159.59, 151.51, 146.15, 129.
Compound 3a. C2 (49.0 mg, 0.0130 mmol), thioglycolic acid (82.8 mg, 0.90 mmol), and the photo-initiator Irgacure 2959 (1 mg, 0.0045 mmol) were reacted following the general procedure for step iii. Product: white solid (50.1 mg, 76%). $^1$H NMR (500 MHz, CDCl$_3$, ppm, δ): 8.83 (s, 2H, triazole-$H$), 8.69 (s, 2H, triazole-$H$), 7.82 (m, 8H, triazole-$Ar_m$-$H$), 7.51 (m, 10H, triazole-$Ar_o$-$H$ + CH$_2$NHCO), 6.89 (br, 7H, -COOH), 4.54 (br, 4H, SiCH$_2$CH$_2$OCO), 3.48 (br, 4H, SiCH$_2$CH$_2$CH$_2$NHCO), 3.26 (br, 28H, CH$_2$SCH$_2$COOH), 2.73 (br, 28H, CH$_2$SCH$_2$COOH), 1.93-1.80 (m, 14H, SiCH$_2$CH$_2$C$_6$H$_5$), 1.80-1.72 (m, 4H, SiCH$_2$CH$_2$CH$_2$NHCO), 1.36 (br, 4H, SiCH$_2$CH$_2$OCO), 1.03 (m, 28H, SiCH$_2$CH$_2$S), 1.00-0.90 (m, 86H, SiCH$_2$CH$_2$C$_6$H$_5$), 0.70 (t, 4H, SiCH$_2$CH$_2$CH$_2$NHCO), 0.65-0.56 (m, 28H, SiCH$_2$CH$_2$C$_6$H$_5$). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm, δ): 175.22, 175.06, 160.62, 160.35, 140.50, 135.80, 132.19, 128.29, 125.50, 124.13, 120.61, 41.94, 34.22, 33.39, 30.32, 29.68, 26.60, 25.68, 23.84, 22.88, 22.47, 21.16, 12.17, 9.50.

Compound 3b. C2 (48.0 mg, 0.0128 mmol), 3-mercaptopropionic acid (100 mg, 0.95 mmol), and the photo-initiator Irgacure 2959 (1 mg, 0.0045 mmol) were reacted following the general procedure for step iii. Product: white solid (40.3 mg, 60%). $^1$H NMR (300 MHz, CDCl$_3$, ppm, δ): 9.28 (br, 14H, -COOH), 8.90 (s, 2H, triazole-$H$), 8.66 (s, 2H, triazole-$H$), 8.03 (t, 2H, -CH$_2$NHCO), 7.82 (d, 8H, triazole-$Ar_m$-$H$), 7.52 (d, 8H, triazole-$Ar_o$-$H$), 4.52 (br, 4H, SiCH$_2$CH$_2$OCO), 3.49 (br, 4H, SiCH$_2$CH$_2$CH$_2$NHCO), 2.95-2.45 (m, 84H, CH$_2$SCH$_2$CH$_2$COOH), 1.95-1.65 (m, 18H, SiCH$_2$CH$_2$C$_6$H$_5$ + SiCH$_2$CH$_2$CH$_2$NHCO), 1.25 (m, 4H, SiCH$_2$CH$_2$OCO), 1.10-0.85 (m, 112H, SiCH$_2$CH$_2$S
+ SiCH$_2$CH$_2$H$_6$), 0.74 (t, 4H, SiCH$_3$CH$_2$CH$_2$NHCO), 0.60 (t, 28H, SiCH$_3$CH$_2$H$_6$). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm, δ): 177.40, 160.63, 160.26, 135.72, 132.23, 128.23, 125.21, 120.61, 67.95, 67.35, 34.64, 34.21, 30.30, 29.69, 26.42, 26.01, 25.69, 25.59, 23.85, 22.45, 22.40, 12.73, 9.46.

Compound 3c. C$_2$ (45.0 mg, 0.0120 mmol), 1-thioglycerol (90.4 mg, 0.840 mmol), and the photo-initiator Irgacure 2959 (1 mg, 0.0045 mmol) were reacted following the general procedure for step iii. Product: white solid (40.5 mg, 64%). $^1$H NMR (500 MHz, CDCl$_3$, ppm, δ): 8.74 (s, 2H, triazole-H$_6$), 8.66 (s, 2H, triazole-H$_6$), 7.80 (br, 8H, triazole-Ar$_m$-H$_6$), 7.49 (m, 8H, triazole-Ar$_o$-H$_6$), 7.35 (br, 2H, -CH$_2$NHCO), 4.75-4.25 (m, 32H, SiCH$_2$CH$_2$OCO + SCH$_2$CH(OH)CH$_2$OH), 3.95-3.42 (m, 48H, SCH$_2$CH(OH)CH$_2$OH + SiCH$_3$CH$_2$H$_6$), 2.80-2.55 (m, 56H, CH$_2$SCH$_2$CH(OH)CH$_2$OH), 1.96-1.72 (m, 18H, SiCH$_2$CH$_2$H$_6$ + SiCH$_2$CH$_2$CH$_2$NHCO), 1.04-0.90 (m, 112H, SiCH$_3$CH$_2$S + SiCH$_2$CH$_2$H$_6$), 0.70 (br, 4H, SiCH$_3$CH$_2$CH$_2$NHCO), 0.65-0.56 (m, 28H, SiCH$_3$CH$_2$H$_6$). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm, δ): 143.82, 135.79, 132.06, 128.99, 128.23, 125.48, 125.16, 123.50, 120.74, 120.06, 110.04, 71.18, 65.29, 35.17, 34.21, 30.32, 26.73, 25.67, 23.86, 23.00, 22.45, 21.15, 12.95, 9.52.

Compound 4a. C$_3$ (38.0 mg, 0.0108 mmol), thioglycolic acid (64.4 mg, 0.70 mmol), and the photo-initiator Irgacure 2959 (1 mg, 0.0045 mmol) were reacted following the general procedure for step iii. Product: white solid (37.3 mg, 70%). $^1$H NMR (500 MHz, CD$_3$OD/CDCl$_3$ v/v = 1/1 mixture, ppm, δ): 9.10 (s, 3H, triazole-H$_6$), 8.93 (s, 1H, triazole-H$_6$), 8.10-7.98 (m, 9H, triazole-Ar$_m$-H + CH$_2$NHCO), 7.72 (d, 8H, triazole-Ar$_o$-H$_6$), 4.69 (t, 6H, SiCH$_3$CH$_2$OCO), 3.58 (t, 2H, SiCH$_3$CH$_2$CH$_2$NHCO), 3.43-3.35 (m, 42H, CH$_2$SCH$_2$COOH), 2.95-2.85 (m, 42H, CH$_3$SCH$_2$COOH), 2.05-1.95 (m,
Compound 4b. C3 (38.0 mg, 0.0108 mmol), 3-mercaptopropionic acid (74.2 mg, 0.70 mmol), the photo-initiator Irgacure 2959 (1 mg, 0.0045 mmol) were reacted following the general procedure for step iii. Product: white solid (41.3 mg, 61%). $^1$H NMR (500 MHz, CD$_3$OD/CDCl$_3$ v/v = 1/1 mixture, ppm, δ): 9.08 (s, 3H, triazole-$H$), 8.92 (s, 1H, triazole-$H$), 8.00 (m, 9H, triazole-Ar$_m$-$H$ + CH$_2$NHCO), 7.68 (d, 8H, triazole-Ar$_o$-$H$), 4.66 (t, 6H, SiCH$_2$CH$_2$OCO), 3.53 (t, 2H, SiCH$_2$CH$_2$NHCO), 3.00-2.60 (m, 126H, C$_H$$_2$SC$_H_2$CH$_2$COOH), 2.05-1.80 (m, 9H, SiCH$_2$CH$_2$C$_H_6$ + SiCH$_2$CH$_2$CH$_2$NHCO), 1.36 (m, 6H, SiCH$_2$CH$_2$OCO), 1.25-1.10 (m, 42H, SiCH$_2$CH$_2$S), 1.10-1.00 (m, 42H, SiCH$_2$CH$_2$H$_6$), 0.67 (m, 2H, SiCH$_2$CH$_2$NHCO), 0.75-0.65 (m, 14H, SiCH$_2$CH$_2$H$_6$). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm, δ): 173.78, 159.85, 145.97, 142.90, 139.77, 134.32, 131.51, 125.56, 124.43, 123.24, 119.79, 119.74, 63.76, 60.91, 48.84, 33.80, 33.47, 29.19, 25.98, 25.12, 24.53, 23.15, 22.23, 21.68, 21.61, 11.95, 8.68.

Compound 4c. C3 (38.0 mg, 0.0108 mmol), 1-thioglycerol (74.1 mg, 0.680 mmol), the photo-initiator Irgacure 2959 (1 mg, 0.0045 mmol) were reacted following the general procedure for step iii. Product: white solid (39.2 mg, 63%). $^1$H NMR (500 MHz, CD$_3$OD/CDCl$_3$ v/v = 1/1 mixture, ppm, δ): 9.22 (s, 3H, triazole-$H$), 9.04 (s, 1H, triazole-$H$), 8.17-8.12 (m, 9H, triazole-Ar$_m$-$H$ + CH$_2$NHCO), 7.83 (d, 8H, triazole-Ar$_o$-$H$), 4.82 (t,
6H, SiCH$_2$CH$_2$OCO), 4.50 (br, SCH$_2$CH(OH)CH$_2$OH), 4.05-3.75 (m, 63H, SCH$_2$C(H)OHCH$_2$OH), 3.70 (q, 2H, SiCH$_2$CH$_2$CH$_2$NHCO), 3.00-2.80 (m, 84H, CH$_2$SCH$_2$CH(OH)CH$_2$OH), 2.15-2.05 (m, 7H, SiCH$_2$CHC$_2$H$_6$), 2.05-1.97 (m, 2H, SiCH$_2$CH$_2$CH$_2$NHCO), 1.62 (t, 6H, SiCH$_2$CH$_2$OCO), 1.35-1.25 (m, 42H, SiCH$_3$ CH$_2$S), 1.20 (d, 42H, SiCH$_2$CHC$_2$H$_6$), 0.97 (t, 2H, SiCH$_2$CH$_2$CH$_2$NHCO), 0.86 (t, 14H, SiCH$_2$CHC$_2$H$_6$). $^{13}$C NMR (125 MHz, CD$_3$OD/CDCl$_3$ : 1/1, ppm, δ): 160.03, 159.96, 146.09, 145.85, 143.06, 139.84, 134.60, 134.39, 131.63, 125.65, 124.62, 123.35, 119.97, 119.90, 70.70, 60.50, 64.38, 61.13, 34.51, 29.36, 28.93, 26.05, 24.73, 23.25, 22.34, 21.77, 12.47, 12.22, 8.83.
Figure 3.2. Representative $^1$H-NMR spectra of giant tetrahedra molecules and their precursors. (A) $^1$H-NMR spectrum of B3; (B) $^1$H-NMR spectrum of C3; (C) $^1$H-NMR spectrum of 4a; (D) $^1$H-NMR spectrum of 4b; (E) $^1$H-NMR spectrum of 4c; (F) $^1$H-NMR spectrum of 2a; (G) $^1$H-NMR spectrum of 1.
Figure 3.3. MALDI-TOF mass spectroscopy characterization of giant tetrahedra precursors. (A) MALDI-TOF mass spectra of B1-B3. Due to the facile release of N$_2$ from the azido groups under the experimental conditions, some fragments were also observed; (B) MALDI-TOF mass spectra of C1-C3 and I. For C3, some fragments were observed due to the bond breakage of vinyl groups, but the strongest peak matches well with the calculated molecular weight.
3.4.2 Giant Surfactants

The synthesis of DPOSS-PS, DPOSS-2PS_m and DPOSS-3PS_m series can be referred in the previous literature published by our group and won’t be covered due to the limitation of the dissertation. We will only focus on the synthesis of DPOSS-4PS_m.

![Synthetic scheme of VPOSS-2alkyne.](image)

**Figure 3.4.** Synthetic scheme of VPOSS-2alkyne.

Preparation of VPOSS-2alkyne. To a 100 mL round-bottomed flask equipped with a magnetic stirring bar were added VPOSS-S-2OH (741 mg, 1.0 mmol), 4-pentynoic acid (206 mg, 2.1 mmol), and DMAP (40 mg, 0.20 mmol), followed by the addition of 20 mL freshly dried CH2Cl2 to fully dissolve the solids. The flask was capped with a rubber septum and cooled to 0 °C. With stirring, DIPC (464 μL, 3.0 mmol) was added dropwise into the flask via syringe. The resulting mixture was stirred for 24 h at room temperature. After that, the white precipitate was filtered out, and the filtrate was evaporated by rotary evaporation. The crude product was purified by flash column chromatography on silica gel using CH2Cl2 as the eluent to afford the product (805 mg) as a white powder. Yield: 89%. 1H NMR (CDCl3, 500 MHz, ppm): δ 6.20 - 5.90 (m, 21H), 5.18 (m, 1H), 4.43 (m, 1H), 4.23 (m, 1H), 2.75 - 2.68 (m, 4H), 2.57 (m, 4H), 2.51 (m, 4H), 1.99 (m, 2H), 1.07
(m, 2H). $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 171.22, 170.90, 137.06, 137.04, 137.00, 128.65, 128.62, 128.60, 82.28, 82.24, 70.86, 69.17, 69.16, 63.96, 33.35, 33.22, 31.99, 26.83, 14.36, 14.33, 13.11. MS (MALDI-TOF, m/z): Calc. for C$_{29}$H$_{40}$O$_{16}$SSi$_{8}$: 900.0 Da. Found: 923.2 Da (M+Na)$^+$.  

Figure 3.5. (A) $^1$H NMR and (B) $^{13}$C NMR spectra of VPOSS-2alkyne. Resonance peaks in (A) are assigned. Asterisks indicate corresponding signals from CDCl$_3$ solvent.
Figure 3.6. Synthetic scheme of giant surfactant DPOSS-4PS_m. Reagents and conditions: (i) CuBr, PMDETA, toluene, r.t., overnight, ~ 80%; (ii) 1-thioglycerol, Irgacure 2959, THF, hv, 10 min, ~70 - 85%.

Preparation of VPOSS-4PS. To a 100 mL Schlenk flask equipped with a magnetic stirring bar were added VPOSS-2alkyne (90.0 mg, 0.10 mmol), 2PS_{10}-N\textsubscript{3} (M\textsubscript{NMR} = 2.3 kg/mol, D = 1.07, 500 mg, 0.22 mmol), CuBr (0.05 eq per azide group), and 20 mL
toluene. The solution was degassed by three freeze-pump-thaw cycles before the addition of PMDETA (1 eq per azide group) under the protection of nitrogen gas. The mixture was degassed by one more freeze-pump-thaw cycle and then stirred at room temperature for 12 h. After that, the solution was directly transferred onto a silica gel column. CH$_2$Cl$_2$ was used to remove any unreacted starting materials. Then, a mixture of CH$_2$Cl$_2$ and ethyl acetate (v/v = 1/1) was used to flash the product out of the column. After removal of solvent, the crude product was dissolved in THF and precipitated in cold methanol. The product was collected by vacuum filtration and dried *in vacuo* to afford VPOSS-4PS$_{10}$ as a white powder (450 mg). Yield: 82%. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.40 - 6.30 (m, 202H), 6.25 - 5.80 (m, 21H), 5.14 (m, 1H), 4.37 (m, 1H), 4.19 (m, 1H), 4.05 - 3.64 (m, 4H), 2.97 (m, 4H), 2.70 (m, 8H), 2.50 - 1.00 (m, 138H), 0.94 (m, 4H), 0.76 - 0.62 (m, 24H), 0.30 - 0.50 (m, 6H). $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 171.9, 146.0 - 144.9, 137.1, 137.0, 128.6, 128.6, 129.1 - 124.6, 70.5, 63.8, 52.9, 46.2 - 40.4, 33.6, 33.3, 32.0, 31.5, 31.4, 30.5, 29.9, 29.8, 28.8, 26.8, 24.2, 20.8, 20.2, 19.9, 19.3, 19.2, 18.8, 18.7, 18.5, 13.1, 11.2 - 10.8. FT-IR (KBr) ν (cm$^{-1}$): 3084, 3062, 3027, 2927, 2854, 1945, 1873, 1803, 1730, 1601, 1549, 1492, 1453, 1408, 1364, 1275, 1123 (Si-O-Si asymmetric stretching), 1028, 1006, 971, 908, 760, 731, 700, 584. MS (MALDI-TOF, m/z): Calcd. mono-isotopic mass for [40mer-Ag]$^+$ (C$_{373}$H$_{414}$AgN$_6$O$_{16}$Si$_{10}$): 5651.8. Found 5652.0. $M_{n,NMR}$ = 5.6 kg/mol. SEC: $M_{n,SEC}$ = 5.13 kg/mol, $M_{w,SEC}$ = 5.22 kg/mol, $D$ = 1.02. A series of DPOSS-4PS$_m$ samples with different molecular weights can be similarly obtained from VPOSS-2alkyne and different 2PS$_m$-N$_3$ samples with similar yields.

Preparation of DPOSS-4PS$_{10}$. To an open vial without a stirring bar were added VPOSS-4PS$_{10}$ ($M_{n,NMR}$ = 5.6 kg/mol, $D$ = 1.01, 200 mg, 0.036 mmol), 1-thioglycerol
(10.0 eq per VPOSS cage), Irgacure 2959 (0.10 eq per VPOSS cage, or 0.014 eq per vinyl group), and a minimum amount of THF (~2 mL) to fully dissolve the solids. The reaction was completed after irradiation by 365 nm UV light for 10 min. The resulting mixture was then purified by repeated precipitations from concentrated THF solutions into cold MeOH/water mixture (v/v = 1/1 to 1/5), collected by centrifugation, and dried in vacuo to afford DPOSS-4PS$_{10}$ as a white powder (177 mg). Yield: 78%. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.40 - 6.30 (m, 202H), 5.15 (m, 1H), 4.38 (m, 1H), 4.19 (m, 1H), 4.15 - 3.24 (m, 39H), 2.96 (m, 4H), 2.85 - 2.60 (m, 36H), 2.50 - 1.00 (m, 152H), 0.94 (m, 4H), 0.76 - 0.62 (m, 24H), 0.30 - 0.50 (m, 6H). $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 172.3, 171.8, 146.0 - 144.9, 129.1 - 124.6, 72.6, 71.0, 70.9, 65.4, 64.9, 46.2 - 40.4, 35.5, 33.6, 31.5, 30.4, 29.8, 28.0, 26.8, 26.7, 20.7, 18.6, 18.5, 12.9, 11.3 - 10.8. FT-IR (KBr) ν (cm$^{-1}$): 3389 (br), 3061, 3027, 2926, 1735, 1648, 1601, 1582, 1492, 1454, 1386, 1283, 1182, 1120 (Si-O-Si asymmetric stretching). 1031, 908, 758, 699, 527. $M_{n,NMR} = 6.3$ kg/mol. SEC: $M_{n,SEC} = 5.78$ kg/mol, $M_{w,SEC} = 5.90$ kg/mol, $\mathcal{D} = 1.02$. A series of DPOSS-4PS$_m$ samples with different molecular weights can be similarly obtained from different VPOSS-4PS$_m$ samples with similar yields.
Figure 3.7. $^1$H NMR spectra of (A) VPOSS-4PS$_{10}$ and (B) DPOSS-4PS$_{10}$ with characteristic resonance peaks assigned. Asterisks indicate corresponding signals from residue protons in CDCl$_3$ solvent.
Figure 3.8. $^{13}$C NMR spectra of (A) VPOSS-4PS$_{10}$ and (B) DPOSS-4PS$_{10}$. After the thiol-ene reaction, characteristic resonance peaks from vinyl carbons disappeared. Asterisks indicate corresponding signals from CDCl$_3$. 
Figure 3.9. Normalized SEC overlay of $2\text{PS}_{10}$-$\text{N}_3$ (black curve), VPOSS-$4\text{PS}_{10}$ (red curve), and DPOSS-$4\text{PS}_{10}$ (blue curve).
Figure 3.10. FT-IR spectra of $2\text{PS}_{10}\text{-N}_3$ (black curve), VPOSS-$\text{4PS}_{10}$ (red curve), and DPOSS-$\text{4PS}_{10}$ (blue curve). Characteristic absorbance peaks from azide groups and the Si-O framework of POSS cages were assigned.
Figure 3.11. MALDI–TOF mass spectrum of VPOSS-4PS$_{10}$ with monoisotopic resolution. The inset showed the full spectrum.
3.4.3 Giant Shape Amphiphile

2, 3, 6, 7, 10, 11-Hexa-alkyne-triphenylene. To a solution of 2,3,6,7,10,11-Hexahydroxytriphenylene (100 mg, 0.308 mmol) in THF (10 mL) was added CaCO₃ (100 mg) suspended in THF (10 mL). A solution of Bromoethyne (293.47 mg, 2.464 mmol) in THF (10 mL) was then added to the mixture. The resulting mixture was stirred at room temperature overnight. The reaction extracted with MeOH. The organic layer was washed with brine, dried over Na₂SO₄ and concentrated. The residue was purified on a silica gel column chromatography to get the compound 7. ¹H NMR (300 MHz, CDCl₃, ppm) δ 8.10–8.08 (s, 6H), 4.99–4.95 (d, 12H), 2.60–2.57 (m, 6H).

Figure 3.12. Synthetic route of Triphenylene-6BPOSS

Azidebenzyl-heptaisobutylPOSS (BPOSS-N3). Choloridebenzyl-heptaisobutylPOSS (BPOSS-Cl) (1.0 g, 1.06 mmol) and sodium azide (207 mg, 3.18 mmol) were dissolved
by 14 mL DMF and 4 mL THF. The solution was stirred for 24h under room temperature. Solvent were evaporated under reduced pressure, the residue was extracted with CH$_2$Cl$_2$. The product was obtained after removing the solvent. $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ 7.75-7.65 (d, 2H), 7.39-7.31 (d, 2H), 4.42-4.32 (s, 2H), 2.01-1.79 (m, 7H), 1.15-0.90 (m, 42H), 0.78-0.59 (m, 14H). $^{13}$C NMR (300 MHz, CDCl$_3$, ppm) δ 137.34, 134.50, 131.96, 127.26, 54.79, 25.73, 23.72, 22.37

2, 3, 6, 7, 10, 11-Hexa-BPOSS-Ar-triphenylene (triphenylene-6BPOSS). BPOSS-N3 (250 mg, 0.263 mmol) and 2, 3, 6, 7, 10, 11-Hexa-alkyne-triphenylene (17.16 mg, 0.033 mmol) were added to a 100 mL Schlenk flask and dissolved by 10 mL purified THF. CuBr (about 2 mg) was then added to the solution. The solution was degassed on the vacuum line for 3 freeze-degas-unfreeze cycles. Two drops of PMDETA was added to the solution under N$_2$ flow. The system was degassed once more. Then the solution was stirred at room temperature for 12h. The product was obtained after purification by column chromatography on silica gel eluting with hexane: EA (v:v = 2:1 ). $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ 8.23-8.14 (s, 6H), 7.84 (s, 6H), 7.70-7.62 (d, 12H), 7.32-7.24 (d, 12H), 5.56-5.48 (d, 12H), 1.96-1.79 (m, 42H), 1.02-0.90 (m, 252H), 0.67-0.60 (m, 84H). $^{13}$C NMR (300 MHz, CDCl$_3$, ppm) δ 148.12, 144.59, 136.54, 135.77, 134.78, 132.55, 127.18, 124.04, 123.58, 30.26, 25.83, 23.77, 22.47
Figure 3.13. $^1$H-NMR of triphenylene-6BPOSS
CHAPTER IV

SELECTIVE-ASSEMBLIES OF GIANT TETRAHEDRA VIA PRECISELY
CONTROLLED POSITIONAL INTERACTIONS

Recent computer simulation studies, based on the entropic driving force, have revealed the possible ordered structures, such as crystals and liquid crystals, for the packing scheme of polyhedra. In particular, hard tetrahedron building blocks have been shown to form quasicrystal and crystal phases with high packing fractions. However, experimental investigation on rigid, nano-sized giant polyhedra with precisely defined symmetry and functionality (positional interactions) to form ordered superlattices remains largely unexplored. Utilizing polyhedron building blocks to selectively assemble into ordered structures is a promising approach to discover unexpected structure formation mechanisms and encourage novel technological innovations. Among all the polyhedra, tetrahedron is the simplest one to start with. Rigid, nano-sized tetrahedra molecules with designed symmetry breaking on accurately controlled positional interactions are distinguished from the known dendrimer and block copolymer systems by excluding any flexible alkyl or polymeric chains. The lack of the soft “squishy surface layers” will also introduce different enthalpic and entropic interactions in the self-assembly process.
Molecular nanoparticles (MNPs) offer great opportunities to construct nano-sized giant tetrahedra with atomic precision due to their unique nanometer sizes and shape persistency. In this chapter, we present an experimental approximation of giant tetrahedra by coupling four POSS cages with different functionalities to a rigid tetrahedral core: hydrophobic POSS cages with seven isobutyl groups (BPOSS) and hydrophilic POSS cages with hydroxyl or carboxylic acid groups (see figure 4.1). As shown in figure 3.1 in chapter III, syntheses of these giant tetrahedra were achieved by sequentially combining two “click” reactions: the copper-catalyzed azide-alkyne \([3 + 2]\) cycloaddition reaction and the thiol-ene reaction. Fig. 2 shows the chemical structures and space-filling models of four categories of nano-sized giant tetrahedra with different partitions of hydrophobic and hydrophilic POSS cages. Incorporation of different POSS cages results in designed symmetry breaking of the accurately controlled positional interactions generated by the collective (multiple) hydrogen bonding among the hydrophilic POSS cages and the crystallization of the hydrophobic POSS cages. NMR and mass spectral results (Figs. xx and xx) confirm that they are indeed precisely defined macromolecules with high purity. It is rather intriguing to study how the symmetry breaking of the positional interactions dictates their selective assembly to form diverse ordered superlattices in these giant tetrahedra. Furthermore, they serve as the basis to understand how different nano-sized giant polyhedra, as an extension of known soft materials, self-assemble into functional structures.
Figure 4.1. Chemical structures of the four categories of giant tetrahedra (the space-filling model also illustrated in the shadow). Four cartoons in the left corner are corresponding simplifications of these four giant tetrahedra in which the dark blue spheres represent hydrophilic POSS cages and the dark red spheres represent hydrophobic BPOSS cages.

4.1 Sample Preparation

The single crystal of 1 was obtained by slow evaporation from its dilute solution on mica substrate in a solvent-saturated atmosphere. A chamber with a 1,2-dichloroethane (CH₂ClCH₂Cl) saturated atmosphere was constructed in a glass Petri culture dish with a
carbon-coated mica put on a steel cylindrical mount. About 4 mL 1,2-dichloroethane was added into the dish. The chamber was sealed at room temperature for 1 hour for the atmosphere to reach saturation. Then, several drops of the 0.02 wt% dilute solution of 1 in 1,2-dichloroethane was quickly dropped on the surface of the mica, followed by sealing the chamber. The chamber was then left to allow for the solvent to completely evaporate in 1-2 days.

For SAED experiments, the single crystals of 1 on carbon coated mica were transferred onto a water surface. Clean TEM copper grids (300 mesh, SPI) were then used to pick up the carbon film with samples. Before TEM measurement, samples were put into a vacuum oven for 12 h to remove the residual solvent and moisture. BF TEM images and SAED patterns were then taken. The \( d \)-spacings were calibrated using a TlCl standard.

Crystalline samples of 1, 2a-2d and 3a-3c for X-ray experiments were prepared by first dissolving about 15 mg samples in a THF/MeCN (v/v = 1/1) mixed solvent. The solution was then allowed to slowly evaporate in two days at room temperature to give bulk powder samples, which were further dried \textit{in vacuo} overnight. The dried powder samples were sealed into an aluminum sample holder with a hole of 5 mm diameter for SAXS and WAXD measurements. Powder samples treated by the same procedure were also transferred to an aluminum DSC pan with a weight of about 3 mg for DSC measurements.

To prepare thermally annealed samples at higher temperatures, 2a-2d were first heated to 180 °C, followed by immediate cooling to 140 °C at 5 °C/min, and then annealed at 140 °C for 12 h. All thermal annealing procedures were performed under
nitrogen atmosphere. After cooled to room temperature, the samples were used in SAXS and WAXD measurements. Due to the stronger crystallizing ability, 3a-3c were annealed at 180 °C for 3 h and then directly quenched in liquid nitrogen to avoid recrystallization of the BPOSS cages. The collected samples were used in SAXS and WAXD measurements. Samples of 4a-4c without any solvent crystallization treatment were directly annealed at 130 °C for 12 h. After that, samples were cooled to room temperature and used for SAXS and WAXD measurements.

Thin slices of the bulk samples suitable for TEM experiments were obtained using a Reichert Ultracut S (Leica) microtome on evaporated or annealed samples embedded in epoxy monolith at room temperature. The slices were transferred to carbon coated copper grids for TEM experiments. The thickness of these thin slices was around 70–100 nm. When necessary, staining of the samples was performed at room temperature by using RuO$_4$ for the APOSS cages containing carboxylic acid groups for 0.5 h or OsO$_4$ for HPOSS and DPOSS cages containing hydroxyl groups for 12 h.

Fourier Filtering. Fourier filtering of the TEM image was carried out with the FFTW implementation. A circular mask of a radius of 0.0225 nm$^{-1}$ was applied to the central peak in the frequency domain, and circular masks of radius of 0.0096 nm$^{-1}$ were applied to the diffraction peaks (maxima in the frequency domain) up to the 4$^{th}$ order. All unmasked Fourier spectrum terms were set to zero, while the masked terms remained intact. Inversed fast Fourier transform (IFFT) on the processed Fourier spectrum yields the filtered spatial image.
4.2 Self-assembly Behavior of Giant Tetrahedron 1

Giant tetrahedron 1 contains four identical BPOSS cages and therefore, an ordered crystalline structure is expected. Indeed, a crystal superlattice with a triclinic unit cell and a space group of $P\text{i}$ has been determined, based on the combination of selected area electron diffraction (SAED, figure 4.2A) results from the single crystals and wide angle X-ray diffraction (WAXD, figure. 4.2B) results from the bulk samples. Figure 4.2A-4.2B shows the structure determination of this giant tetrahedron via both selected area electron diffraction (SAED) of the single crystals grown from solvent evaporation and synchrotron WAXD pattern of the bulk sample of 1. The crystal parameters are determined to be $a = 3.72$ nm, $b = 3.56$ nm, $c = 1.05$ nm, $\alpha = 97.8^\circ$, $\beta = 90.3^\circ$, and $\gamma = 71.7^\circ$. The comparison between measured and calculated scattering angles as well as $d$-spacings based on the determined superlattice parameters are listed in table 4.1. The determined unit cell parameters were confirmed by tilting experiment in reciprocal space (figure 4.2F). Diffraction patterns from the [1$\overline{1}0$] zone was acquired by tilting $34^\circ$ along the $c^*$ axis at [100], which matched the calculated tilting angle ($34^\circ$). In the simulated molecular packing model, the tetrahedral cores adopted an interpenetrated stacking to form geometrically locked columns at the molecular level, which were surrounded by a shell of BPOSS cages (figure 4.2D). The included angle between $a$- and $b$-axes is $71.7^\circ$ (figure 4.2E), which is deviated from $60^\circ$ (the angle for hexagonally packed columns). This observation suggests that the crystallization of BPOSS cages, within and between columns, distorts the hexagonally packing of columns, resulting in a triclinic superlattice with lower symmetry. The generated ED pattern along the [001] zone (figure 4.2C) matches well with the experimentally observed one as shown in figure 4.2B. To confirm
the supramolecular structure, the structural information in real space was also acquired on BF TEM images with large magnification. Figure 4.2G shows the BF TEM image of flat crystal. It displays stripes with periodicity of ca. 3 nm (see the inset FFT image), which corresponds to the \{110\} plane of the supramolecular structure. On the other hand, the cross-sectioned thin slice samples of the crystals were obtained by microtome, and the BF TEM image is shown in figure 4.2H. It displays a honeycomb-like structure with BPOSS cages as dark regions and tetrahedral cores as light regions. This observation matches the determined structure very well in both real and reciprocal space as illustrated in the \textit{ab}-plane along the <001> direction in figure 4.2G.
Figure 4.2. Crystal structure determination and simulation of giant tetrahedron 1. (A) Synchrotron X-ray powder diffraction pattern of 1. (B) SAED of a single crystal of 1 along the [100] zone. (C) Simulated diffraction pattern at [100] by Cerius². (D) Side view of a column consisted of 1. (E) Simulated molecular packing model in the triclinic crystal lattice of 1 projected on the ab-plane, the bc-plane, and the ac-plane with 2×2×2 repeated unit cells. The BPOSS cages are shown in brown and the tetrahedral core are shown in blue and grey. The aliphatic spacers are neglected in the simulation. (F) SAED of a single crystal of 1 along the [1̅10] zone acquired by tilting 34° along the c₀ axis at [100]. (G) BF TEM image of a flat crystal with an FFT image as the inset, showing the side view on columns. (H) BF TEM image of the microtomed thin slice of the crystals showing the cross section of the columns. The upper right inset is the corresponding FFT image, and the lower right inset is the Fourier filtered image.
Table 4.1. Crystallographic parameters of the supramolecular lattice of 1.

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<td>9.49</td>
</tr>
<tr>
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<td>(131)</td>
<td>12.14</td>
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</tr>
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</table>

Note: \(^a\) Experimental values observed in WAXD and TEM data. \(^b\) Calculated based on the triclinic unit cell of \(a = 3.72\) nm, \(b = 3.56\) nm, \(c = 1.05\) nm, \(α = 97.8°\), \(β = 90.3°\), and \(γ = 71.7°\).

4.3 Self-assembly Behavior of Giant Tetrahedron 2a-2d

Replacing one BPOSS cage with a hydrophilic POSS cage in 1 lowers the molecular symmetry into \(C_{3v}\). At 25 °C, density-frustrated lamellar superlattices with a 3-layer packing periodicity were observed for all of these giant tetrahedra (2a-2d). The lamellar structures are supported by the combined small angle X-ray scattering (SAXS)
and WAXD results (Figure 4.3A) with a $q$ value ratio of 1:2:3. The strongest diffraction peak at 1.09 nm in the WAXD pattern (Figure 4.3A) is attributed to the characteristic diffraction of the BPOSS triclinic crystals. It is further confirmed by the bright-field (BF) TEM image of microtomed thin section samples (Figure 4.3B) and its fast Fourier transform (FFT) pattern (the right-up inset of Figure 4.3B). Moreover, the measured periodicities of 4.3-4.7 nm can only accommodate two layers of BPOSS and one interdigitated layer of the hydrophilic POSS cages. The lamellar $d$-spacings and melting temperatures ($T_m$) of samples 2a-2d are summarized in Table 4.2. Disregarding the unmatched numbers of hydrophobic and hydrophilic POSS cages, crystallization of BPOSS cages always prefers to create flat interfaces, leading to the formation of frustrated lamellar superlattice disregarding the density difference.

![Figure 4.3.](image)

**Figure 4.3.** (A) Combined SAXS and WAXD profiles of 2a evaporated from THF/MeCN mixed solvents at 25 °C. (B) BF TEM image of a microtomed thin section confirms the lamellar superlattice. The right-up inset is the corresponding FFT pattern.

After 2a was heated up to 180 °C (above its $T_m$, Table 4.2) and immediately cooled to and annealed at 140 °C for 12 hours, an entirely different SAXS pattern was observed (Figure 4.4A). The WAXD pattern indicates that BPOSS cages were amorphous in this
structure (Figure 4.4B). Both 2b and 2c exhibited virtually identical SAXS patterns upon the same thermal treatment (Figure 4.4C and 4.4D). The observed $q$ value ratios are $\sqrt{2}:\sqrt{4}:\sqrt{5}:\sqrt{6}$, which is characteristic of the A15 phase. A cubic unit cell with $a = 13.2$ nm can be deduced for 2a. The lattice assignment is further validated by TEM images of the microtomed, RuO$_4$-stained thin-sectioned samples of 2a (~ 80 nm thick). The BF TEM image in Figure 4.4E exhibits the arrangement of spheres along the $<100>$ direction of the A15 phase in real space. Its FFT pattern is shown in the inset of Figure 4.4E with major diffractions assigned. Fourier filtering treatment provides a clear view of the regular 2D $4^4$ tiling pattern along the $<100>$ direction (Figure 4.4F). From this image, the measured distance between two closest neighboring squares is 13.2 nm, which is consistent with the value calculated from the SAXS result. Setting Figure 4.4F in inverse contrast makes it easier to identify the fine features of the spherical packing (Figure 4.4G).
Figure 4.4. (A) SAXS pattern and (B) WAXD pattern of 2a after the sample was heated to above its $T_m$ and annealed at 140 °C for 12 hours. (C) and (D) are the SAXS patterns of 2b and 2c after similar sample treatment. (E) {100} plane of an A15 superlattice was identified by the BF TEM image after the thin section sample was stained by RuO$_4$. The inset is the FFT pattern of this image. (F) Fourier filtering of the image shown in (E) resulted in a clear view of the 2D $4^4$ tiling along the $<100>$ direction. (G) Inverse colored and magnified image of (F). White spherical regions represent the hydrophilic POSS spherical domains with different sizes. The red-dot circles correspond to the body center and vertex positioned domains in the A15 unit cell. The left-top inset is the simulated projection view along the $<100>$ direction. (H) BF TEM image of thin-sectioned 2a sample showing the {210} plane of the A15 structure. (G) Schematic selective assembly mechanism and molecular packing model in the A15 superlattice.

It is observed that spheres in the red-dot circles (figure 4.4G), which correspond to the Kasper polyhedra with CN = 12, possess smaller sizes compared to their neighbors (Kasper polyhedra with CN = 14). To analyze the size ratio of the two different types of
spheres observed in Figure 4.4G, we denote the composition of the A15 phase as A3B (A-type spheres CN14, while B-type spheres CN 12). A total number of 334 unit cells (2338 spheres) were examined on the Fourier filtered image. The average diameter of A-type spheres is 3.4 ± 0.2 nm, while the average diameter of B-type spheres is 3.1 ± 0.2 nm (the limits of confidence intervals are represented by the standard deviations). We calculated the size ratio for each of those 334 unit cells and then, obtained an average value of the size ratio (the ratio of the radius of A-type spheres over that of B type spheres) is 1.1 ± 0.06. We assume that the ratio between numbers of the tetrahedral molecules in A-type spheres and B-type spheres is identical as the volume ratio between A-type spheres and B-type spheres. Assume that the total molecule number in one A15 unit cell including six A-type spheres and two B-type spheres is \( N \), and that the radius ratio of A-type spheres over B-type spheres is \( x \), then the volume ratio (also the ratio of numbers of molecules in each sphere) between A-type spheres and B-type sphere is \( x^3 \). We can therefore have the following equation:

\[
2n + 6nx^3 = N,
\]

where \( n \) is the number of molecules in each B-type sphere. Therefore, we have

\[
n = N / (2 + 6x^3),
\]

And the number of molecules in each A-type sphere \( m \) could be calculated as

\[
m = N \cdot x^3 / (2 + 6x^3).
\]
The density of 2a, 2b, 2c were measured as 1.23, 1.24, 1.26, and 1.20 g/cm$^3$ respectively. The $N$ values in 2a, 2b and 2c are 376, 456, and 486, as calculated from the density values and the unit cell parameter of their A15 phases in Table 4.2. With the measured $\chi$ value (1.1± 0.06) from the image, we can calculate the corresponding $m$ and $n$ values, as summarized in table 4.2.

Based on the average size ratio between these two types of spheres (1.1 ± 0.06), we estimate that in 2a these two types of spheres contain 38 and 50 giant tetrahedra, respectively. These results support the existence of two types of spheres with different coordination environments in a single-component system, in contrast to metal alloys with different types of atoms. Moreover, the number of giant tetrahedra in each sphere is found to increase with increasing strength of the collective hydrogen bonding interactions and the molecular masses from 2a to 2c (table 4.2). The sphere arrangement on the {210} plane is also clearly observed, as shown in Figure 4.4H. It is observed that the A15 superlattice can be formed quickly via the melting of the lamellar BPOSS crystals, but much slower or even impossible deriving from the condition that the BPOSS parts are completely in amorphous phase. Based on the above analysis, formation mechanism of the A15 phase is schematically illustrated in figure 4.4I. When the frustrated lamellar crystals melt, the hydrophilic POSS cages form spherical aggregates via collective hydrogen bonding, while BPOSS cages originally located in the neighboring top and bottom lamellar layers undergo a 2D scrolling to form the shell. The self-assembled spheres finally pack into the A15 supramolecular lattice.

Dendrimers with a poly(benzyl ether) core and dodecyl corona are known to form spheres that further pack into A15 lattices, which can be explained by the soft “squishy
surface layers” that promote deformation of the spheres to maximize entropy and minimize interfaces. The molecular geometry of giant tetrahedra 2a to 2c also prefers the formation of spheres in the first step. Without any flexible chains, it is proposed that extra degrees of freedom (such as the excluded volume of BPOSS cages and the non-close packing of the hydrophilic POSS cages via hydrogen bonding) contribute to the size differentiations of the assembled spherical motifs, which entropically favor more space and looser packing to form the A15 phase. Furthermore, it is believed that the deformability is associated with the size of the spheres, because the interstitial gaps become larger as the size of spheres increases.

To prove this assumption, we synthesized 2d (figure 4.5A) containing a hydrophilic POSS cage with the weakest hydrogen-bonding interaction and the smallest molar mass among 2a to 2d. After similar thermal treatment, a body centered cubic (BCC) lattice composed of only one type of spheres was found (figure 4.5B, C, D, and E). Each sphere contains 44 giant tetrahedra 2d. This number provides a reasonable estimation of the upper size limit of non-deformable spheres assembled from this series of giant tetrahedra, because a small fraction of the A15 phase can also be identified from the TEM image of thin sectioned 2d samples (figure 4.5F). Any spheres larger than this size would deform as the result of non-close packing of the hydrophilic POSS cages at the spherical center to better fit into the supramolecular lattice-packing requirements with lower symmetry.
Figure 4.5. High temperature self-assembled structures of giant tetrahedron 2d. (A) Chemical structure of 2d with seven hydroxyl groups on the hydrophilic POSS cage. (B) SAXS profile of 2d after melting and thermally annealing at 140 °C for 12 h. The bcc structure was proved by the observed q value ratio of 1:√2:√3:√4. (C) A bcc packing model showing one unit cell. (D,E) BF TEM images of thin-sectioned 2d samples (D) along the {100} plane, and (E) along the {111} plane. The inset images at the right up corner are the corresponding FFT patterns. (F) BF TEM image of occasionally found {100} plane of an A15 structure in thin-sectioned 2d samples. This indicates that spheres self-assembled from 2d reaches the upper limit of the non-deformable size of the spheres.

4.4 Self-assembly Behavior of Giant Tetrahedron 3a-3c

When replacing another BPOSS by a second hydrophilic POSS cage, the giant tetrahedron became more symmetric in terms of both volume fractions and interactions. “Double layered” lamellar superlattices for all the 3a-3c at 25 °C are observed owing to the dominating BPOSS crystallization (see figure 4.6A for SAXS and figure 4.6D for BF TEM image). After being annealed above their \( T_m \) at 180 °C for 3 hours and quenched to...
liquid nitrogen, crystallization of BPOSS in 3a-3c was suppressed. From the SAXS and TEM results (figures 4.6B and 4.6E), the lamellar superlattices of 3b and 3c remained, due to the $C_{2v}$ symmetry with their close hydrophilic/hydrophobic volume fractions. However, compared to their room temperature structures, increased lamellae $d$-spacings were observed, which can be mainly attributed to the disordered BPOSS packing and thermal expansion. On the other hand, a highly ordered double gyroid superlattice (space group $Ia3d$) formed in 3a (figure 4.6C for SAXS pattern and figure 4.6F for BF TEM image viewing along the $<111>$ direction) after high temperature thermal treatment and subsequent quenching. In the TEM image (figure 4.6F), the darker regions are hydrophilic POSS domains embedded in the hydrophobic matrix composed of BPOSS cages and the tetrahedral cores. Formation of such a double-gyroid phase from the rigid and symmetric giant tetrahedron 3a reflects the ubiquity of the gyroid structure, implying the subtle influence of the slightly different volume fractions and interactions on the selective assembly of these giant tetrahedra (figure 4.6G).
Figure 4.6. Characterization data of the self-assembled structures from giant tetrahedra 3a-c. (A) Combined SAXS and WAXD patterns of 3c evaporated from THF/MeCN mixed solvents at 25 °C indicating a lamellar structure of 3c. (B) SAXS pattern of 3c taken at 25 °C after thermal annealing at 130 °C and quenched in liquid nitrogen to avoid BPOSS crystallization. (C) SAXS pattern of 3a after the identical sample preparation process. (D) BF TEM image of a thin-sectioned 3a sample showing a lamellar structure at 25 °C with a thickness of 5.4 nm. (E) BF TEM image of thin sectioned 3c with the lamellar superlattice identical to that deduced by the SAXS result shown in (B). (F) BF TEM image of thin sectioned and RuO4-stained 3a with the double gyroid superlattice identical to that deduced from the SAXS result shown in (C). In (E) and (F) the insets are the FFT patterns of the TEM images. (G) Schematic assembly mechanisms and packing models of 3a-3c.
4.5 Self-assembly behavior of giant tetrahedron 4a-4c

With three hydrophilic POSS cages and only one hydrophobic BPOSS cage, the giant tetrahedra 4a-4c failed to crystallize in similar solvent evaporation processes. The low volume fraction of the BPOSS cages does not favor the formation of continuous 2D flat BPOSS crystals (figure 4.7B). At such a low BPOSS volume fraction, inverse spherical phase such as BCC or A15 superlattice was expected. However, after thermal annealing at 130 °C, only ordered hexagonal cylinder superlattices were observed in 4a-4c, which are revealed by the $q$ value ratio of 1:$\sqrt{3}$:$\sqrt{4}$ in their SAXS patterns (figures. 4.7A, 4.7E and 4.7F for 4b, 4a, and 4c, respectively). The honeycomb-like hexagonal pattern observed in real space BF TEM image (figure 4.7C for the columns perpendicular to the substrate, and figure 4.7 D for the columns parallel to the substrate) also confirms the structural assignment for 4c. A molecular packing model for the hexagonal cylinder superlattice is proposed in figure 4.7G. In this model, the BPOSS cages are wrapped into the center of columns, while the hydrophilic POSS cages with strong collective hydrogen bonding are located in the continuous matrix domain. In strong contrast to the packing of 2a-2c molecules at higher temperatures, maximizing the contact of the hydrophilic POSS cages will increase the number of collective hydrogen bonding formation and thus contribute to minimizing the overall free energy of the system. A hexagonal cylinder packing could have a 2D packing efficiency of 91%, which is much higher than a 3D packing efficiency of 74% in fcc and hcp closest packing, or 52% in A15 packing scheme. Interactions of the collective hydrogen bonding (the enthalpic term) thus play a dominant role in directing this selective assembly of 4a-4c.
Figure 4.7. (A) SAXS pattern and (B) WAXD pattern of 4b after the sample was directly annealed at 130 °C. (C) and (D) show BF TEM images of thin sectioned 4c with the honeycomb-like hexagonal superlattice identical to that deduced by SAXS result shown in (A). (E) and (F) show the SAXS patterns of 4a and 4c after the sample was directly annealed at 130 °C. (G) Schematic assembly mechanisms and packing models of 4a-4c.
4.7 Summary

In summary, symmetry breaking on accurately controlled positional interactions of nano-sized giant tetrahedra has been employed to construct the Frank-Kasper A15 phase and other regular superlattices. The summary superlattice analysis of all of the molecular giant tetrahedra with different symmetry is in table 4.2. The observation of A15 superlattice in these giant tetrahedra reveals that single-component systems are also promising in building supramolecular “alloys” in soft materials via the deformability of the selectively assembled spheres and shape polydispersity. More importantly, such molecular systems are highly tunable in terms of their composition and feature sizes. In general, we expect that the concept and formation mechanisms of these giant tetrahedra could be extended to other giant polyhedra building blocks with different topologies and chemical compositions. The approach to drive rigid giant polyhedra into diverse superlattices including the “alloy”-like Frank-Kasper structure opens up a wide field of supramolecular self-assembly with unexpected structure and properties. For example, we are currently exploring the functional properties of the intriguing light ceramic materials with soft-matter characteristics, so-called “soft-ceramics”, which may result from the thermal incineration of the precursor structures.
Table 4.2. Superlattice analysis of all of the molecular giant tetrahedra with different symmetry. Lattice I structures were formed by slow evaporation of the sample solutions in THF/MeCN mixed solvents at 25°C; lattice II structures were formed after annealing treatment. \( d_1 \) is the determined periodicity of the lamellar structures.

<table>
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<th>Molecule</th>
<th>Lattice I</th>
<th>( T_m ) (°C)</th>
<th>( d_1 ) (nm)</th>
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<th>( d_{II} ) (nm)</th>
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*Dimensions of the A15 or bcc unit cells. †Lamellar periodicities in supramolecular lattice II. ‡The corresponding principal (01) spacing between the cylinders in the honeycomb-like hexagonal lattices. §Calculated numbers of giant tetrahedra in two types of spheres in the A15 lattice (the size ratios of two types of spheres in 2b and 2c are assumed to be 1.1, the same as in 2a) or in each sphere in the bcc lattice. #Average number of giant tetrahedra within 1-nm-thick cross section of the cylinders in the honeycomb-like hexagonal supramolecular lattices.
CHAPTER V

TOPOLOGY-INDUCED EVOLUTION TOWARDS “SOFT” FRANK-KASPER AND QUASICRYSTALLINE PHASES IN GIANT SURFACTANTS

In addition to the close packing schemes of identical atoms (such as hexagonal close-packing and face-centered cubic), atoms with different sizes and electron states in some metal alloys are able to pack into more complex spherical phases, such as the Frank-Kasper (FK) phases, which combine the Frank lattice (icosahedron with a coordination number of 12) and the Kasper lattice (with higher coordination numbers of 14, 15 and 16).\textsuperscript{61,62} Specifically, a few FK phases such as the A15 (space group of $Pm\bar{3}n$) and $\sigma$ (space group of $P4_2/mnm$) phases are viewed as periodic approximates of aperiodic “quasicrystals”, which are first identified in supercooled metal alloys and possess 5-, 7-, 8-, 10- or 12-fold rotational symmetry but no translational operations.\textsuperscript{65,68,71,73,130} These unconventional spherical packing schemes open up possibilities to design materials with different properties. Stabilization of these phases originates from both geometric factors and the tendency to enhance the low orbital electron sharing due to less interface contacts among the atoms.

A variety of FK phases have also been identified in soft matters, such as small molecule surfactants\textsuperscript{75,85-87,91,93,131}, block copolymers\textsuperscript{76,96,97,106-108}, dendrimers\textsuperscript{18,76,77,81},
liquid crystals\textsuperscript{58,78,102,104}, colloidal particles\textsuperscript{109-111} and very recently, molecular giant tetrahedra\textsuperscript{28}. In contrast to metal alloys that use atomic spheres as the motifs, those organic/hybrid molecules first self-assemble into spherical motifs that further organize into supramolecular lattices. Formation of the FK phases results from the subtle competitions between thermodynamic driving forces (both enthalpic and entropic origins) and molecular shapes.\textsuperscript{119,120,122} Recent advances have also revealed dodecagonal quasicrystals (DQC) with 12-fold rotational symmetry on the mesoscale range (several to tens of nanometers) in soft matters. Representative examples are mesoporous silica constructed from small molecule surfactant micelles\textsuperscript{94}, as well as specifically designed single-component dendrimers\textsuperscript{84} and tetra-block copolymers\textsuperscript{108}.

Despite of the successes, observations of these unconventional spherical packing phases in soft materials largely rely on serendipity. A grand challenge is to understand the structural evolution pathways and relationships among these different phases, and to predict as well as control the spatial packing of the supramolecular spherical motifs into designated phase structures. Self-assembling polymeric materials (such as block copolymers) offer unlimited freedom to tailor the chemical structures of the materials and control the size and packing symmetry of the phase-separated nanodomains. Notably, the geometric/topological effect on phase diagram of diblock copolymers has been theoretically assessed. It is argued that besides the commonly observed body-centered cubic (BCC) phase in linear diblock copolymers, the A15 and σ phases could become stable in linear-branched diblock copolymers with large conformational asymmetry.\textsuperscript{116,119,121} Experimental explorations on these predictions, however, are
necessities to provide insights on the formation mechanism and relative stability of these spherical phases.

In this chapter, we present an experimental study on the self-assembly of four series of POSS-based giant surfactants with different molecular topologies by attaching one to four identical PS tails onto a hydrophilic POSS cage (DPOSS-NPS\textsubscript{m}, N is the number of tails and m is the average degree of polymerization of each PS tail, see figure 5.1). Nanophase separation between the hydrophilic POSS cages and the hydrophobic PS tails drives the formation of various highly ordered supramolecular structures in the bulk. We observe that the self-assembly phase boundaries are significantly affected by not only volume fraction of the PS tails (v\textsubscript{fPS}) but also molecular topology. In particular, the phase transitions at N = 1 or 2 of the giant surfactants display similar sequence as traditional diblock copolymers with shifted phase boundaries; whereas when N reaches 3 or 4, stable FK A15, σ and DQC phases are identified in the spherical phase formation region, resulting in a distinct phase transition sequence. We believe that these results reveal the critical role of molecular topology in dictating the packing schemes of the “soft” spherical motifs.
Figure 5.1. Chemical structures of the DPOSS-NPS$_m$ giant surfactants with topological variations. In each molecule, the PS tails are of the same statistical length. Cartoons in the boxes are corresponding simplifications to emphasize their molecular topology.

5.1 Design and Synthesis of Giant Surfactants with Multi-tails

As shown in the figure 5.1, four series of samples with one DPOSS head and different number of tails are designed and studied. The simplest DPOSS-PS single tail giant surfactant has already been studied very clearly and published. We focus more on the multi-tailed samples with m = 2-4. To get more well-defined polymer tails, anionic polymerization which can provide the best control of polydispersity especially low molecular weight region was utilized. Table 5.1 lists out the characterization of all the synthesized giant surfactants in very systematic way, with VPOSS-NPS$_m$, which only has vinyl groups on POSS cages, and thus is the precursor of DPOSS-NPS$_m$ without performing last thiol-ene reaction to introduce hydroxyl groups.
Giant surfactants DPOSS-NPS$_m$ are synthesized following the sequential “click” approaches with precisely defined chemical compositions, molecular topology, and narrow dispersity. Fourteen hydroxyl groups are tethered at the periphery of the POSS cages to provide sufficient immiscibility and drive phase separation. Detailed Synthesis and molecular characterization results are shown in the chapter III. These samples reflect a systematic, two-fold control in the primary chemical structures. Within each series, the POSS head is fixed, whereas the lengths of the PS tails are increased to tune the relative $v_f^{PS}$ of each sample. Among the different series, the change of tail number leads to different molecular topology (figure. 5.1). Thermal annealing processes are applied to generate self-assembled supramolecular structures of the DPOSS-NPS$_m$ samples, and their phase structures are studied via combined experiments of small angle X-ray scattering (SAXS) (in reciprocal space) on the bulk samples and bright-field (BF) transmission electron microscopy (TEM) (in real space) on micromted bulk sample sections5.2 Self-assembly of DPOSS-PS$_m$ and DPOSS-4PS$_m$
<table>
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<th>$M_{\text{MALDI,PS}}$</th>
<th>$M_{\text{NMR,PS}}$</th>
<th>$M_{\text{SEC,PS}}$</th>
<th>$M_w/M_n$</th>
<th>$N_{PS}$</th>
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<td>(kg/mol)</td>
<td>(kg/mol)</td>
<td>(kg/mol)</td>
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$^a$MW for the VPOSS-NPS$_m$ measured by MALDI-TOF; $^b$MW of each PS tail calculated from MALDI-TOF results; $^c$MW of each separate PS tail calculated from 500M $^1$H-NMR results; $^d$MW of each separate PS tail calculated from 500M $^1$H-NMR results.
NMR of VPOSS-NPS\textsubscript{m}; \textsuperscript{d}MW of each separate PS tail from SEC results; \textsuperscript{e}The repeat unit in each PS tail is determined according to the MW determined by MALDI-TOF results;

5.2 Self-assembly of DPOSS-PS\textsubscript{m} and DPOSS-4PS\textsubscript{m}

The phase transition sequence of the DPOSS-1PS\textsubscript{m} giant surfactants has been recently reported to be similar to those of flexible diblock copolymers and also discussed in the background chapter (figure 2.11 in section 2.3). With increasing length of the PS tails, the phase structure sequence follows lamellae (LAM) \(\rightarrow\) double gyroids (DG) \(\rightarrow\) (space group of \(\text{la}\bar{3}d\)) \(\rightarrow\) hexagonally packed cylinders (HEX) \(\rightarrow\) BCC phase (space group of \(\text{Im}3\text{m}\)). However, a visible character is that the phase boundary diagram is asymmetric in terms of \(v_{f}^{\text{PS}}\), and can be attributed to the geometric asymmetry at the interfaces between the POSS head and PS tail.

In order to explore different and new supramolecular structures, we start with the DPOSS-4PS\textsubscript{m} samples with the most distinct topological variation. The DPOSS-4PS\textsubscript{6} sample with the shortest PS tail length shows a HEX phase at \(v_{f}^{\text{PS}} = 0.75\) based on the SAXS pattern with scattering vector \(q\) ratios of \(1:\sqrt{3}:\sqrt{4}\): (figure. 5.2A). This assignment is confirmed by the BF TEM image (figure. 5.2F) with a HEX packing scheme of columns, as revealed by the fast Fourier transformation (FFT) diffraction of the TEM image (insert of figure. 5.2F). However, with further increasing the MW of PS tails all the other DPOSS-4PS\textsubscript{m} samples with longer tails than PS\textsubscript{6} fall into the spherical phase region, and show a rich palette of different supramolecular lattices, such as A15, \(\sigma\) and DQC phases before reaching the BCC phase.
Figure 5.2. Self-assembly phase structures of DPOSS-4PS$_m$ giant surfactants. SAXS patterns and BF TEM images of five representative DPOSS-4PS$_m$ samples showing (A and F) HEX, (B and G) A15, (C and H) $\sigma$, (D and I) DQC, and (E and J) BCC phases. The TEM images are taken along the [0001] zone of HEX phase in (F), the $<001>$ zone of A15 phase in (G), the [001] zone of $\sigma$ phase in (H), the [00001] zone of DQC phase in (I), and the $<001>$ zone of BCC phase in (J). Insets of the TEM images are corresponding FFT patterns. 2D tilting patterns of (K) the A15 phase, (L) the $\sigma$ phase, and (M) the DQC phase are abstracted from the TEM images bounded by the red-lined squares shown in (G to I), respectively. Their elements observed and tilting numbers are summarized in the boxes.

Specifically, DPOSS-4PS$_{10}$ ($\nu_{PS} = 0.82$) shows $q$ ratios of $\sqrt{2}:\sqrt{4}:\sqrt{5}:\sqrt{6}:\sqrt{8}:\sqrt{10}:\sqrt{17}:\sqrt{21}$ in its SAXS pattern (figure. 5.2B), suggesting the formation of a highly ordered A15 phase with a cubic unit cell ($a = 13.1$ nm). A BF TEM image (figure. 5.2G) confirmed the characteristic square $4^4$ tiling and the FFT diffraction pattern of this image exhibited major diffractions in square lattice, in according with the
A15 structure along <001> direction (figure 5.2K). The image acquired after doing the Fourier filtering of figure 5.2 G showed in the bottom left inset is rather clear for the $4^4$ tiling pattern.

For DPOSS-4PS$_{13}$ ($\nu_f^{PS} = 0.86$), an entirely different SAXS pattern (figure. 5.2C) with many diffraction peaks is recorded, which perfectly matches the pattern of a $\sigma$ phase having a tetragonal unit cell ($a = 25.7$ nm, $c = 13.4$ nm, space group $P4_2/mnm$). Well resolved the diffraction peaks can be clearly indexed (figure 5.3 and table 5.2). The corresponding BF TEM image along the [001] zone (figure. 5.2H) displays a typical $3^2.4.3.4$ tiling number (figure 5.2L), and the FFT diffraction pattern (figure. 5.2H, inset) exhibits sharp tetragonal lattice of the $\sigma$ phase.
Figure 5.3. SAXS pattern of the $\sigma$ phase found in DPOSS-4PS$_{13}$. 

$\sigma$ Phase ($P4_2/mnm)$

$a = 25.7$ nm, $c = 13.4$ nm
Table 5.2 Index of the σ phase found in DPOSS-4PS$_{13}$

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For DPOSS-4PS$_{15}$ ($v_f^{PS} = 0.87$), it is a DQC phase based on their SAXS pattern (figure 5.2D) and BT TEM (figure 5.2I) observations. The SAXS pattern has nearly the identical features and $q$ value ratios to those of the reported DQC phase in the dendrimer system, which can be indexed using a 5D reciprocal lattice (figure 5.4) as we discussed in the background of DQC in chapter II. Especially, the twelve strong diffraction spots in the FFT diffraction pattern reveal the 12-fold rotational symmetry (figure 5.2I, inset). The BF TEM image in the red dot square of figure 5.2I was picked out for reconstruction of 2D schematic tiling using three basic tiling units. From the obtained 2D schematic tiling along the [00001] zone (figure 5.2M), representative tiling numbers of $3^2.4.3.4$, $3^3.4^2$, $4^4$ and $3^6$, can be identified, further supporting the formation of an aperiodic DQC phase.

![Figure 5.4. SAXS pattern of the DQC phase found in DPOSS-4PS$_{15}$.](image)

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</table>

The roughness of sphere edge largely blurs the high order FFT peaks of DQC tiling observed under BF TEM, as the hazy high order diffraction spots can be observed except
for the 12 strong peaks in figure 5.5A. Regarding with the rough interface between spheres, we replaced the distorted or irregular 2D projections of supramolecular spheres with perfect circular dots in the center (schemed in figure 5.5B), and then only pick out the position of the supramolecular spheres (figure 5.5C). The FFT diffraction of the newly constructed sphere packing pattern is shown in figure 5.5D, exhibiting hundreds of high order diffraction spots with obvious 12 fold symmetry. The diffraction pattern matches very well with the peak positions calculated from perfect 2D dodecagonal quasicrystal tiling with the 4D projection algorithm, shown by thin brown circles on top in figure 5.5D. Besides, three main diffraction peaks of 9.5 nm, 6.6 nm and 4.7 nm close to beam stop in reciprocal space are marked in figure 5.5D. The real space d-spacing for 9.5 nm corresponds to the closest distance between spheres on the same secondary layer, while the 4.7 nm is the closest 2D projected distance between the sphere centers on primary layer and secondary layer, as illustrated in figure 5.5E. Furthermore, the random tiling of this DQC in 2D which contains four types tiling methods, $3^2.4.3.4$, $3^3.4^2$, $4^4$ and $3^6$, can be described by four basic vectors colored with white, green, red and brown lines. Each set of non-periodically parallel planes tilts 30° and generates aperiodic diffraction spots along 1 dimension. The linear combination of 4 sets of reciprocal vectors gives rise to the 12-fold symmetric pattern.
Figure 5.5. Analysis of random tiling DQC. (A) Original BF TEM image of DQC along [00001] direction. Replacing the 2D projections of supramolecular spheres with perfect circular dots in the center creates (B), and only the position information of the supramolecular spheres is picked out in (C). (D) is the FFT pattern of (C), compared with the calculated 2D DQC tiling diffraction peaks. (E) illustrated the d-spacing in real space. (F) 2D tiling scheme described by four vectors.

Finally, in DPOSS-4PS$_{17}$ ($v_f^{PS} = 0.88$), a BCC phase appears based on the $q$ ratio of $1 : \sqrt{2} : \sqrt{3} : \sqrt{5}$ in the SAXS pattern (figure 5.2E), as well as the BF TEM image with the FFT diffraction pattern ($a = 8.46$ nm, figure. 5.2J and inset). The phase structure identifications and several parameters are summarized in table 5.4.

The clear topology-induced difference in phase transition sequences drives us to investigate another two series of DPOSS-3PS$_m$ and DPOSS-2PS$_m$ giant surfactants for comprehensive understandings.
5.3 Self-assembly of DPOSS-3PS\textsubscript{m} and DPOSS-2PS\textsubscript{m}

For the series of DPOSS-3PS\textsubscript{m}, the phase structures appeared at even the shortest PS tail length (m = 11) step into the spherical phase region. The phase structures start from A15 (m = 11, \(v_f^{PS} = 0.82\)) as evidenced by figure 5.6A and 5.6E. It is followed by a \(\sigma\) phase (m = 13, and \(v_f^{PS} = 0.83\)) with a space group of \(P4_2/mnm\) and the projection view along the [001] direction exhibits a tilting number of \(3^2.4.3.4\) (figure 5.6B and 5.6F). The index of this \(\sigma\) phase indicates a very small fraction of A15 phase coexisted (figure 5.7 and table 5.3). Further increasing the MW of PS tail, DQC phases occurred (\(v_f^{PS}\) between 0.85-0.89, m = 15-20) possessing a non-crystallographic symmetry of 12-folds within stacking plans, but with rotational symmetries perpendicular to these planes (figure 5.6C and 5.6G). Beyond \(v_f^{PS} = 0.89\) finally, the bcc phase reaches (figure 5.6D and 5.6H).
Figure 5.6. Self-assembly phase structures of DPOSS-3PS\textsubscript{m} giant surfactants. SAXS patterns and BF TEM images of four representative DPOSS-3PS\textsubscript{m} samples showing (A and E) A15, (B and F) $\sigma$, (C and G) DQC, and (D and H) BCC phases. The TEM images are taken along the $<001>$ zone of A15 phase in (E), the [001] zone of $\sigma$ phase in (F), the [00001] zone of DQC phase in (G), and the $<001>$ zone of BCC phase in (H). Insets of the TEM images are corresponding FFT patterns.
Figure 5.7. SAXS pattern of the $\sigma$ phase found in DPOSS-3PS$_{15}$. The peaks indicated by the red number belong to A15 phase in a small fraction.
<table>
<thead>
<tr>
<th>NO</th>
<th>$q_{\text{exp}}$ (1/Å)</th>
<th>Intensity</th>
<th>(hkl)</th>
<th>$d_{\text{exp}}$ (Å)</th>
<th>$d_{\text{calc}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0705</td>
<td>610</td>
<td>(310)</td>
<td>89.12</td>
<td>89.17</td>
</tr>
<tr>
<td>2</td>
<td>0.0758</td>
<td>588</td>
<td>(221)</td>
<td>82.89</td>
<td>82.81</td>
</tr>
<tr>
<td>3</td>
<td>0.0802</td>
<td>803</td>
<td>(320)</td>
<td>78.34</td>
<td>78.21</td>
</tr>
<tr>
<td>4</td>
<td>0.0820</td>
<td>1000</td>
<td>(311)</td>
<td>76.62</td>
<td>76.48</td>
</tr>
<tr>
<td>5</td>
<td>0.0845</td>
<td>1325</td>
<td>(002)</td>
<td>74.36</td>
<td>74.35</td>
</tr>
<tr>
<td>6</td>
<td>0.0853</td>
<td>1090</td>
<td>(200)$_{A15}$</td>
<td>73.66</td>
<td>73.66</td>
</tr>
<tr>
<td>7</td>
<td>0.0915</td>
<td>2830</td>
<td>(410)</td>
<td>68.67</td>
<td>68.40</td>
</tr>
<tr>
<td>8</td>
<td>0.0944</td>
<td>2600</td>
<td>(330)</td>
<td>66.56</td>
<td>66.49</td>
</tr>
<tr>
<td>9</td>
<td>0.0951</td>
<td>2720</td>
<td>(202)</td>
<td>66.07</td>
<td>65.77</td>
</tr>
<tr>
<td>10</td>
<td>0.0963</td>
<td>2150</td>
<td>(210)$_{A15}$</td>
<td>65.25</td>
<td>65.80</td>
</tr>
<tr>
<td>11</td>
<td>0.0978</td>
<td>2420</td>
<td>(212)</td>
<td>64.25</td>
<td>64.05</td>
</tr>
<tr>
<td>12</td>
<td>0.1008</td>
<td>2120</td>
<td>(411)</td>
<td>62.33</td>
<td>62.14</td>
</tr>
<tr>
<td>13</td>
<td>0.1033</td>
<td>1340</td>
<td>(331)</td>
<td>60.82</td>
<td>60.68</td>
</tr>
<tr>
<td>14</td>
<td>0.1050</td>
<td>670</td>
<td>(222)</td>
<td>59.84</td>
<td>59.6</td>
</tr>
<tr>
<td>15</td>
<td>0.1094</td>
<td>410</td>
<td>(312)</td>
<td>57.43</td>
<td>57.11</td>
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<tr>
<td>16</td>
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<td>0.1187</td>
<td>200</td>
<td>(501)</td>
<td>52.93</td>
<td>52.73</td>
</tr>
<tr>
<td>18</td>
<td>0.1206</td>
<td>180</td>
<td>(511)</td>
<td>52.10</td>
<td>51.84</td>
</tr>
</tbody>
</table>
For the series of DPOSS-2PS\textsubscript{m} giant surfactants, their phase behaviors are identified based on the SAXS and BF TEM observations. The similar phase sequence to the set of DPOSS-PS\textsubscript{m} is found. Again, their LAM phase \(v_{f}^{PS} = 0.61-0.70\) with a scattering vector \(q\) ratio of 1:2:3 (figure 5.8A and 5.8E), DG phase \(v_{f}^{PS} = 0.70\) with a \(q\) ratio of \(\sqrt{6}:\sqrt{8}:\sqrt{20}:\sqrt{22}\) (figure 5.8B and 5.8F), HEX phase \(v_{f}^{PS} = 0.77-0.85\) with a \(q\) ratio of 1: \(\sqrt{3}:\sqrt{4}\) (figure 5.8C and 5.8G), and BCC phase \(v_{f}^{PS}\) above 0.85 are observed (figure 5.8D and 5.8H) with increasing the length of two PS tails. The overall assessment of this series of DPOSS-2PS\textsubscript{m} reveals that the dimension of \(\phi\) starts changing from 1D to 2D and finally 3D. Furthermore, the \(v_{f}^{PS}\) at which the lam phase changes to hex phase is found to be smaller compared with its counterpart of DPOSS-PS\textsubscript{m}. 
Figure 5.8. Self-assembly phase structures of DPOSS-2PS$_m$ giant surfactants. SAXS patterns and BF TEM images of four representative DPOSS-2PS$_m$ samples showing (A and E) LAM, (B and F) DG, (C and G) HEX, and (D and H) BCC phases. The TEM images are taken along the the $\langle111\rangle$ zone of DG phase in (F), the $[0001]$ zone of HEX phase in (G), and the $\langle001\rangle$ zone of BCC phase in (H). Insets of the TEM images are corresponding FFT patterns.

5.4 Discussion of the Phase Diagram

All the structure information and related calculation are listed in table 5.4, together with the explanation for all the parameters.
Table 5.4 Summary of molecular characterizations of the DPOSS-NPS\textsubscript{m} samples

<table>
<thead>
<tr>
<th>DPOSS-NPS\textsubscript{m}</th>
<th>(v_1)\textsuperscript{a}</th>
<th>Lattice</th>
<th>(a(\text{nm}))\textsuperscript{b}</th>
<th>(D_{\text{exp}}(\text{nm}))\textsuperscript{c}</th>
<th>(\mu)</th>
<th>(\alpha(\text{o}))\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPOSS-PS\textsubscript{33}</td>
<td>0.76</td>
<td>LAM</td>
<td>9.00</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>DPOSS-PS\textsubscript{35}</td>
<td>0.78</td>
<td>DG</td>
<td>20.57</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DPOSS-PS\textsubscript{44}</td>
<td>0.81</td>
<td>HEX</td>
<td>10.28</td>
<td>10.28</td>
<td>9.9</td>
<td>36.3</td>
</tr>
<tr>
<td>DPOSS-PS\textsubscript{91}</td>
<td>0.90</td>
<td>HEX</td>
<td>13.05</td>
<td>13.05</td>
<td>8.6</td>
<td>42.1</td>
</tr>
<tr>
<td>DPOSS-PS\textsubscript{140}</td>
<td>0.93</td>
<td>BCC</td>
<td>16.40</td>
<td>16.15</td>
<td>86.0</td>
<td>4.2</td>
</tr>
<tr>
<td>DPOSS-2PS\textsubscript{6}</td>
<td>0.61</td>
<td>LAM</td>
<td>5.84</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>DPOSS-2PS\textsubscript{10}</td>
<td>0.70</td>
<td>DG</td>
<td>15.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DPOSS-2PS\textsubscript{14}</td>
<td>0.77</td>
<td>HEX</td>
<td>7.49</td>
<td>7.49e</td>
<td>7.0f</td>
<td>51.7</td>
</tr>
<tr>
<td>DPOSS-2PS\textsubscript{17}</td>
<td>0.79</td>
<td>HEX</td>
<td>7.74</td>
<td>7.74e</td>
<td>6.7f</td>
<td>53.6</td>
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<tr>
<td>DPOSS-2PS\textsubscript{20}</td>
<td>0.82</td>
<td>HEX</td>
<td>8.52</td>
<td>8.52e</td>
<td>7.1f</td>
<td>51.0</td>
</tr>
<tr>
<td>DPOSS-2PS\textsubscript{27}</td>
<td>0.85</td>
<td>BCC</td>
<td>10.46</td>
<td>10.30d</td>
<td>51.1f</td>
<td>7.0</td>
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<tr>
<td>DPOSS-2PS\textsubscript{39}</td>
<td>0.89</td>
<td>BCC</td>
<td>11.98</td>
<td>11.80d</td>
<td>55.7f</td>
<td>6.5</td>
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<tr>
<td>DPOSS-3PS\textsubscript{11}</td>
<td>0.82</td>
<td>A15</td>
<td>14.32</td>
<td>8.88d</td>
<td>41.8f</td>
<td>8.6</td>
</tr>
<tr>
<td>DPOSS-3PS\textsubscript{13}</td>
<td>0.83</td>
<td>(\sigma)</td>
<td>28.25\times14.9</td>
<td>9.10d</td>
<td>41.3f</td>
<td>8.7</td>
</tr>
<tr>
<td>DPOSS-3PS\textsubscript{15}</td>
<td>0.85</td>
<td>DQC</td>
<td>7.48</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DPOSS-3PS\textsubscript{18}</td>
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<td>DQC</td>
<td>7.49</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DPOSS-3PS\textsubscript{20}</td>
<td>0.88</td>
<td>DQC</td>
<td>7.64</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DPOSS-3PS\textsubscript{24}</td>
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<td>BCC</td>
<td>10.15</td>
<td>10.00d</td>
<td>34.4f</td>
<td>10.5</td>
</tr>
<tr>
<td>DPOSS-4PS\textsubscript{6}</td>
<td>0.75</td>
<td>HEX</td>
<td>6.46</td>
<td>6.46e</td>
<td>5.70f</td>
<td>63.2</td>
</tr>
<tr>
<td>DPOSS-4PS\textsubscript{10}</td>
<td>0.82</td>
<td>A15</td>
<td>13.10</td>
<td>8.13d</td>
<td>30.5f</td>
<td>11.8</td>
</tr>
<tr>
<td>DPOSS-4PS\textsubscript{12}</td>
<td>0.85</td>
<td>A15+(\sigma)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DPOSS-4PS\textsubscript{13}</td>
<td>0.86</td>
<td>(\sigma)</td>
<td>25.75\times13.4</td>
<td>8.26d</td>
<td>25.6f</td>
<td>14.1</td>
</tr>
<tr>
<td>DPOSS-4PS\textsubscript{15}</td>
<td>0.87</td>
<td>DQC</td>
<td>6.79</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DPOSS-4PS\textsubscript{17}</td>
<td>0.88</td>
<td>BCC</td>
<td>8.46</td>
<td>8.33d</td>
<td>21.6f</td>
<td>16.6</td>
</tr>
<tr>
<td>DPOSS-4PS\textsubscript{19}</td>
<td>0.89</td>
<td>BCC</td>
<td>8.71</td>
<td>8.58d</td>
<td>21.4f</td>
<td>16.8</td>
</tr>
</tbody>
</table>
The volume fraction of PS is given by \( \nu_{\text{PS}} = \frac{M_{\text{PS}}/\rho_{\text{PS}}}{M_{\text{PS}}/\rho_{\text{PS}} + M_{\text{DPOSS}}/\rho_{\text{DPOSS}}} \), where the density values are 1.05 g/cm\(^3\) for PS and 1.43 g/cm\(^3\) for the DPOSS cage; \(^b\) These values are the corresponding hexagonal columnar lattice parameters in the HEX lattices, cubic lattice parameters in DG, BCC or A15 lattices, tetragonal lattice parameters perpendicular to and along 4\(_2\) screw axis in \( \sigma \) phase, and the d-spacing values of the first peaks in DQC phase; \(^c\) Columnar diameter in HEX lattices; \(^d\) Spherical diameter in the A15, \( \sigma \) or BCC lattices; \(^e\) These values are the average number of giant surfactants within 1-nm-thick cross-section of the cylinders in the hexagonal columnar lattices; \(^f\) \( \mu \) values are the calculated average numbers of giant surfactants per supramolecular sphere in the A15, \( \sigma \) or BCC lattices; \(^g\) Projection of the solid angle for giant surfactants in columnar lattice or spherical phases, \( \alpha = 360/\mu \) (deg).

Based on all the phase identifications of DPOSS-NPS\(_m\) (\( N = 1 \) to 4), we are able to construct a phase boundary diagram to summarize the phase structures and transitions of all the studied samples as shown in figure 5.9. It is evident that the phase boundaries of the conventional phases (LAM, DG, HEX, and spherical phases) move towards lower \( \nu_{\text{PS}} \) values with increasing number of PS tails from one to four. This phenomenon is associated with the fact that the presence of more than one tail at the junction point creates shape asymmetry at the interfaces, which also contributed to the interfacial curvature between the immiscible nanodomains in addition to volume fraction. The resulting tilted phase boundary lines are thus the origin of observed topological isomers, which refer to the giant surfactants with different numbers of tails but identical \( \nu_{\text{PS}} \) value.
that possesses distinct supramolecular lattices. For example, in the pair of topological isomers of DPOSS-1PS_{14} and DPOSS-4PS_{11}, the former forms a HEX phase and the latter shows an A15 phase. More importantly, when the number of tails increases to 3 and 4, a window in the spherical phase region is opened for observing FK and quasicrystalline phases, resulting in a distinct phase transition sequence of HEX → A15 → \( \sigma \) → DQC → BCC as increasing \( \nu_f^{PS} \). The same sequence is validated in both DPOSS-3PS\(_m\) and DPOSS-4PS\(_m\) samples.

Figure 5.9. Phase boundary diagrams of the four series of giant surfactants with different molecular topology. The overall phase boundary diagram with four different LAM (aqua), DG (yellow), HEX (green) and spherical (rest of the colors) phase regions is represented. Note that the phase boundary lines are tilted with respect to the number of PS tails. The window opened in the spherical phase region is opened for DPOSS-NPS\(_m\) with \( N = 3 \) and 4. The detailed phase boundaries of the A15 (blue), \( \sigma \) (red), DQC (purple) and BCC (brown) phases within the spherical phase region are shown by different colors. The black dots represent experimentally accessed data points.
In this spherical phase formation region, the relatively rigid cores of the spherical motifs are formed by aggregations of the hydrophilic DPOSS heads via collective hydrogen bonding interactions, which are surrounded by the PS tails as the shells. The distinct chemical compositions result in surface tension between the nanophase separated DPOSS cores and PS shells, which contributes to the stability of the spherical motif. Although the PS shells possess identical density, the individual PS tail may possess different conformations depending on the tail length and confined space provided. The short PS tails may exhibit more stretched conformations, yet with increasing the PS tail length the stretched conformations become progressively relaxed towards away from the spherical core.

In constructing the FK and DQC phases via the spherical motifs, theoretical results suggest that compared to the BCC phase, the A15 and $\sigma$ phases reduce contacting areas among neighboring spherical motifs. In our system, the phase formation is an entropy of PS tails directed self-assembly process. Namely, when the spherical motifs with shorter and relatively stretched PS chains in the shell deform into the Voronoi or Wigner-Seitz polyhedra, it is penalized by the relative high stretching energy. The A15 and $\sigma$ lattices which possess reduced contacting areas are thus preferable due to the smaller overlaps among stretched PS shells, which generate larger orientational entropy. At the same $v_t^{PS}$, increasing the number of PS tails would make each PS tail being shorter and spatially more crowded, the PS tails could then be more stretched and lead to decreased deformation ability of the spherical motifs, and help stabilizing the FK A15 and $\sigma$ phases in DPOSS-3PS$_m$ and DPOSS-4PS$_m$ series. As the PS tails becomes longer, they approach to more relaxed conformations. The BCC phase facilitates minimize the stretching energy
and thus, becomes stable. Specifically, existence of the DQC phase between the \( \sigma \) and BCC phases must be originated by a disordered process of the \( \sigma \) phase via forming variety of polyhedra to provide the combined tilting numbers before entering the ordered BCC phase. These results reveal more possibilities for theoretical developments to understand the topological effects in single-component, soft matter systems.
We have discussed highly diverse hierarchical structures constructed from the self-assembly of asymmetric giant polyhedra and giant surfactants. Such easy access to the complicated Frank-Kasper phase and quasicrystal phase in these systems is really surprising, considering very few systems exhibiting these phase structures are reported. We have introduced in a lot of details that these phases are intrinsically different topological closed packing methods of soft spheres. The building blocks used to create supramolecular spheres are cone-shape molecules, both in giant tetrahedra and giant surfactants. This soft sphere fabrication approach is also mostly used in other similar systems, such as dendrimer system.

In order to better understand how the primary chemical structure of dendrons and dendronized polymers govern their final self-assembly, Percec et al introduced the parameter $\alpha'$. It is defined as the projection of the solid angle $\alpha$ of a dendron on a plane (figure 6.1).\cite{18,80} For a conical dendron, its solid angle $\alpha$ is defined as $\alpha = 4\pi/\mu$, where $\mu$ is the number of dendron molecules involved to build one complete supramolecular column or sphere. The $\alpha'$ of a conical dendron, projection of the solid angle $\alpha$ of a conical
dendron is thus defined as \( \alpha' = \alpha/2 = 2\pi/\mu \). Note that for a planar Dendron taper, \( \alpha' \) is the same as \( \alpha \). The value of \( \alpha' \) gives a direct view of overall geometry shape of dendrons. It is quite straightforward that columnar structure is favored from the tapered dendrons with small sized branched groups in the periphery or at low generation number. Following the increasing of periphery group size and generation number, \( \alpha' \) would increase and a transition from tapered shape to conical shape would occur, accompanying with the transition from columnar phase to spherical phase. At this transition point, \( \alpha' \) value decrease largely, and further increase with the more branching and higher generation number.

Figure 6.1. The evolution of a dendron shape from tapered to conical shapes and the correlation with the projection of the solid angle \( \alpha' \).\textsuperscript{18,80} Reproduced with permission from Ref 18. Copyright 2014 Royal Society of Chemistry.

According to the analysis of molecular shape and related \( \alpha' \), the flat shape molecule is believed to self-assemble into columnar structure. Imaging in another extreme case that a disk like flat building block has many rather bulky periphery groups, we can expect that columnar structure is difficult to form due to strong steric hinderance. What the structure would form if this flat molecule has only some bulk periphery group, which can be
treated as the intermediate case? The answer is supramolecular oligomers with only several molecules stack together can be obtained, which are able to further pack into spherical phases. Percec et al has reported that dendronized cyclotrimeratrylenes which exhibited crown conformations self-assembled into spherical A15 and σ phase\textsuperscript{132}, and A15 phase is also found in dendronized triphenylene molecular system\textsuperscript{133}. Each supramolecular sphere contains about five dendrons in these two flat-molecular systems.

In the chapter II, we have defined the giant shape amphiphile as giant molecules upon covalently linking different MNPs of distinct shapes and competing interactions. In this chapter, a novel giant shape amphiphile constructed by the center disk-like triphenylene building block and six periphery rigid BPOSS cages is designed and synthesized (triphenylene-6BPOSS, see figure 6.2A) through [3+2] cyclo-addition click reaction. The self-assemble of this type of giant shape amphiphile would be discussed in the following part.

A previous study of a triphenylene bearing a fullerene on its side chain shows that columnar mesophase with hexagonal packing could form.\textsuperscript{134} The triphenylene-6BPOSS with six designed bulky BPOSS cages are expected to prevent columnar structure formation. After annealed at 160 °C for several hours and cooled to room temperature, the sample exhibited the SAXS profile shown in figure 6.2B. Four sharp diffraction peaks were recorded, with \( q \) value ratio being \( \sqrt{2} : \sqrt{4} : \sqrt{5} : \sqrt{6} \), which is characteristic feature of the A15 phase as discussed in chapter IV. The four peaks can be identified as (110), (200), (210) and (211), respectively, in a cubic unit cell with size \( a = 6.54 \) nm. Figure 6.2C shows the corresponding WAXD pattern with only amorphous halos, indicating no
crystallization of BPOSS cage. It is quite surprising that the \( \pi-\pi \) interaction between triphenylene cores is such strong to override the strong BPOSS crystallization.

Figure 6.2. (A) Chemical structure of triphenylene-6BPOSS; (B) SAXS pattern of triphenylene-6BPOSS annealed at 160 °C and corresponding WAXD pattern in (C).

The structure determination and lattice assignment were further validated by TEM images of the microtomed thin-sectioned samples (~ 80 nm thick). The BF TEM image in figure 6.3A exhibits the arrangement of spheres along the \( <100> \) direction of the A15 phase in real space. Its FFT pattern is shown in the inset of figure 6.3A, and is the characteristic diffraction of A15 structure along \( <100> \) direction with 12 major diffractions in the square lattice. Since both BPOSS and triphenylene are difficult to stain, the contrast in figure 6.3A is not very high. Fourier filtering treatment provides a more clear view of the regular 2D 4\(^4\) tiling pattern along the \( <100> \) direction (figure 6.3B). From this image, the measured distance between two closest neighboring squares is about 6.5 nm, which is consistent with the value calculated from the SAXS result. In this image, the dark region is attributed to BPOSS domain (higher electron density) and the white region is in triphenylene domain. Figure 6.3A and 6.3B have inverse contrast comparing with the TEM image of A15 phase in giant tetrahedra (3BPOSS-DPOSS, 2a-2c) and
giant surfactants (DPOSS-4PS or DPOSS-3PS). This is reasonable considering that in 2a-2c or DPOSS-4PS, the core of supramolecular sphere is composed of DPOSS which has much higher electron density after staining by RuO4 than the corona structure composed of BPOSS or PS, while in the supramolecular sphere constructed by triphylene-6BPOSS triphenylene core has lower electron density than the BPOSS corona. This explanation is confirmed by the fact that setting figure 6.3B in inverse contrast makes it similar image feature observed in 2a-2c or DPOSS-4PS system. The relatively strong three peaks with $q$ value ratio $\sqrt{4} : \sqrt{5} : \sqrt{6}$ all have d-spacing around 3 nm, which is in the measurable d-spacing range of TEM diffraction. Figure 6.3D shows the SAED pattern of the area exhibiting features in BF TEM image 6.3A. Three diffraction rings close to the beam stop were observed, with the calculated d-spacing having the exact ratio of $\sqrt{4} : \sqrt{5} : \sqrt{6}$.

Figure 6.3. (A) {100} plane of an A15 superlattice was identified by the BF TEM image from the microtomed thin-section of triphenylene-6BPOSS. The top right inset is the FFT of this image. (B) Fourier filtering of the image shown in (A) resulted in a clear view of the 2D $4^4$ tiling along the <100> direction. (C) Inverse colored image of (B). (D) Selected area electron diffraction of triphenylene-6BPOSS.
Thus, through the characteristic SAXS pattern and TEM image, we can determine 
the order structure of triphenylene-6BPOSS as A15 structure and the dimension of this 
cubic lattice was calculated to be $a = 6.54$ nm. With the uniform density, the average 
diameter of each supramolecular sphere can be calculated by this equation:

\[ D_{\text{sphere}} = 2a/(32\pi/3)^{1/3} \]

The average diameter is estimated as 4.06 nm. After measuring the density, the number 
of molecules in each unit cell is further calculated as 30.5, and thus each separate 
supramolecular sphere has average 3.8 molecules. The next question is the formation 
mechanism of supramolecular sphere constructed from about 4 triphenylene-6BPOSS 
molecules. Figure 6.4 illustrated the two possible packing models, of which only the 
triphenylene cores are shown (the BPOSS shell of sphere is not drawn). Model A takes 
the similar packing method of dendrons or giant surfactants, in which each molecule 
takes a conical shape. The four triphenylenes form a polyhedron like core structure while 
the BPOSS cages pend in the corona via the bending of flexible linker between 
triphenylene and BPOSS. In model B, four triphenylene disks (marked as molecules 1-4) 
stack together along one dimension to facilitate the $\pi$-$\pi$ interaction. On the other hand, the 
six BPOSS cages belonging to molecule 1 curl up and six BPOSS cages of molecule 4 
undergo scroll to form the shell of entire spherical structure. Comparing the diameter of 
supramolecular sphere in model A self-assembled from the conical conformer of 
triphenylene-6BPOSS (about 5.0 nm estimated with Cerius$^2$) with the supramolecular 
sphere in model B assembled from a fragment of column (about 4.0 nm), the model B 
with diameter closed to that obtained from SAXS (4.06 nm) is apparently preferred. In 
addition, model B can maximize the $\pi$-$\pi$ interaction between triphenylene. The possible
creation of porous space in the center of sphere in model A also makes it less stable comparing with model B.

Figure 6.4 Molecular models of the supramolecular sphere assembled from triphenylene-6BPOSS.
CHAPTER VII

SUMMARY AND OUTLOOK

In the fields of chemistry and material science, the design and development of novel self-assembling materials is a central piece in advancing our understandings of their thermodynamic driving forces, kinetic pathways and nano-structure formations as well as exploring potential applications. The emerging requirement of nano-building blocks possessing relatively independent, well-defined three-dimensional (3D) structure and shape is increasing to make their further assembly into variety of hierarchal structures at different length scales more predictable and robust.

In this dissertation, we have discussed a novel approach to construct precise macromolecules utilizing molecular nanoparticles (MNPs) which are shape- and volume-persistent nano-objects with well-defined molecular structure and specific symmetry. The T₈-POSS cages were especially focused on. By covalently connecting different MNPs in a controlled manner, new macromolecules are built, named giant molecules to distinguish from the natural macromolecules. In general, three basic categories of giant molecules are proposed: “giant polyhedra” (conjugates of MNPs in polyhedral framework), “giant surfactants” (conjugates of MNP and polymer tail), and “giant shape amphiphiles”. Three series of giant molecules span over all the three categories were designed, synthesized,
and studied for their self-assembly behaviors. The collective physical secondary interactions from the functional groups on the periphery of POSS cages constitute the driving force to further assemble MNPs into hierarchal structures under the packing constraints imposed by the overall giant molecular shapes. Specifically, unusual FK phases and DQC phase were discovered in all the three categories of giant molecules.

Experimental approximation of giant tetrahedra was presented by coupling four POSS cages with different functionalities to a rigid tetrahedral core: hydrophobic POSS cages with seven isobutyl groups (BPOSS) and hydrophilic POSS cages with hydroxyl or carboxylic acid groups. Syntheses of these giant tetrahedra were achieved by sequentially combining two “click” reactions: the copper-catalyzed azide-alkyne \([3 + 2]\) cycloaddition reaction and the thiol-ene reaction. Incorporation of different POSS cages results in designed symmetry breaking of the accurately controlled positional interactions generated by the collective (multiple) hydrogen bonding among the hydrophilic POSS cages and the crystallization of the hydrophobic POSS cages. Designed symmetry breaking of these giant tetrahedra accurately controlled the positional interactions, leading to diverse selectively assembled, highly ordered superlattices. In particular, a FK A15 superlattice was obtained from a series of giant tetrahedra with three hydrophobic and one hydrophilic POSS cages, which resembled the essential structure of certain metal alloys, but with tunable feature sizes at much larger length scales. Formation of the A15 phase is due primarily to the deformability of the self-assembled spherical building blocks that allows size polydispersity from monodisperse giant tetrahedra. More importantly, such molecular systems are highly tunable in terms of their composition and feature sizes. In general, it is expected that the concept and formation mechanisms of
these giant tetrahedra could be extended to other giant polyhedra building blocks with different topologies (e.g. giant octahedron, or even giant icosahedron) and chemical compositions (e.g. diverse functionality on POSS periphery with optical or electric properties, or even other MPNs like C_{60} and POM).

Another experimental study focused on the self-assembly of four series of POSS-based giant surfactants with different molecular topologies by attaching one to four identical PS tails onto a hydrophilic POSS cage (DPOSS-NPS\textsubscript{m}) was carried out. Nanophase separation between the hydrophilic POSS cages and the hydrophobic PS tails drives the formation of various highly ordered supramolecular structures in the bulk. We observe that the self-assembly phase boundaries are significantly affected by not only volume fraction of the PS tails (\(v_f^{PS}\)) but also molecular topology. In particular, the phase transitions at \(N = 1\) or \(2\) of the giant surfactants display similar sequence as traditional diblock copolymers with shifted phase boundaries; whereas when \(N\) reaches \(3\) or \(4\), stable FK A15, \(\sigma\) and DQC phases are identified in the spherical phase formation region, resulting in a distinct phase transition sequence. We believe that these results reveal the critical role of molecular topology in dictating the packing schemes of the “soft” spherical motifs. The roughly “V” shape of the window exhibiting FK A15, \(\sigma\) and DQC phases makes us curious of the complete phase diagram shape involving much more branched tail structure. Further study would be focused to DPOSS-5PS\textsubscript{m}, DPOSS-6PS\textsubscript{m} or even DPOSS-8PS\textsubscript{m}.

In the last part, a novel giant shape amphiphile constructed by conjugating the center disk-like triphenylene building block and six periphery rigid BPOSS cages is designed and synthesized (triphenylene-6BPOSS). The self-assemble of this type of giant
shape amphiphile resulted in A15 phase structure. The formation mechanism is believed to be that four triphenylene disks stack together along one dimension to facilitate the π-π interaction, while the six BPOSS cages belonging to up molecule curl up and six BPOSS cages of bottom molecule undergo scroll to form the shell of entire spherical structure. Due to the small free energy difference between FK A15, σ and DQC phases, we can anticipate other complicated spherical structures in this series of molecules by changing the molecular structure. Actually, σ phase has already been found by tuning the linker length between triphenylene core and periphery BPOSS cages. Systematic study will be done in the future. Furthermore, other flat disk-like core structures (figure 7.1) with stronger π-π interaction and higher symmetries are expected to present other complicated spherical phase structures with larger sizes.
Figure 7.1. Flat disk-like core structures with different symmetries.

To briefly conclude, unusual Frank-Kasper phases or dodecagonal quasicrystals phase were discovered experimentally in all the three categories of giant molecules, which are distinct from all the systems discussed in background review exhibiting the Frank-Kasper and quasicrystal phases in soft matters. The simple chemical structures and relatively rigid conformation facilitate us to make deeper understanding of the relationship between these phases. The common features existing in all the three giant molecule systems can be identified: the well-defined chemical structure with very narrow polydispersity or even single molecular weight, the molecular shapes toward supramolecular spherical micelle formation (conical shapes or disk shape with bulky groups in the periphery), and the shell of spherical micelles with appropriate stiffness and deformability.

Yet the story is, certainly, not completed. There are a lot of important issues remained to be explored. Regarding the common features summarized in these three giant molecular systems, we can design other novel systems to step into Frank-Kasper and quasicrystal phases utilizing building blocks with certain optic, electric, or magnetic
properties. One way is to functionalize the POSS cage with diverse functional groups or replace with other MNPs, to change the properties of core structures in the supramolecular micelles. The other way is tuning the shell properties. A promising approach is to introduce functional semi-conducting oligomers/polymers with precise/well-defined chemical structures, which can satisfy the mentioned conditions. The field is completely blank for the property study of functional polymers or macromolecules arranged in the intriguing Frank-Kasper and quasicrystal phases. The more interesting issue deserve much attention: will other Frank-Kasper phases such as three types of Laves phase occur in our giant molecule system? How about the quasicrystal phases with other symmetries such as 5-fold, 10-fold or even 3D icosahedral quasicrystals? Definitely with the further development of all other existing and novel building blocks to be developed, the study on Frank-Kasper and quasicrystal phases based on giant molecules would open the gate to numerous exciting research topics.
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