Giant Polyhedra and Giant Surfactants based on "Nano-atoms": Tuning from Crystals to Frank-Kasper Phases and Quasicrystals

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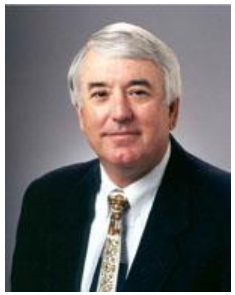
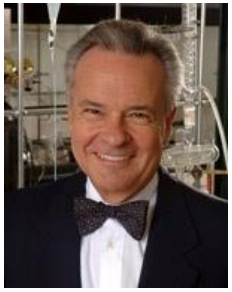
July 14, 2015

Acknowledgements

- All of my former and current students, postdoctorals and coworkers
- Prof. Fumian Li at Peking University
- Prof. Frank W. Harris and his groups at University of Akron
- Prof. Roderic P. Quirk and his students at University of Akron
- Prof. Chrys Wesdemiotis and his students at University of Akron
- Prof. George Newkome and his students at University of Akron
- Prof. Takozu Aida, University of Tokyo, Japan
- Prof. Bernard Lotz, Institute Charles Sadron, Strasburg, France
- Prof. An-Chang Shi, McMaster University, Canada
- Prof. Edwin L. Thomas, Rice University
- The National Science Foundation, US Air Force, and Many agencies and Industries
- High qualified X-ray experiments were carried out at APS, ANL.





Where is our Beginning?

"What would the properties of materials be if we could really arrange the atoms the way we want them?"

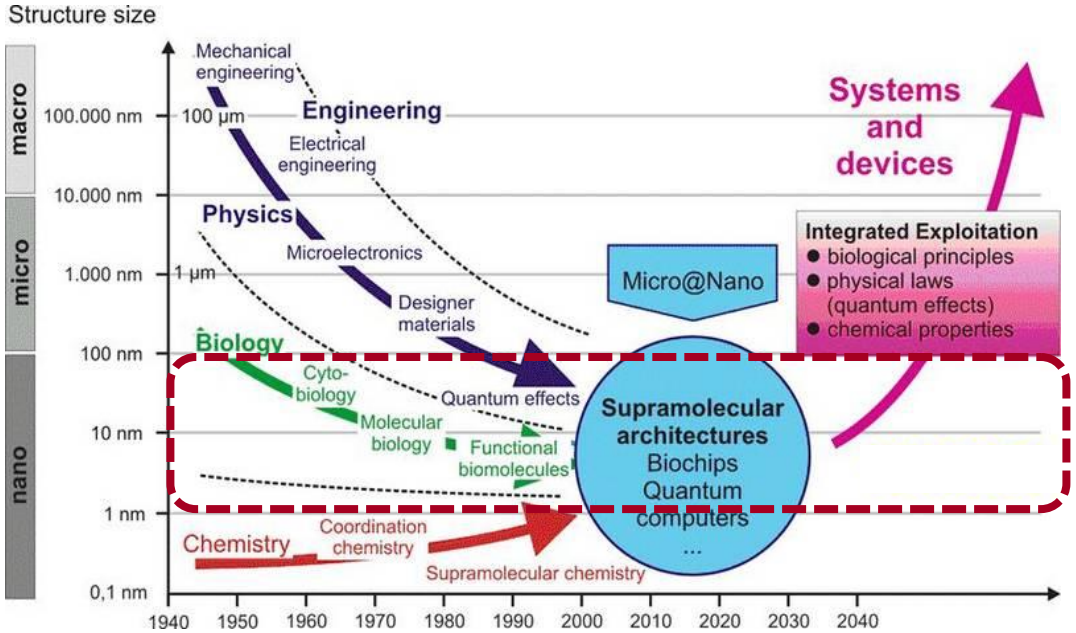
Feynman, R. P. *Eng. Sci.* ***1960***, *23, 22.*

$\sum$ Molecular functions → ? → Macroscopic Properties

(via hierarchical structures)

Hierarchical structure is important in transferring and amplifying molecular functions to a property at a specific length scale.

Top-down & Bottom-up Approaches



The structures in the length scale of 1 to 100 nm are the key to determine transferring and amplifying the functionality to macroscopic properties.

- **Chemical Reactions**

  "Click" Chemistry and other Efficient Transformations

- **Physical Interactions**

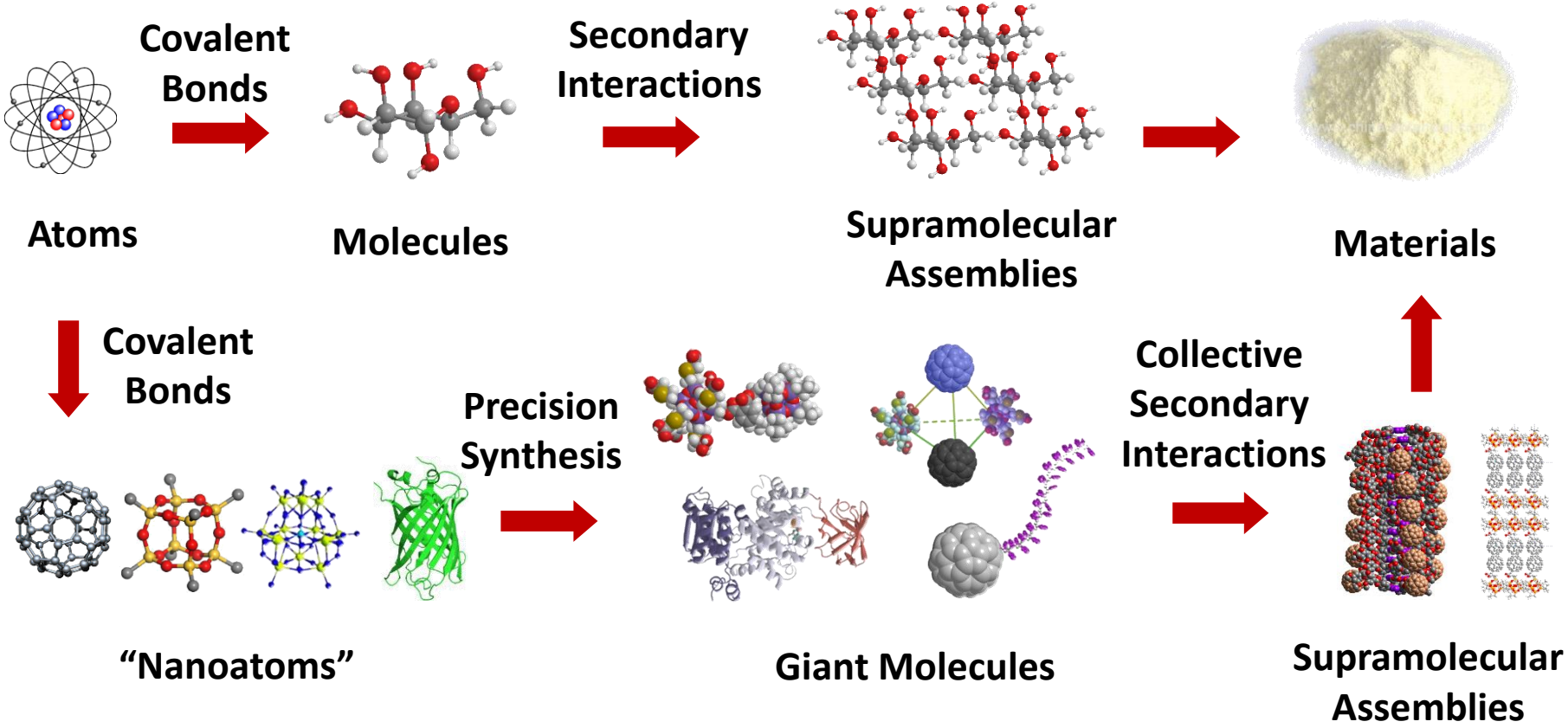
  Supramolecular Engineering to Hierarchical Structures

https://pchem.univie.ac.at/materialwissenschaftliches-zentrum-fuer-nanotechnologien/

From Molecules to Materials

➢ From Microscopic Functionality to Macroscopic Properties

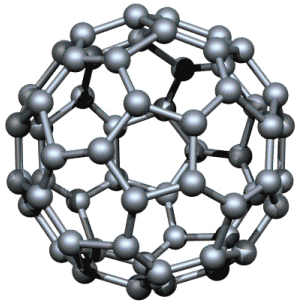
■ Atom-based Molecules



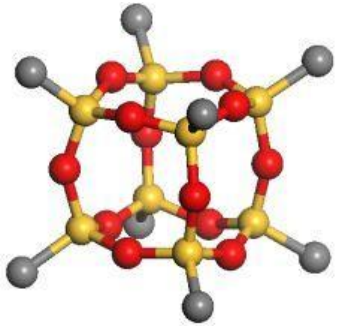
■ "Nano-atom"-based Precisely-defined Giant Molecules

“Nano-Atoms”

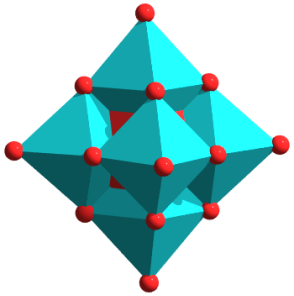
➢ “Nano-atoms” are **compact** and **rigid** molecular particles that possess **precisely-defined symmetry** and **surface functionalities** which are able to form “bonds” in specific positions and geometry.



- Fullerenes
- Carbon allotrope
- Sphere Diameter: ~ 1 nm
- Organic
- Functional Properties
- Versatile Functionalization



- Polyhedral Oligosilsesquioxane
- Center core across: ~ 1 nm
- Inorganic
- Versatile periphery functionality
- Cage provides rigid structural support
- High thermal stability

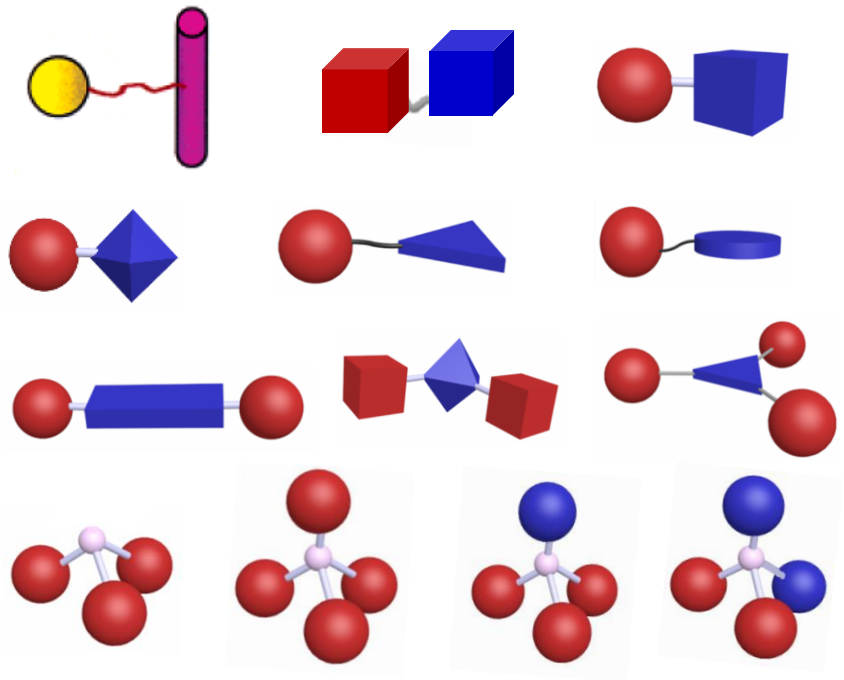


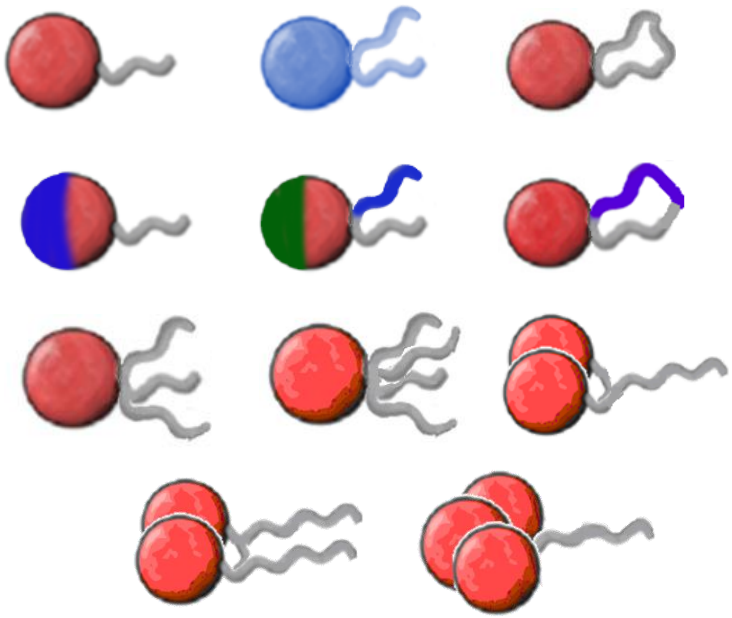
- Hexamolybdate (Lindqvist)
- End-to-end distance ~ 1 nm
- Two delocalized negative charges
- Facile but versatile functionality strategies
- Good thermal stability

Giant Molecules

- **Giant molecules are precisely defined macromolecules constructed by "nano-atoms"**

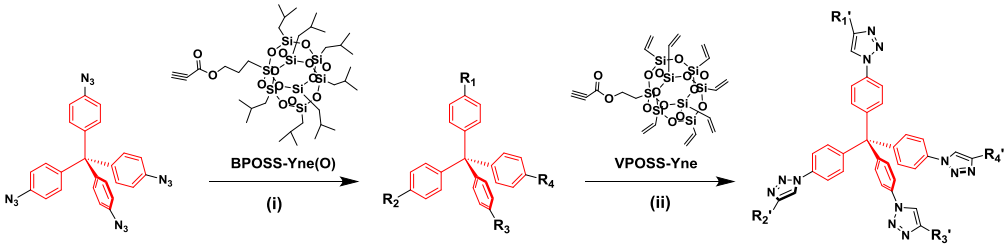
It includes shape amphiphiles, giant polyhedrons, giant surfactants and lipids…





- **"Click" Chemistry**
- **Physical Interactions**

Giant Shape Tetrahedron



1a R_1 = BPOSS-triazole
$R_2 = R_3 = R_4 = N_3$

1b $R_1 = R_2$ = BPOSS-triazole
$R_3 = R_4 = N_3$

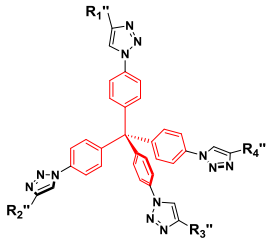
1c $R_1 = R_2 = R_3$ = BPOSS-triazole
$R_4 = N_3$

2a $R_1' = $ BPOSS
$R_2' = R_3' = R_4' = $ VPOSS

2b $R_1' = R_2' = $ BPOSS
$R_3' = R_4' = $ VPOSS

1c $R_1' = R_2' = R_3' = $ BPOSS
$R_4' = $ VPOSS

(iii)



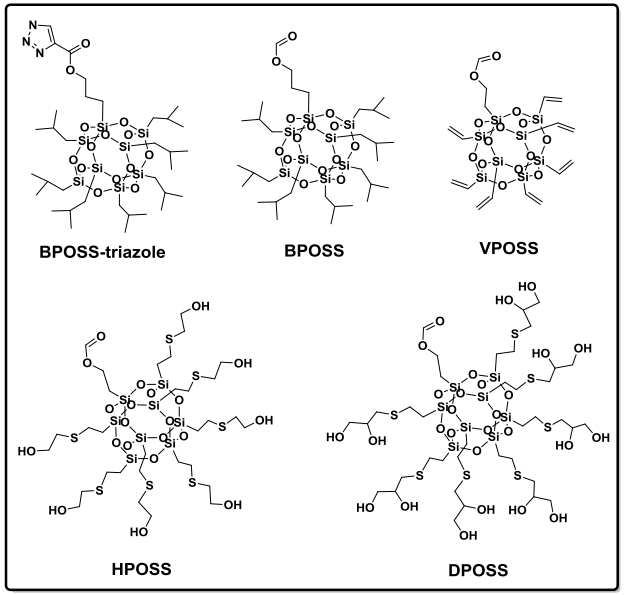
3a-H (BH_3)
$R_1'' = $ BPOSS
$R_2'' = R_3'' = R_4'' = $ HPOSS

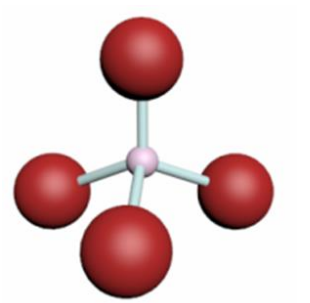
3a-D (BD_3)
$R_1'' = $ BPOSS
$R_2'' = R_3'' = R_4'' = $ DPOSS

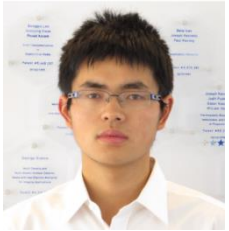
3b-H (H_2B_2)
$R_1'' = R_2'' = $ BPOSS
$R_3'' = R_4'' = $ HPOSS

3c-H (B_3H)
$R_1'' = R_2'' = R_3'' = $ BPOSS
$R_4'' = $ HPOSS

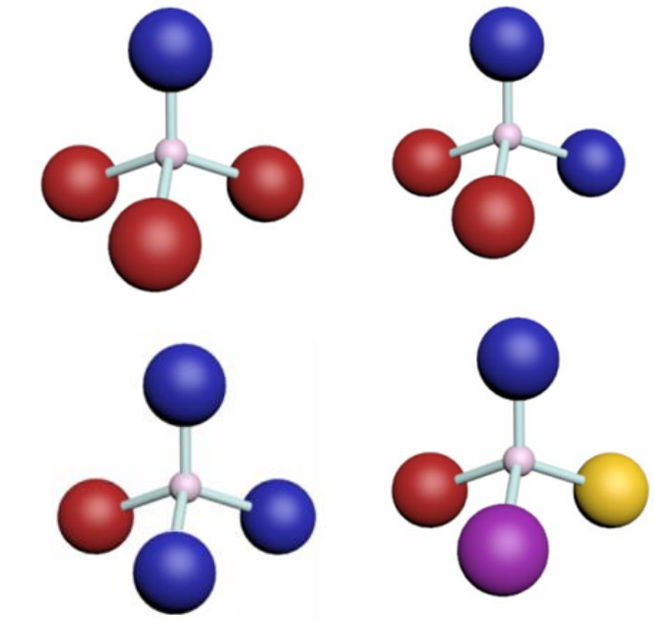
3c-D (B_3D)
$R_1'' = R_2'' = R_3'' = $ BPOSS
$R_4'' = $ DPOSS





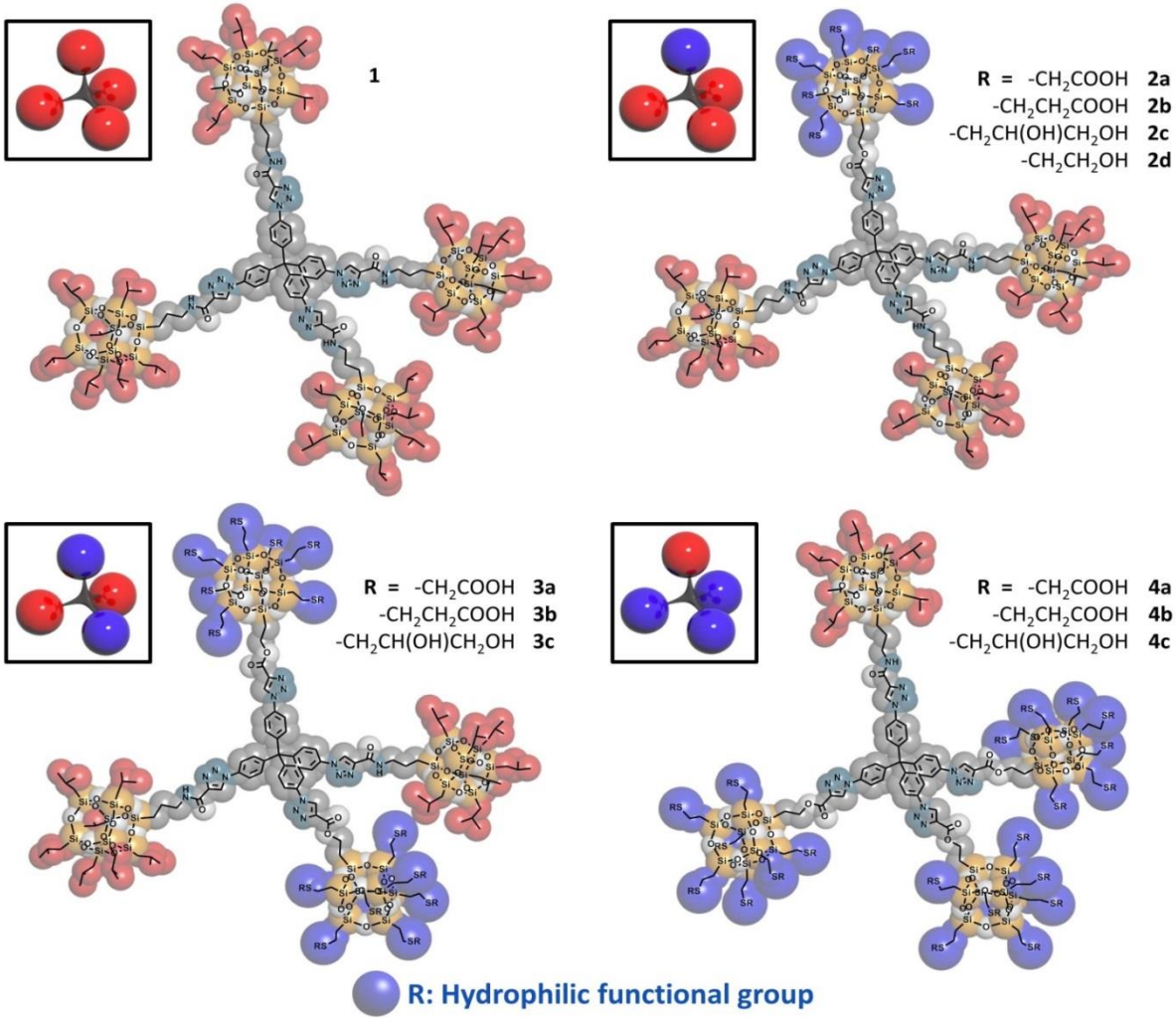


Mingjun Huang



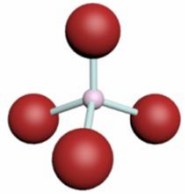
Red: BPOSS, Hydrophobic;
Blue: DPOSS or HPOSS, Hydrophilic

Chemical Structures and Molecular Models

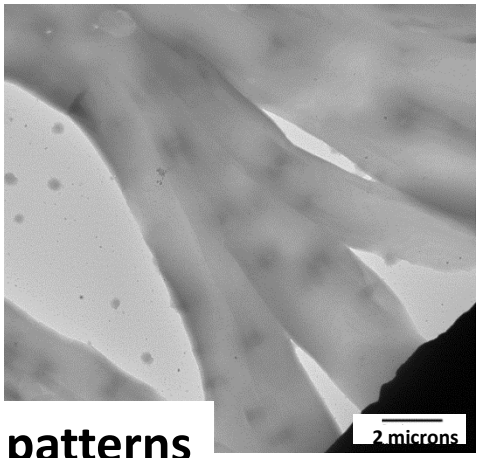


Ref. Huang, M.; Hsu, C.-H.; Zhang, W.-B.; Yue, K.; Cheng, Z. D. *et al*. *Science* **2015**, *348*, 424-428.

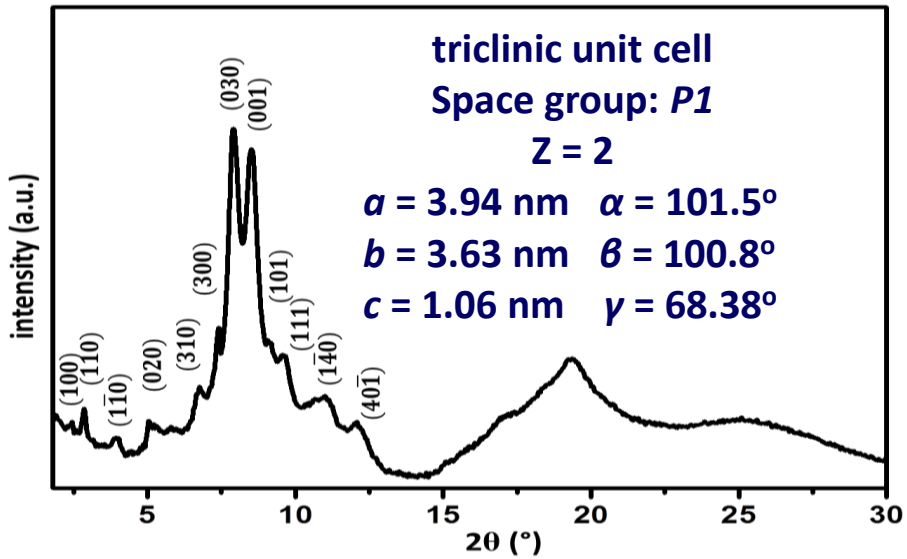
Crystal Structure of Giant Tetrahedron



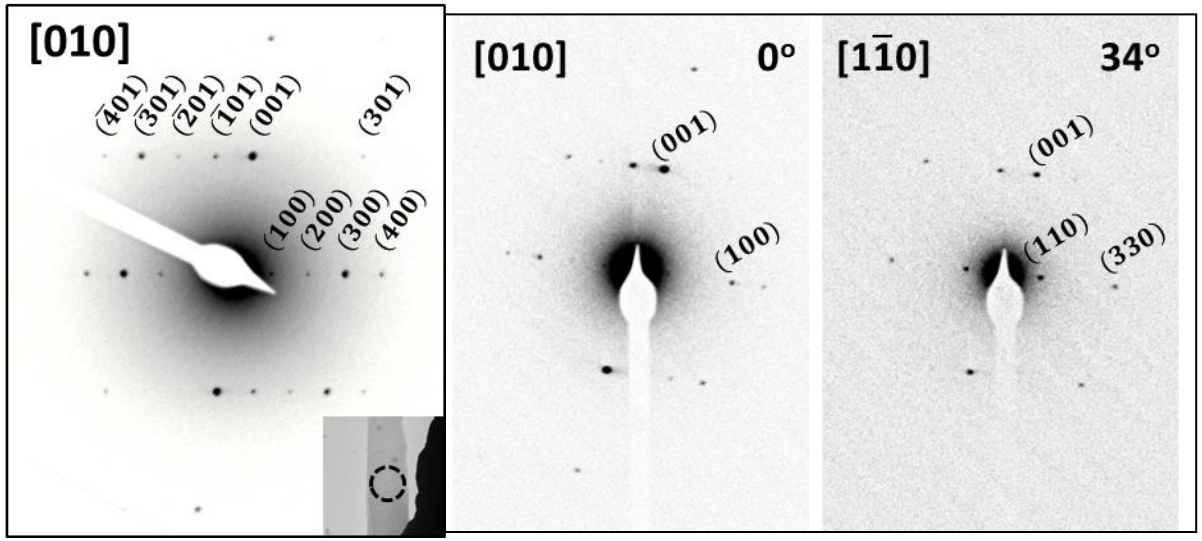
Bright-field TEM image (samples were slowly evaporated from 0.02(wt)% dichloroethene solution.

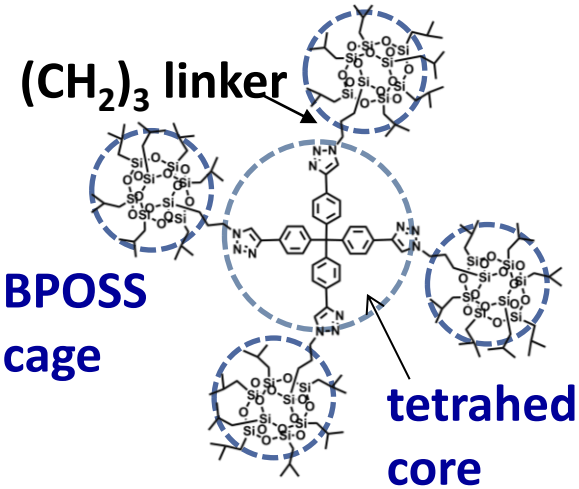


ED tilting patterns

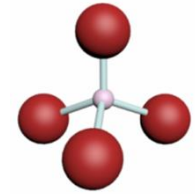


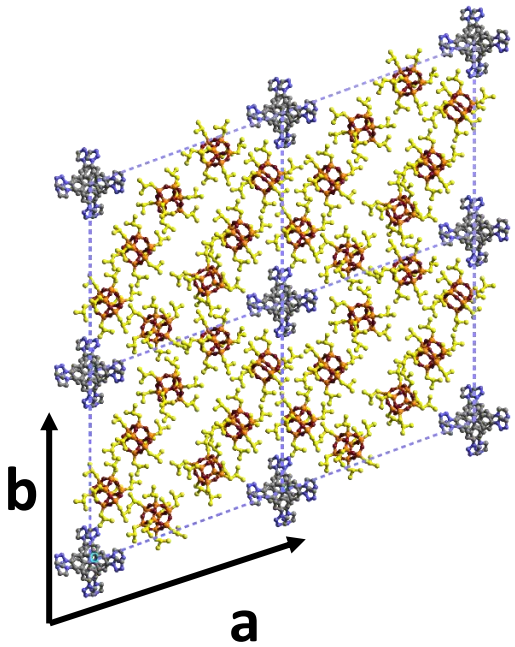
ED patterns



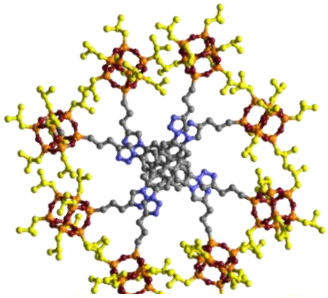


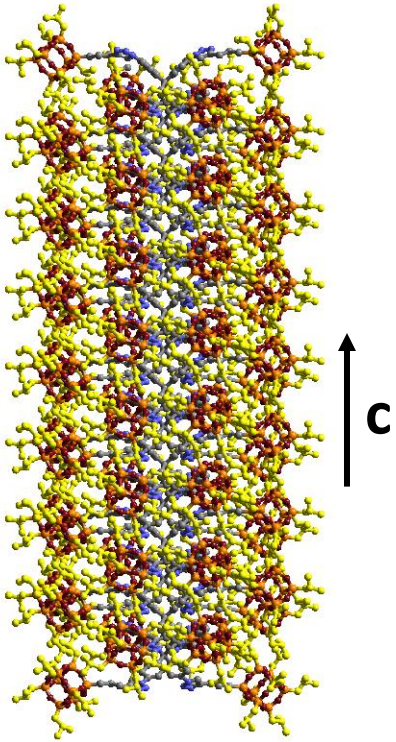
Molecular Packing Model



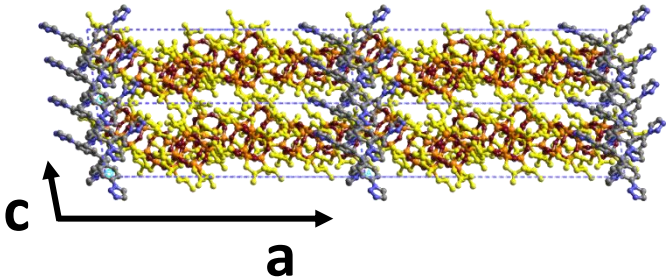


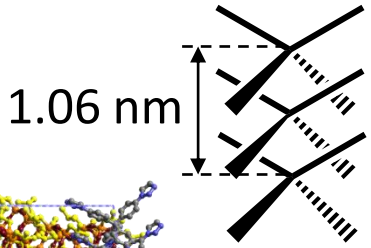
Chih-Hao Hsu



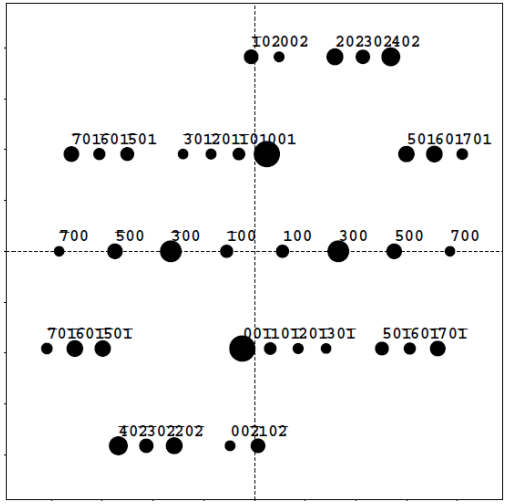


triclinic unit cell
Space group: *P1*
Z = 2
a = 3.94 nm α = 101.5°
b = 3.63 nm β = 100.8°
c = 1.06 nm γ = 68.38°



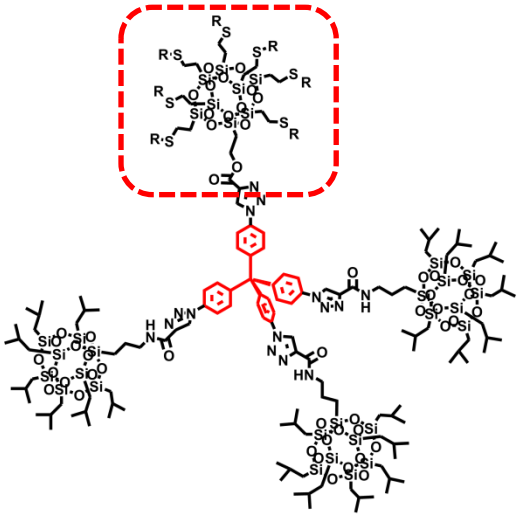


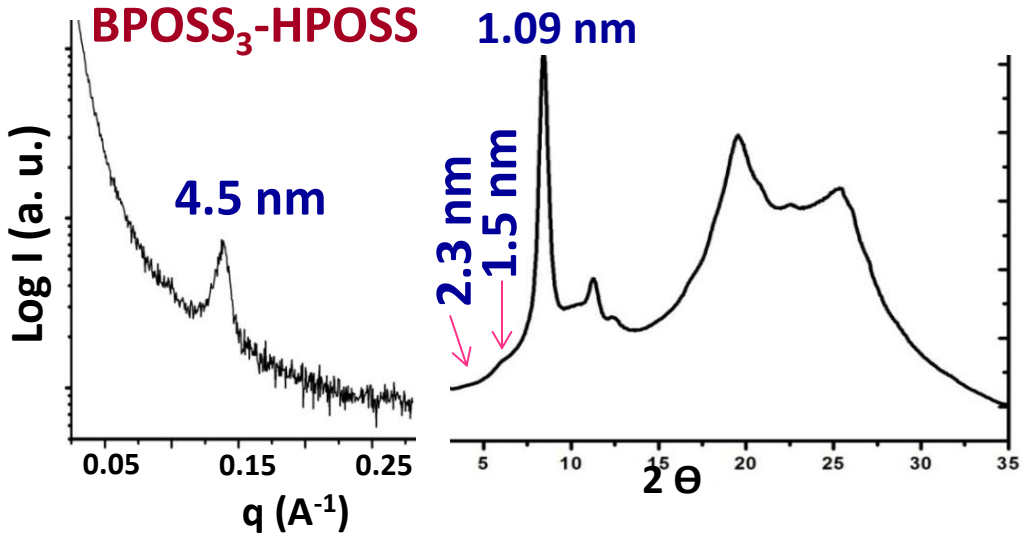
Simulated ED Pattern



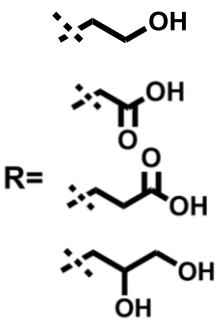
Crystallization of BPOSS distorts the hexagonally cylindrical packing.

Amphiphilic $BPOSS_3$-XPOSS at R.T.





d-spacing for lamellae:



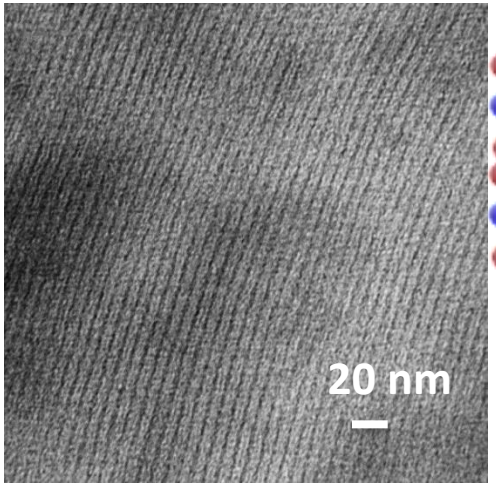
$BPOSS_3$-HPOSS: 4.50 nm

$BPOSS_3$-APOSS: 4.38 nm

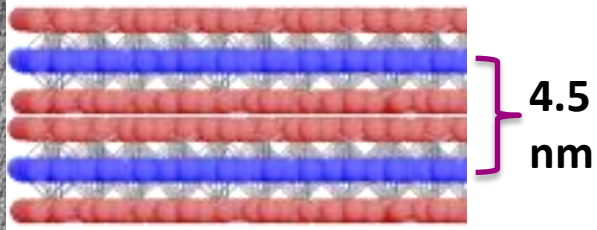
$BPOSS_3$-APOSS-C3: 4.60 nm

$BPOSS_3$-DPOSS: 4.67 nm

At room temperature, BPOSS crystallizes, dominating over hydrogen bonding



Microtome TEM at R.T.

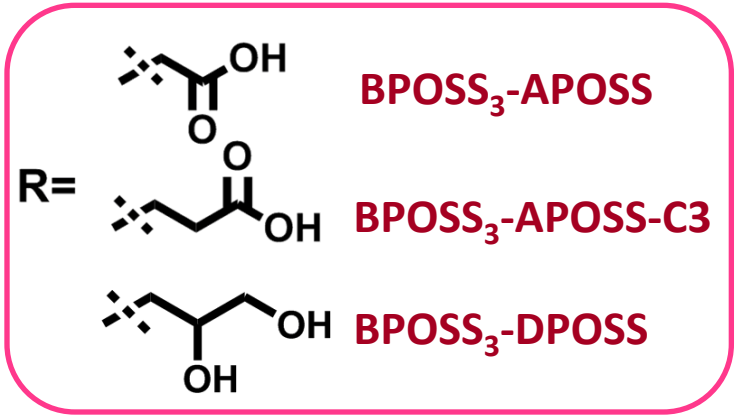


1.5 layer structure

Frustrated Lamellae!

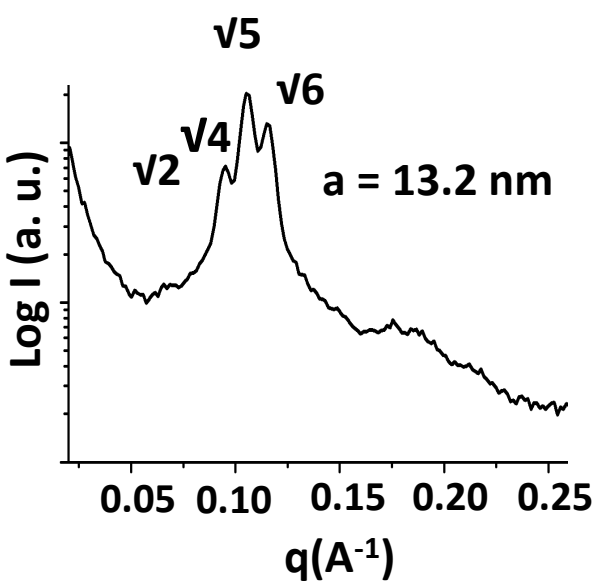
Amphiphilic BPOSS3-XPOSS

$BPOSS_3$-APOSS annealed slightly above the melting temperature of BPOSS crystals.

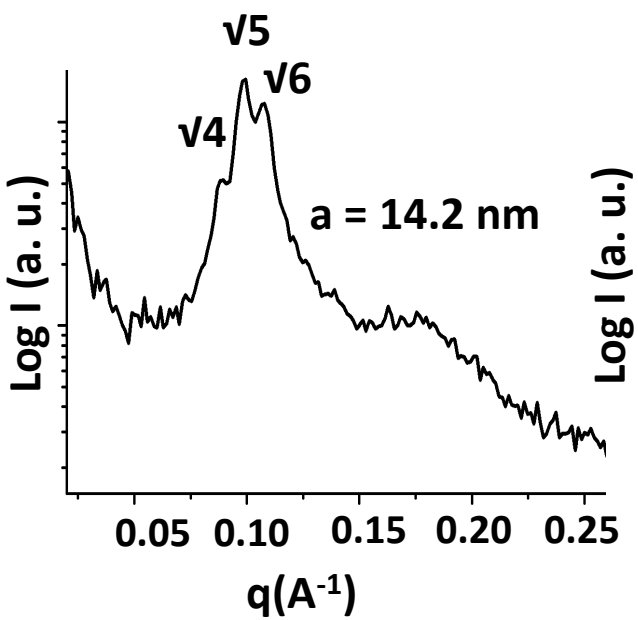


T_m of BPOSS crystals are 120 °C - 150 °C. Annealing temperature is above T_m.

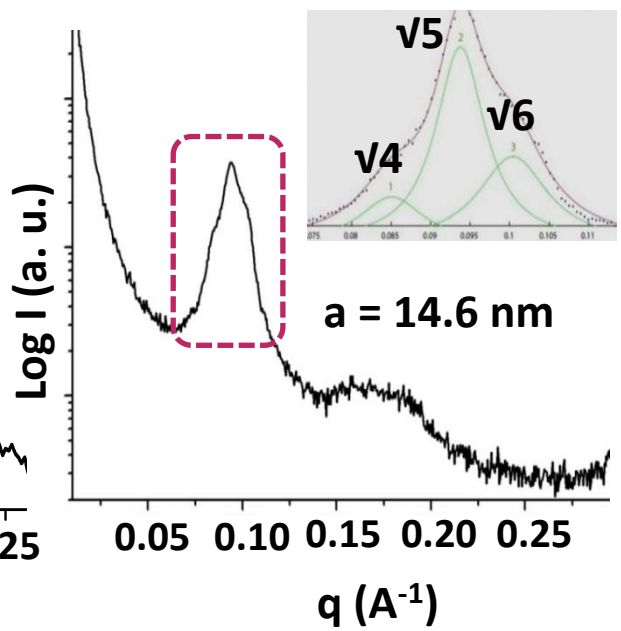
A15 phase



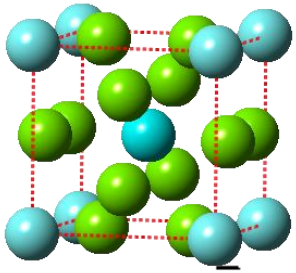
$BPOSS_3$-APOSS-C3



$BPOSS_3$-DPOSS



Frank-Kasper A15 Phase Structure

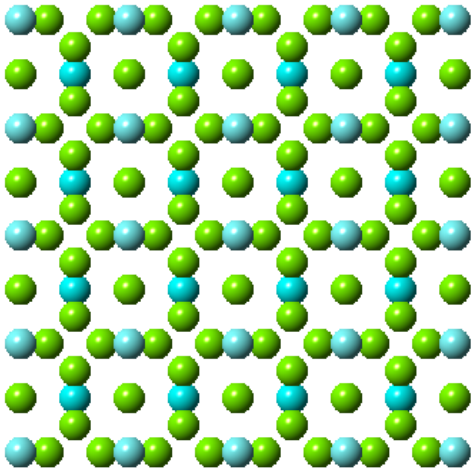


A15($Pm3n$)

Atom positions:

(0, 0, 0), (½, ½, ½)
(½, 0, ¾), (½, 0, ¼)
(0, ¾, ½), (0, ¼, ½)
(¼, ½, 0), (¾, ½, 0)

$BPOSS_3$-APOSS



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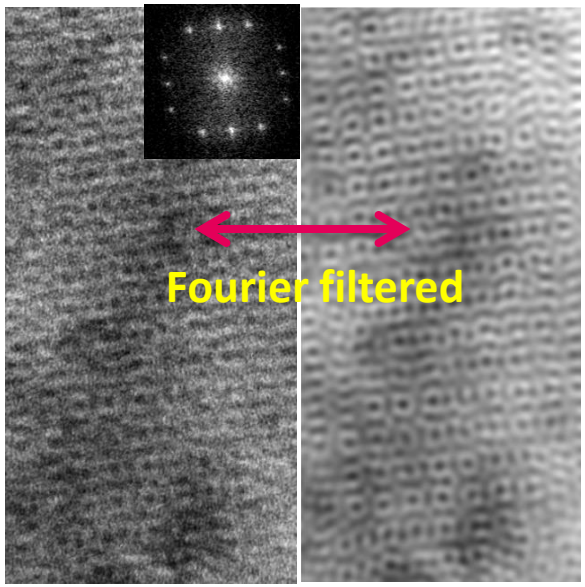

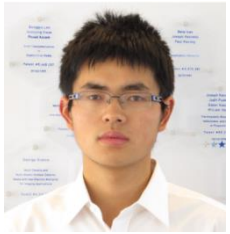

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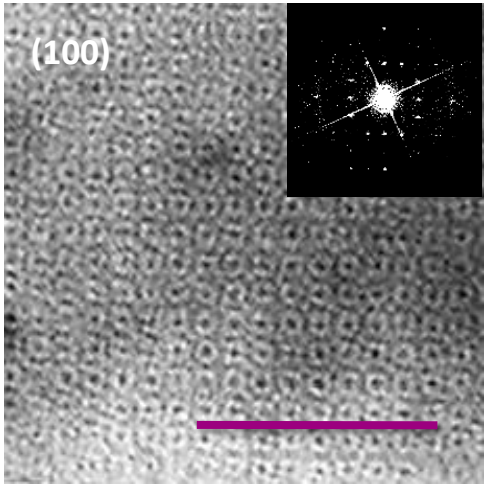
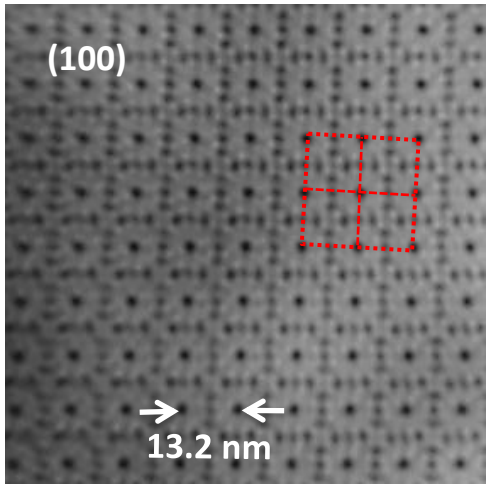
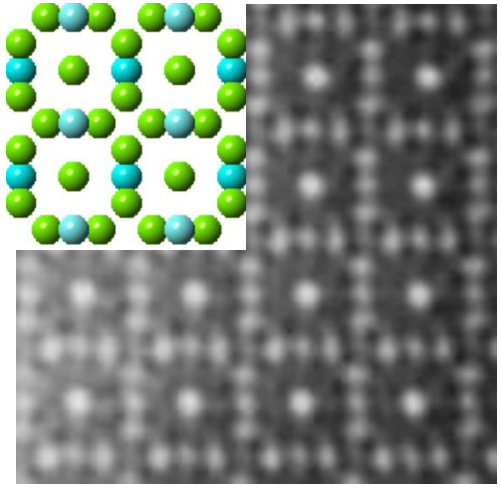
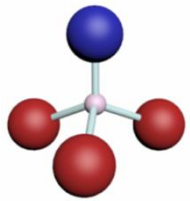
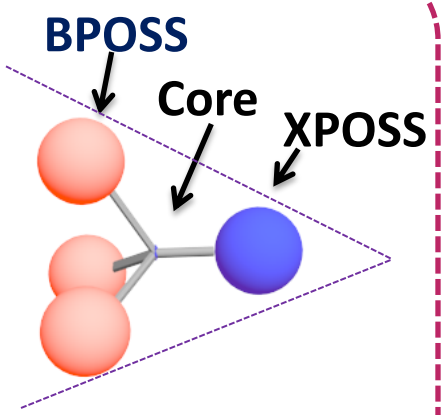






Scheme of $BPOSS_3$-XPOSS Structure





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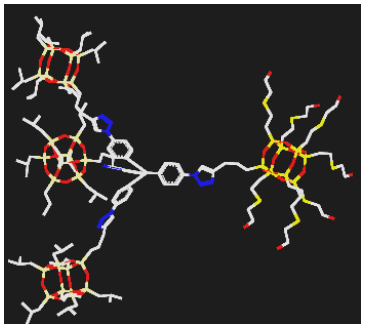
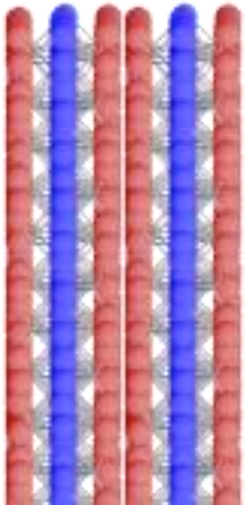
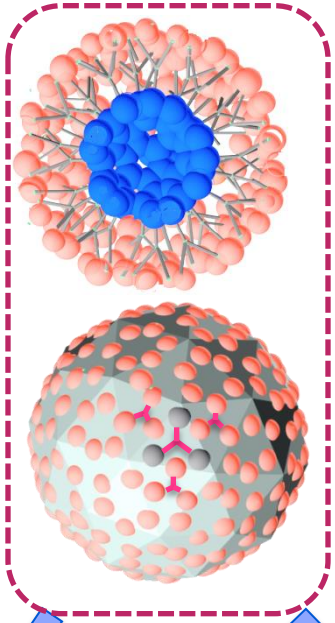


Crystalize



Frustrated 1.5 layer structure

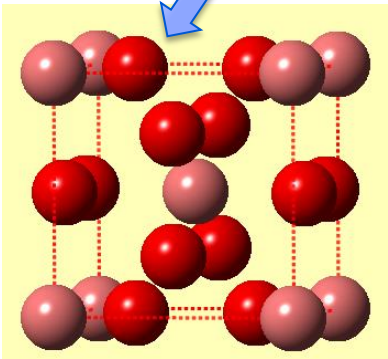
Melting



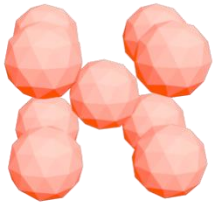
H-bonding Intersection to form spheres

Building Block:

Size and deformability



A15($Pm\bar{3}n$)



BCC

Amphiphilic $BPOSS_2$-$XPOSS_2$ at R. T.

Lamellar structures for BPOSS2-XPOSS2 tetrahedra at room temperature form since BPOSS crystallizes.

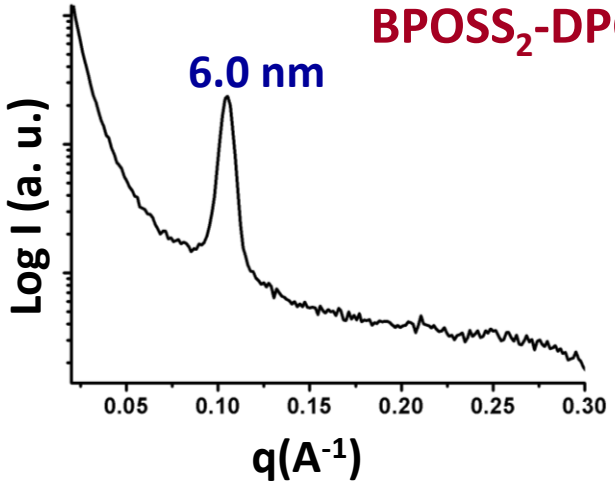
The d-spacings of lamellae at R.T.

$BPOSS_2$-$HPOSS_2$: 5.5 nm

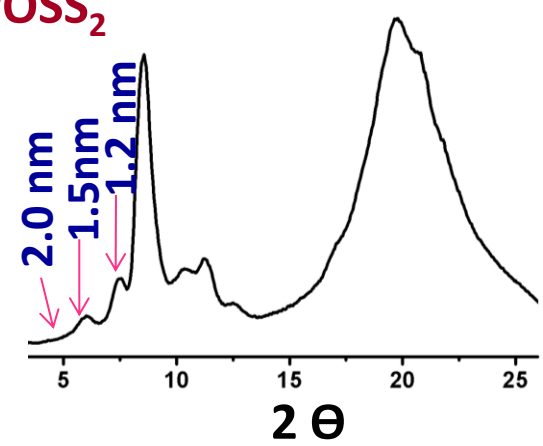
$BPOSS_2$-$APOSS_2$: 5.4 nm

$BPOSS_2$-$APOSS_2$-C_3: 5.9 nm

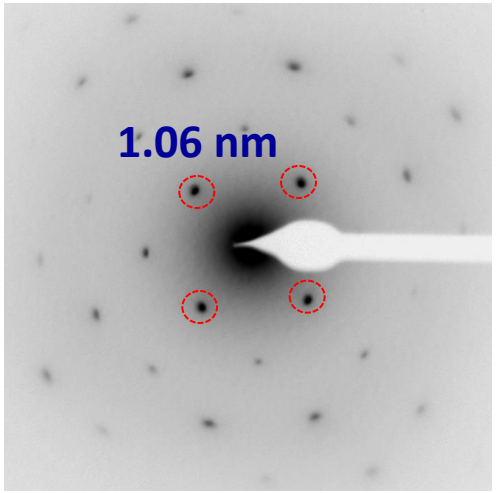
$BPOSS_2$-$DPOSS_2$: 6.0 nm

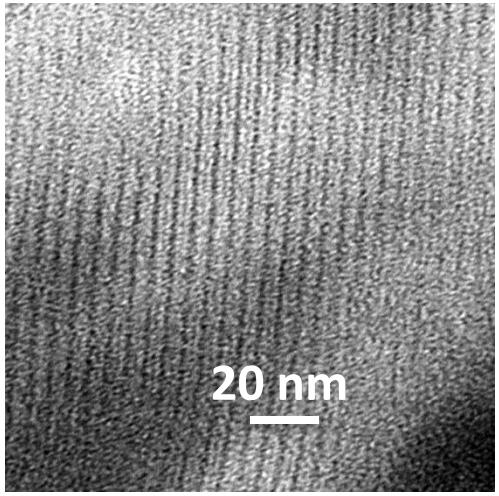


$BPOSS_2$-$DPOSS_2$



ED pattern is close to the simple BPOSS crystal lattice.

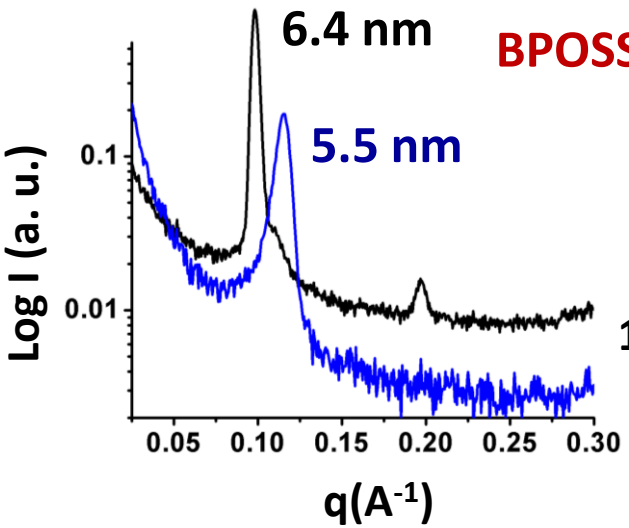


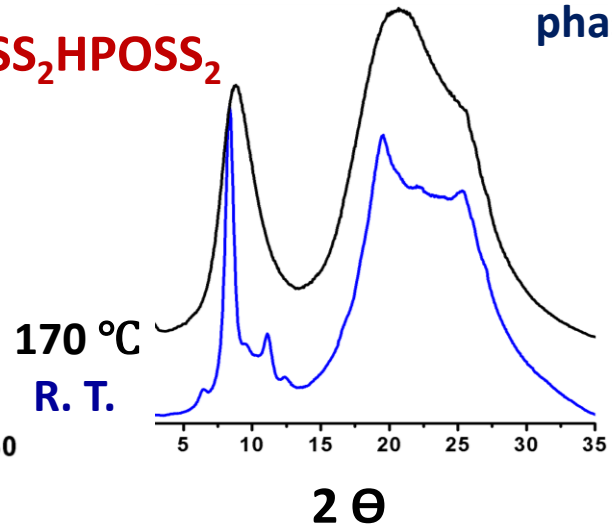


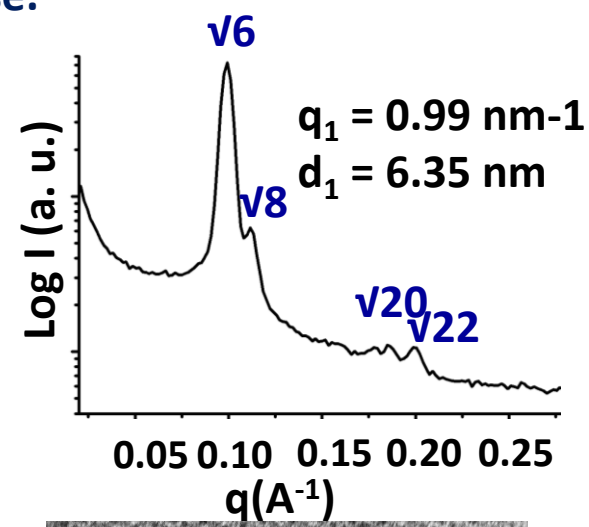
Amphiphilic $BPOSS_2$-$XPOSS_2$ above T_m

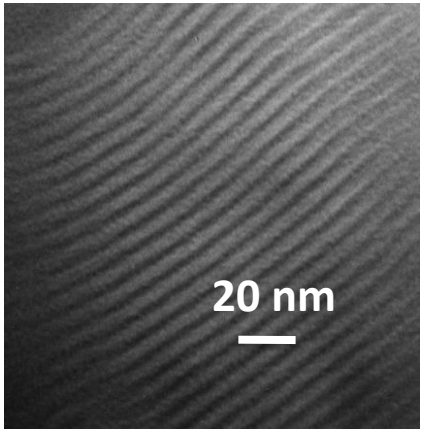
After the BPOSS crystal parts melt, lamellar structures remain for $BPOSS_2$-$HPOSS_2$, $BPOSS_2$-$DPOSS_2$ and $BPOSS_2$-$APOSS_2$-C_3.

For $BPOSS_2$-$APOSS_2$ it become DG phase.









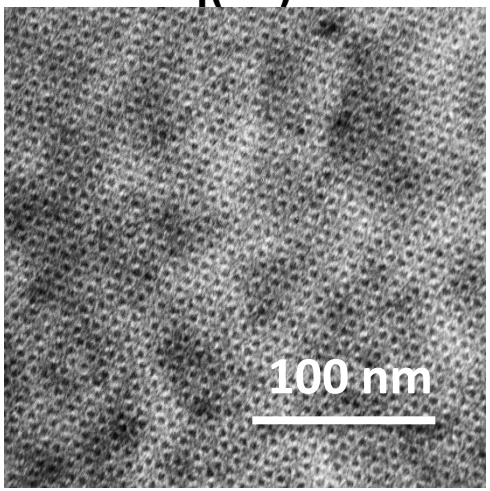
quenched at 170 ℃

Lamellar expansion to:

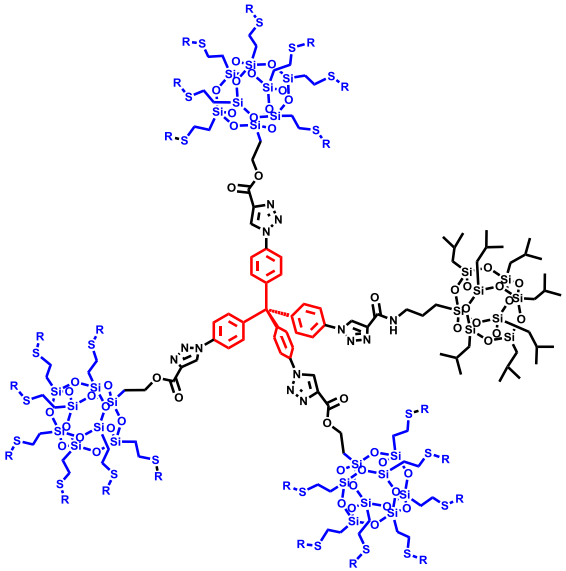
$BPOSS_2$-$HPOSS_2$: 6.40 nm

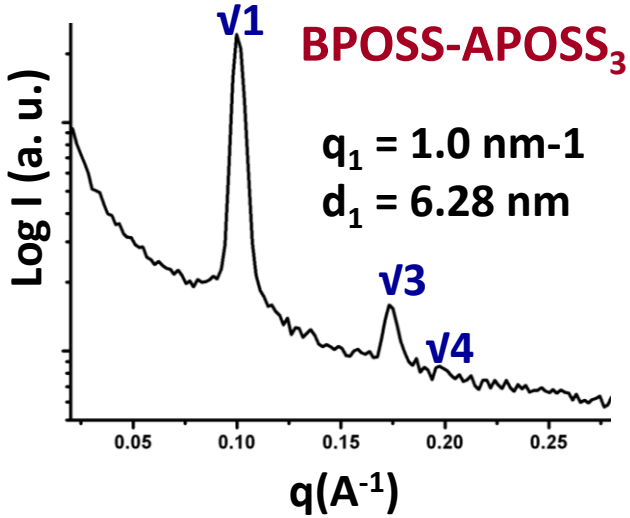
$BPOSS_2$-$APOSS_2$-C_3: 6.40 nm

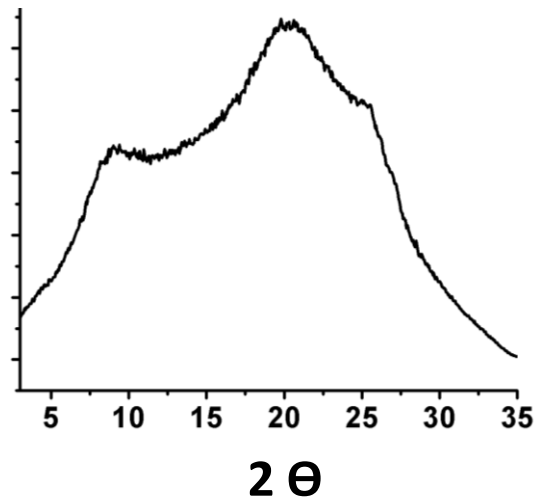
$BPOSS_2$-$DPOSS_2$: 7.24 nm



Amphiphilic BPOSS-XPOSS$_3$







BPOSS number is too few to crystalize

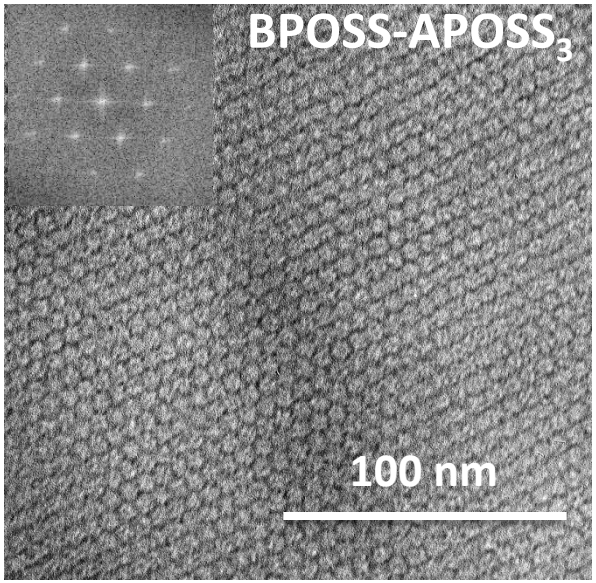
d-spacing for (10):

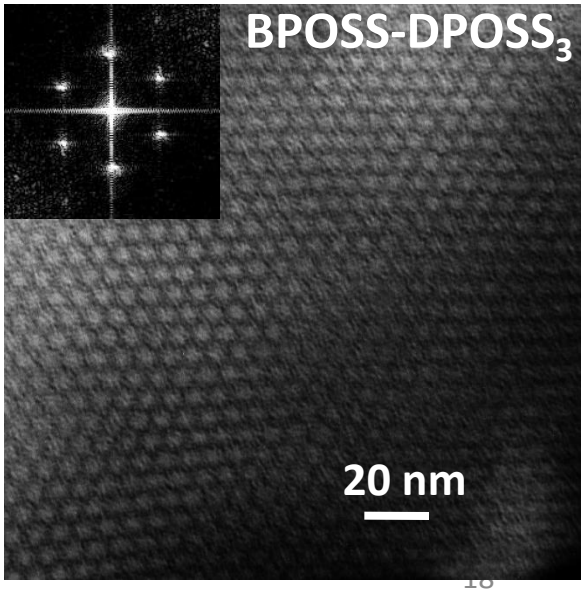
BPOSS-HPOSS$_3$: 6.0 nm

BPOSS-APOSS$_3$: 6.4 nm

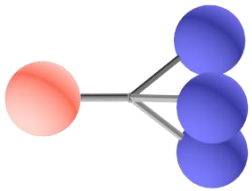
BPOSS-APOSS$_3$-C$_3$: 6.3 nm

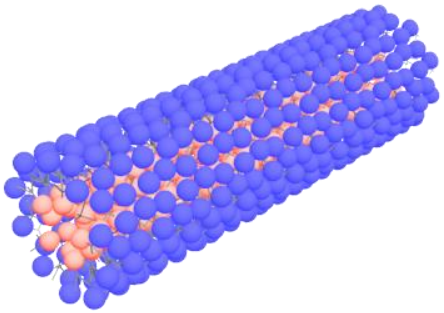
BPOSS-DPOSS$_3$: 6.7 nm

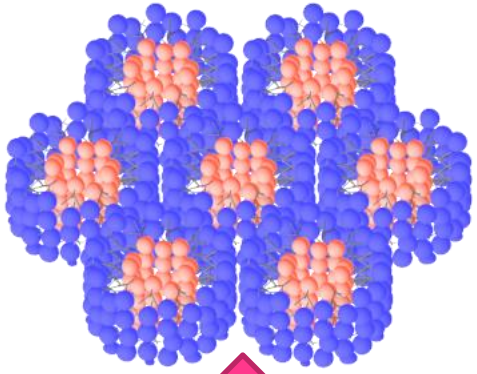




Scheme of BPOSS-XPOSS$_3$ Structure

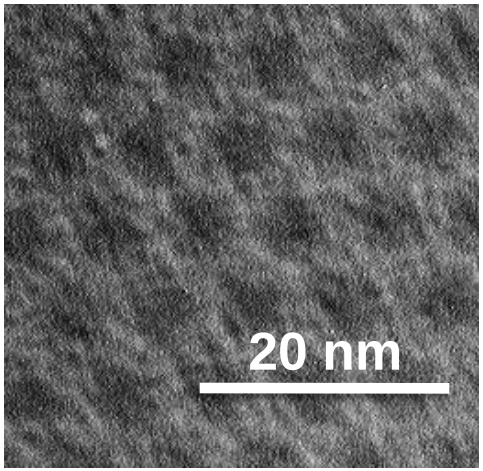






BPOSS-HPOSS$_3$
BPOSS-DPOSS$_3$
BPOSS-APOSS$_3$

Hydrogen bonding prefers more contact between DPOSS, cylinder structure could provide more contact area than sphere structures.

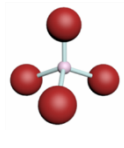
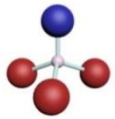
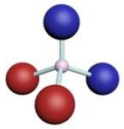
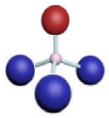


Negative view. Gray: DPOSS
Dark: BPOSS

What we have observed is that the collective secondary interactions become a determining factor to select the sphere packing schemes.

Collective Secondary Interaction Effect on the Supramolecular Structures

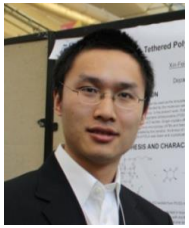
The collective secondary interaction (H-bonding) is the determining Factor for selecting the sphere packing schemes.

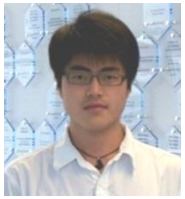
Giant tetrahedrons	Crystallized BPOSS at R.T.	Crystal, d (nm)	After BPOSS crystals melt	Supralattice spacing, d (nm)	μ (Sphere)
$BPOSS_4$	Triclinic	-	Amorphous	-	-
$BPOSS_3$-HPOSS	Lamellae	4.50	BCC	8.2	41
$BPOSS_3$-APOSS	Lamellae	4.38	A15	13.2	34/52
$BPOSS_3$-APOSS-C3	Lamellae	4.60	A15	14.2	41/62
$BPOSS_3$-DPOSS	Lamellae	4.67	A15	14.6	44/67
$BPOSS_2$-$HPOSS_2$	Lamellae	5.5	Lamellae	6.40	-
$BPOSS_2$-$APOSS_2$	Lamellae	5.4	Doub. Gyroid	6.35 (d_1)	-
$BPOSS_2$-$APOSS_2$-C_3	Lamellae	5.9	Lamellae	6.40	-
$BPOSS_2$-$DPOSS_2$	Lamellae	6.0	Lamellae	7.24	-
BPOSS-$HPOSS_3$	Amorphous	-	Cylinder	6.0 (d_1)	-
BPOSS-$APOSS_3$	Amorphous	-	Cylinder	6.4(d_1)	-
BPOSS-$APOSS_3$-C_3	Amorphous	-	Cylinder	6.3(d_1)	-
BPOSS-$DPOSS_3$	Amorphous	-	Cylinder	6.7(d_1)	-

Giant Surfactants and Lipids

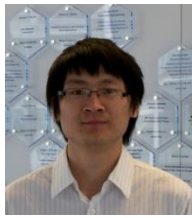
Between Small Molecule Surfactant & Block Copolymer
Role of Surface Chemistry and Shape Persistency



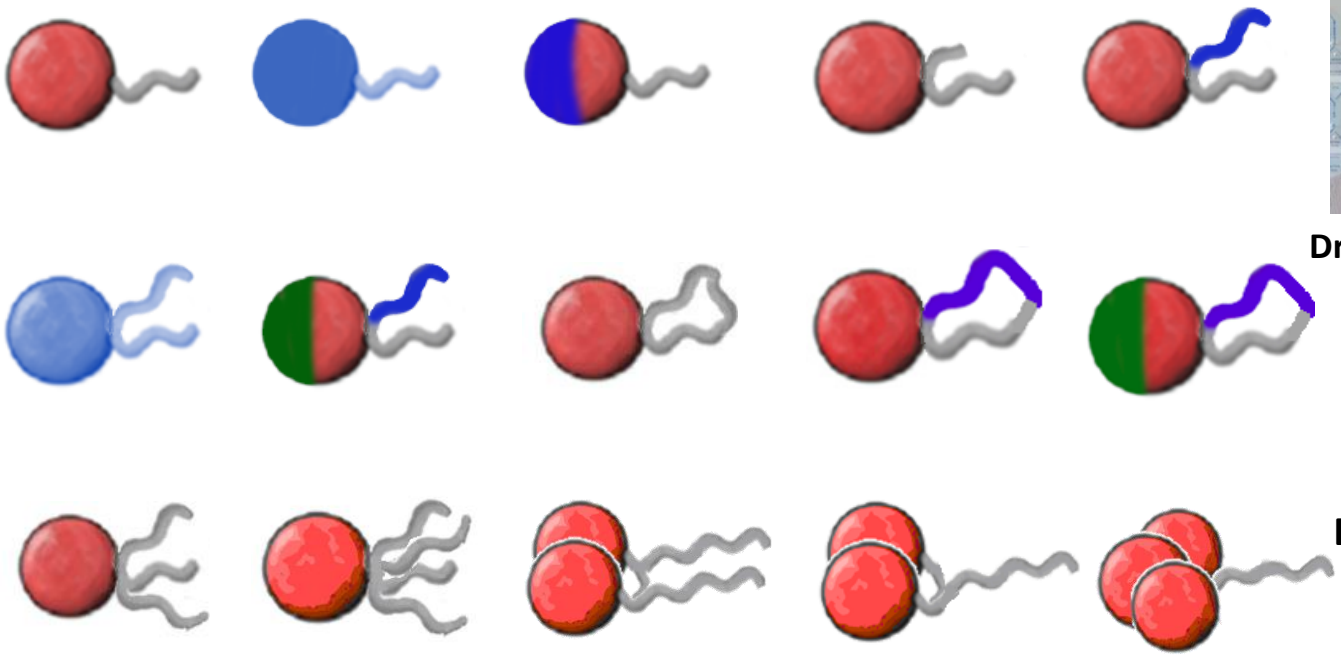
Dr. Xinfei Yu

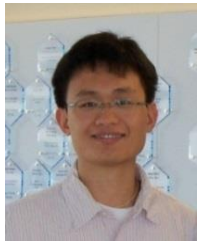


Dr. Xuehui Dong



Dr. Kan Yue





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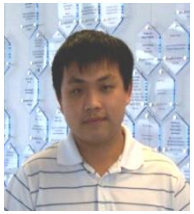


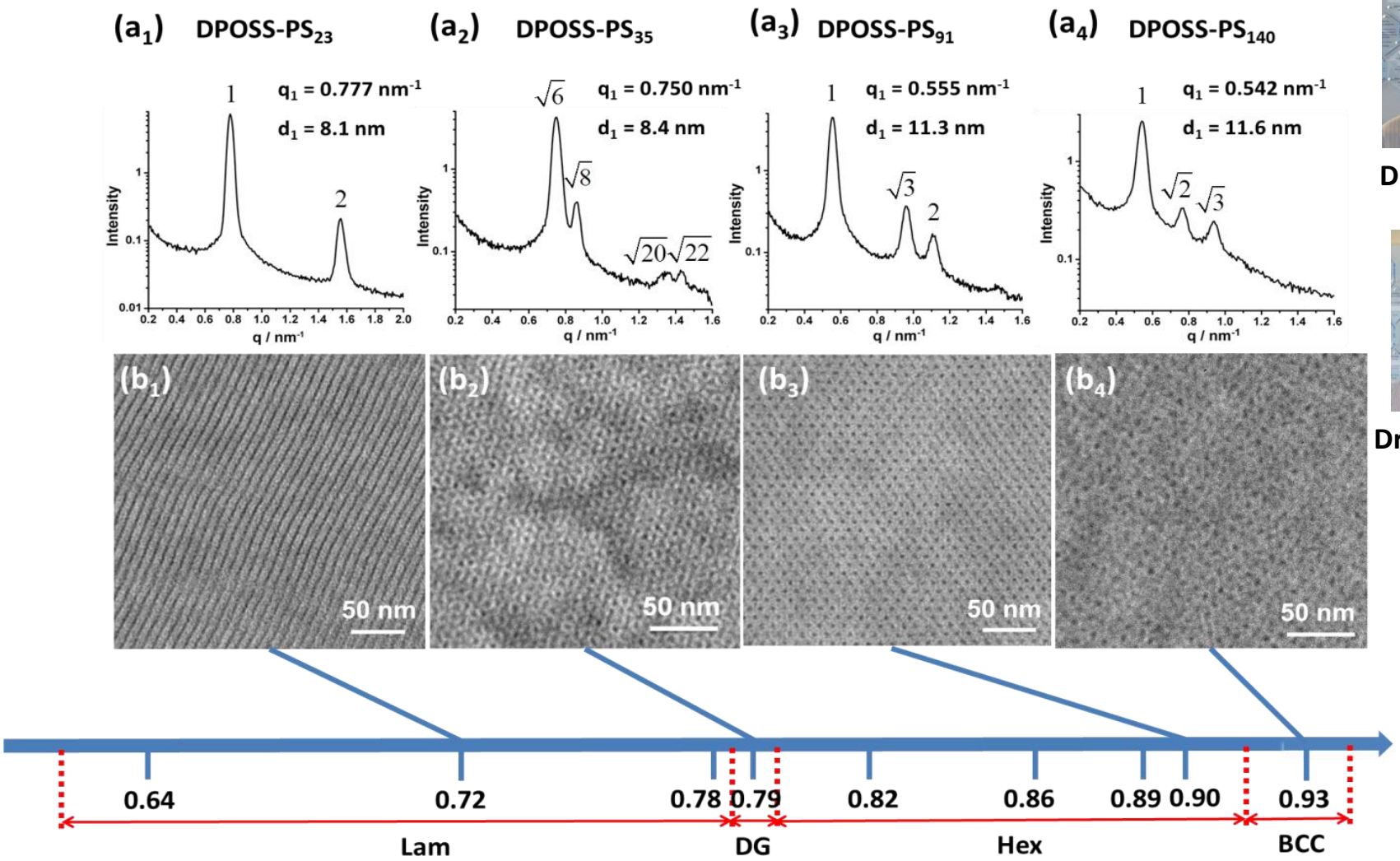
Dr. Yiwen Li

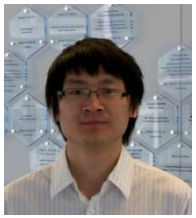
Hao Liu

Ref. Yu, X.; Yue, K.; Chen, E.-Q.; Zhang, W.-B., Cheng, Z. S. D. *et al.* *PNAS* **2013**, 110, 10078-10083.

DPOSS-PS Phase Structure of Giant Surfactants in the bulk

- **Duality I: Block-Copolymer-like Behavior in the Bulk.**





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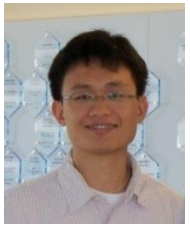

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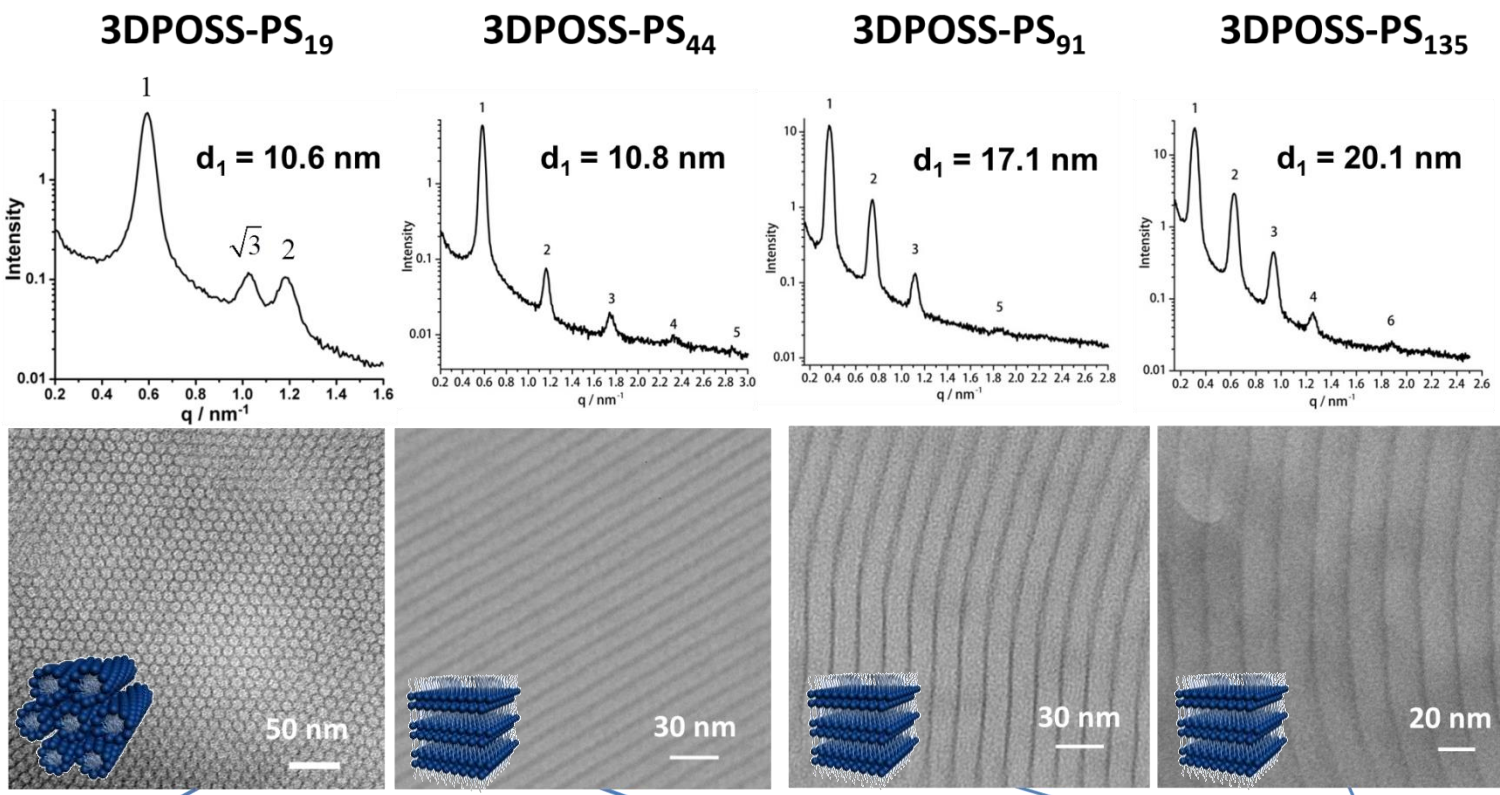
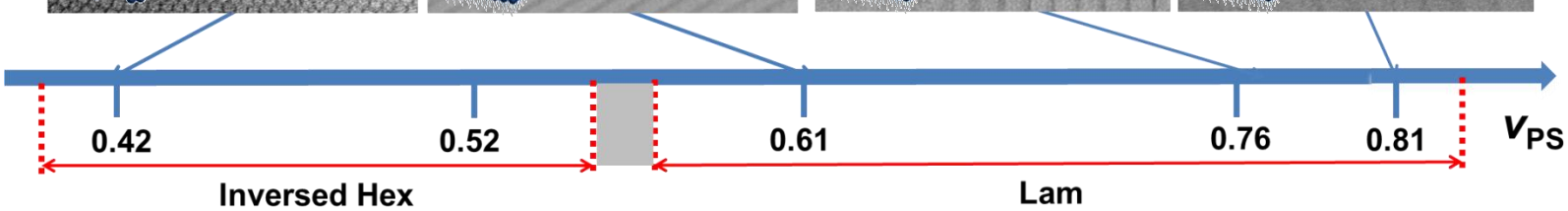
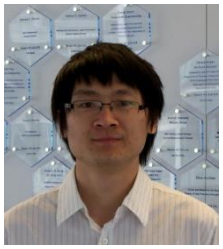
3DPOSS-PS Phase Structure in the Bulk







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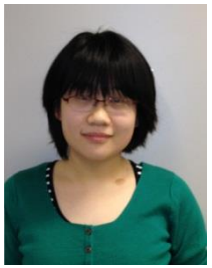
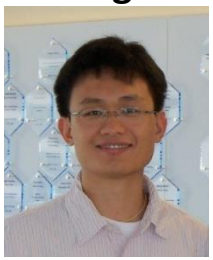


Chang Liu



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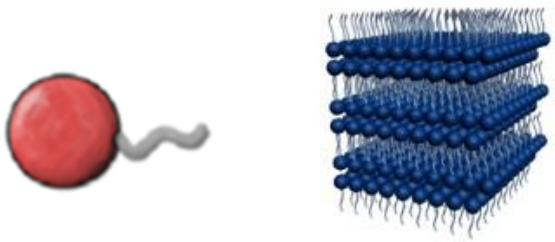
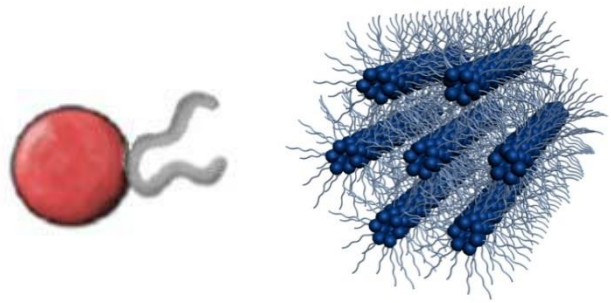
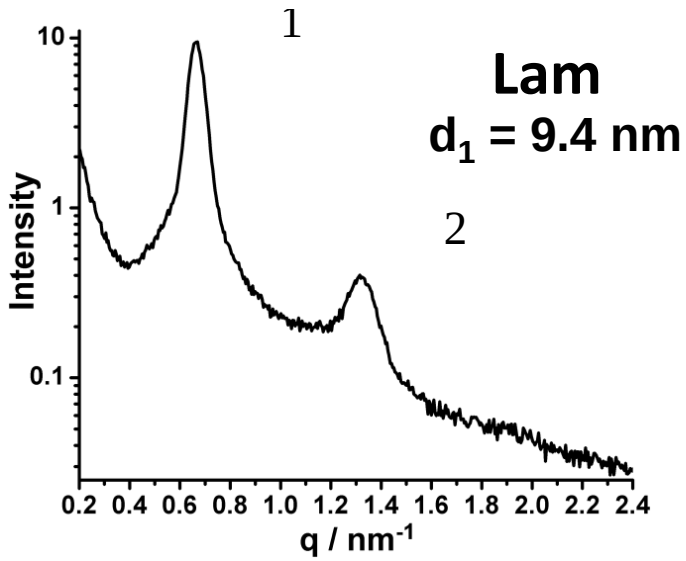
Inversed Hex and Highly Asymmetric Lamellar Phases

Topological Isomers in the Bulk

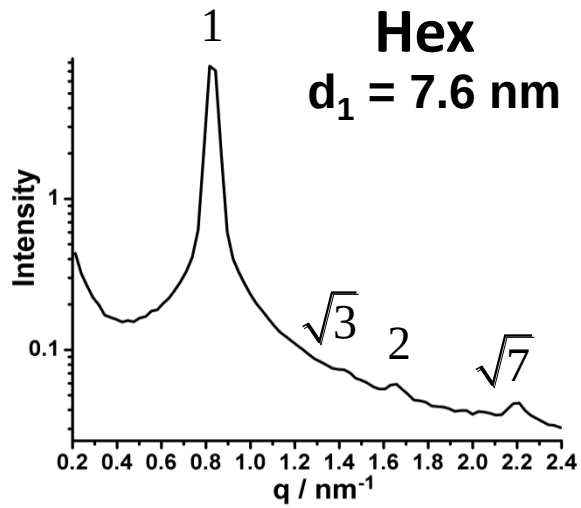
- AC_{60}-PS and AC_{60}-2PS with same PS MW exhibit distinct structures.



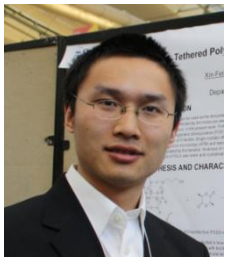




AC_{60}-PS_{44}



AC_{60}-$2PS_{22}$



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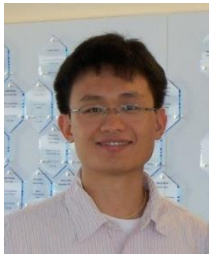

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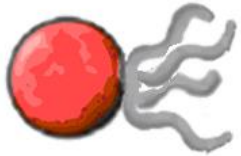
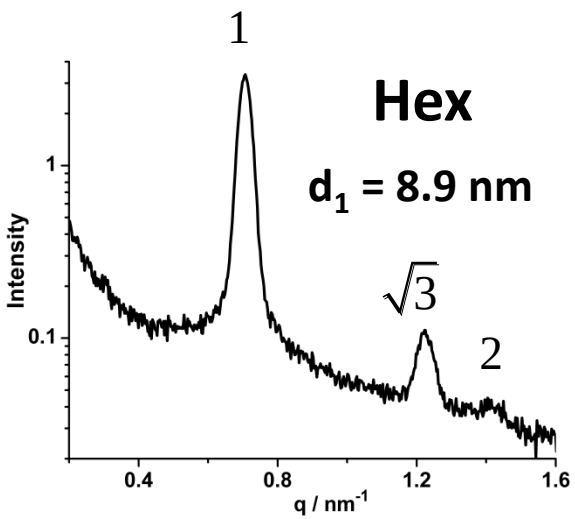
Dr. Ryan Van Horn

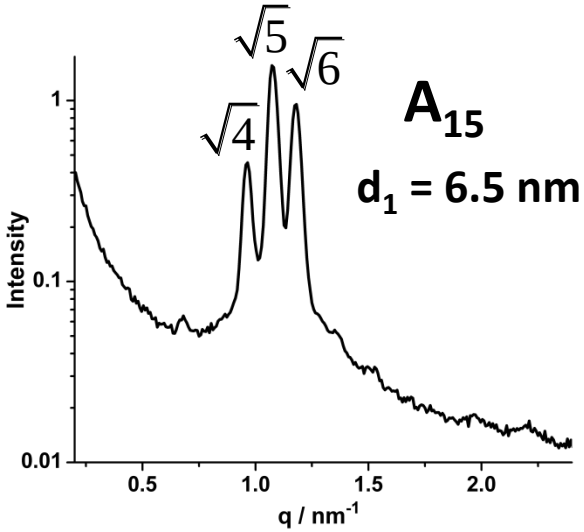
Topological Isomers in the Bulk

- **DPOSS-4PS prefers the formation of more curved phases.**



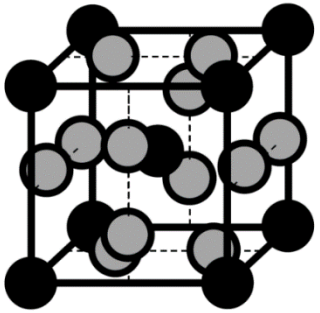


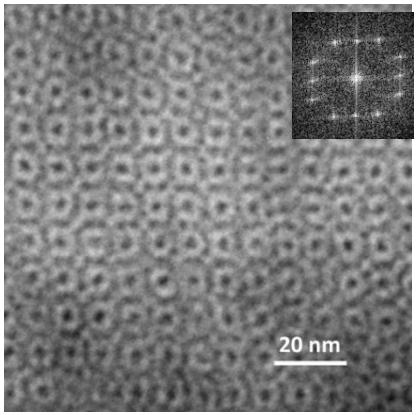
DPOSS-PS$_{44}$



DPOSS-4PS$_{44}$

The A_{15} Phase





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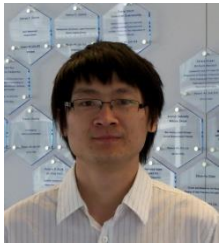
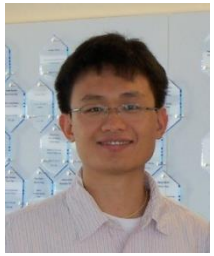
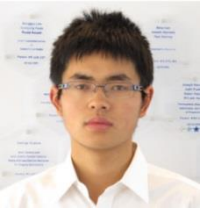


Dr. Kan Yue



Dr. W.-B. Zhang

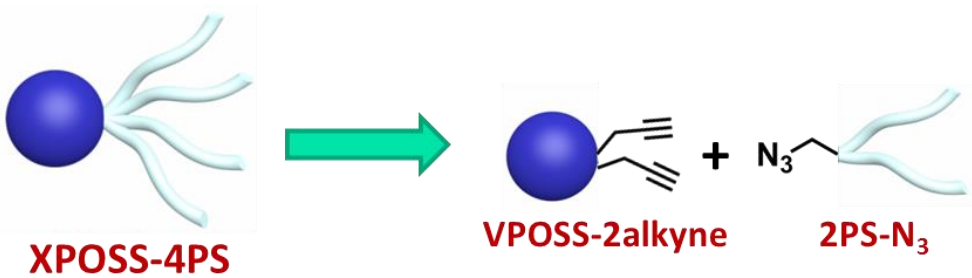


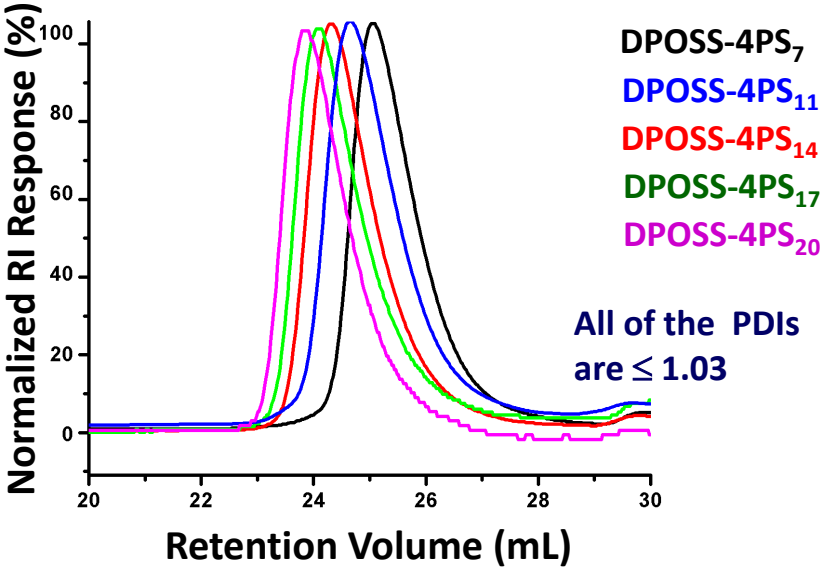
M.J. Huang

The Predicted A_{15} Phase with a Space Group of $Pm\bar{3}n$

Summary of DPOSS-4PS$_n$ Samples

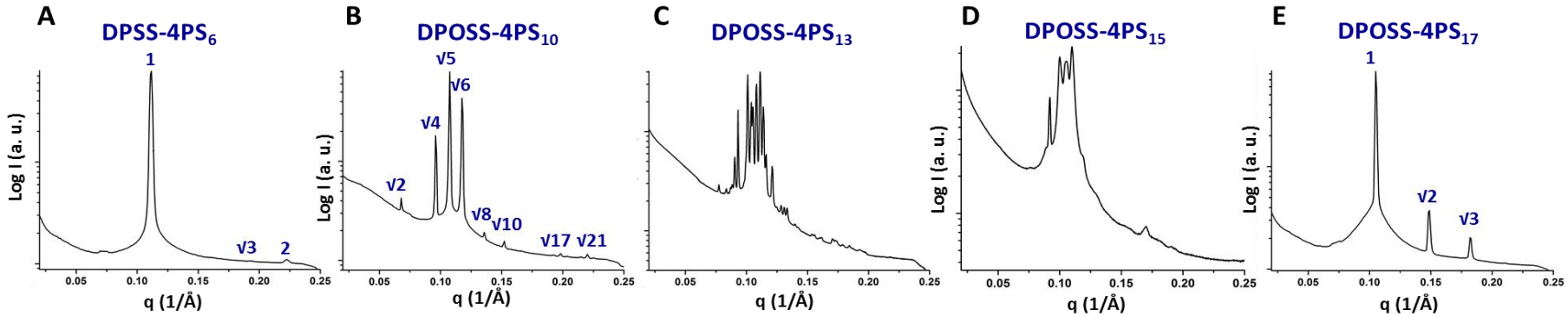
Chemical Synthesis:

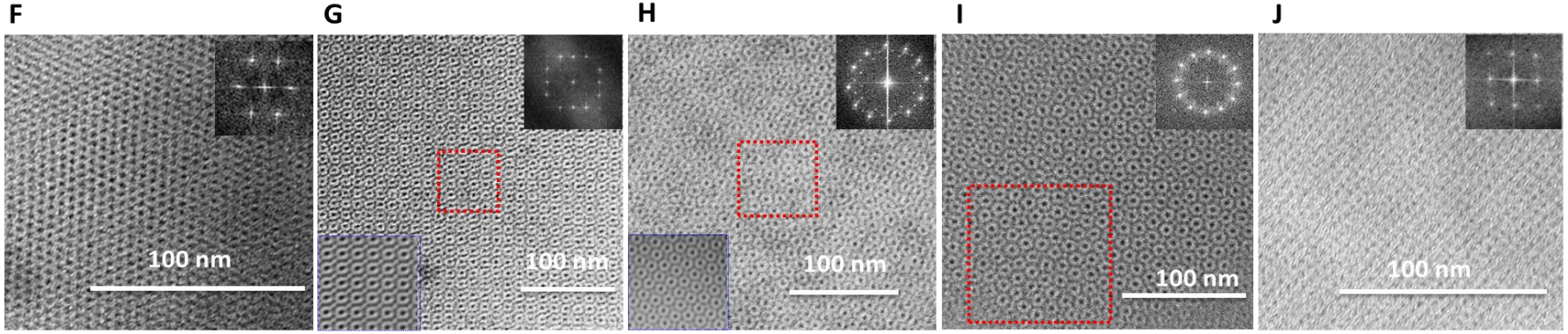


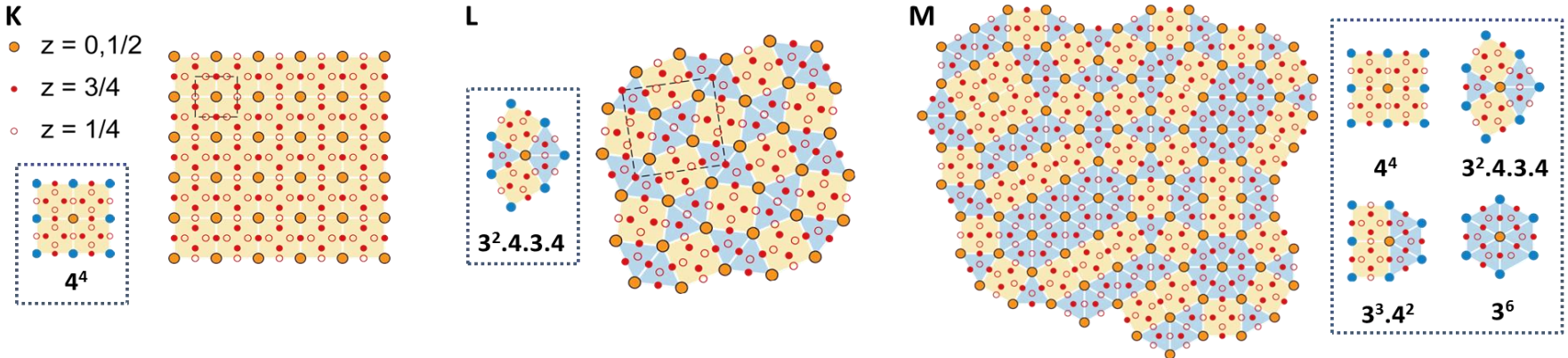


Sample	M_n / kDa	M_{PS} / kDa	f_{PS}	f_{DPOSS}	Phase
DPOSS-4PS$_7$	5.0	3.5	0.76	0.24	hex
DPOSS-4PS$_{11}$	6.7	5.2	0.83	0.17	A15
DPOSS-4PS$_{12}$	7.1	5.6	0.84	0.16	dqc
DPOSS-4PS$_{14}$	7.9	6.4	0.85	0.15	sigma
DPOSS-4PS$_{17}$	9.1	7.6	0.87	0.13	bcc
DPOSS-4PS$_{20}$	10.4	8.9	0.89	0.11	bcc

Phase Diagram of DPOSS-4PS$_n$

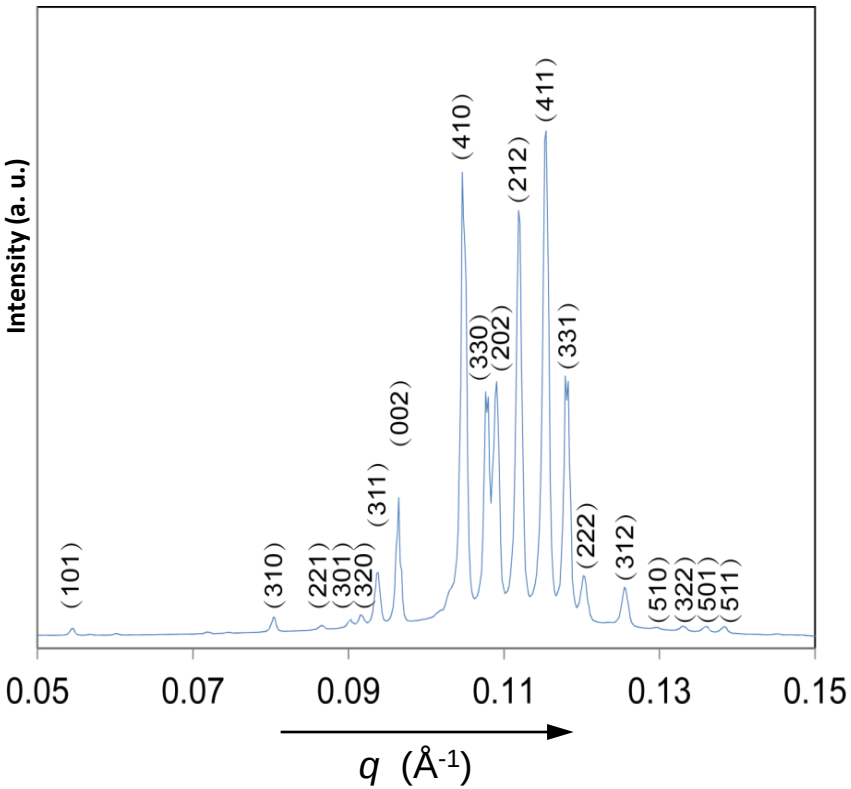


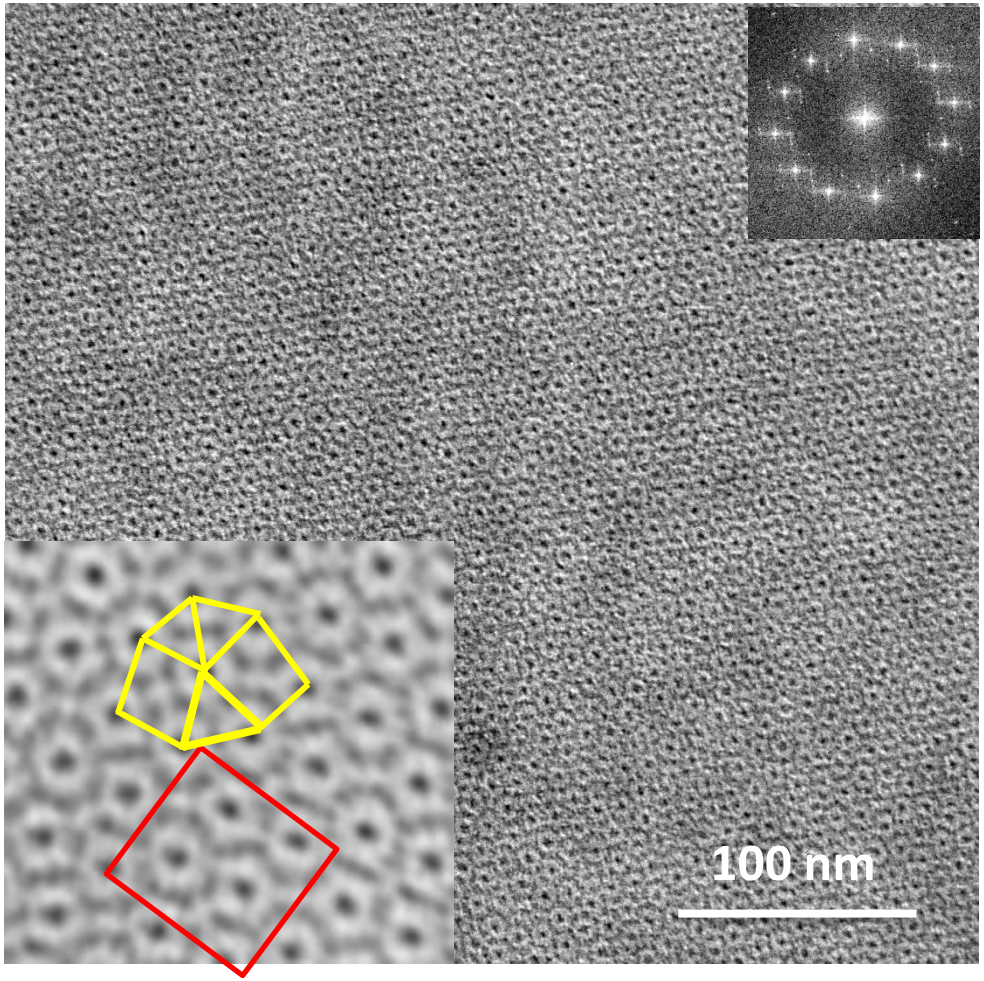




The Sigma phase of DPOSS-4PS$_{14}$

Tetragonal unit cell P4$_2$/mnm: a = 24.8 nm and c = 12.9 nm.

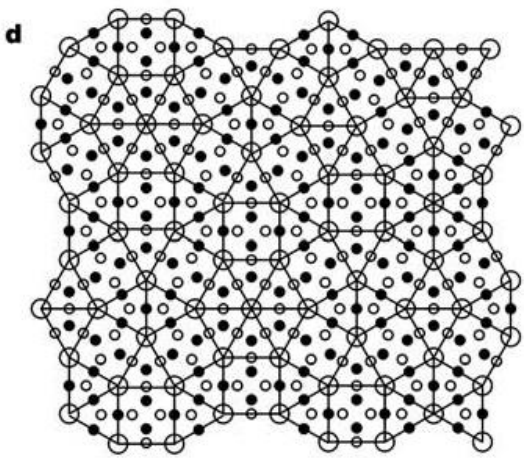




Tetragonal [001] zone

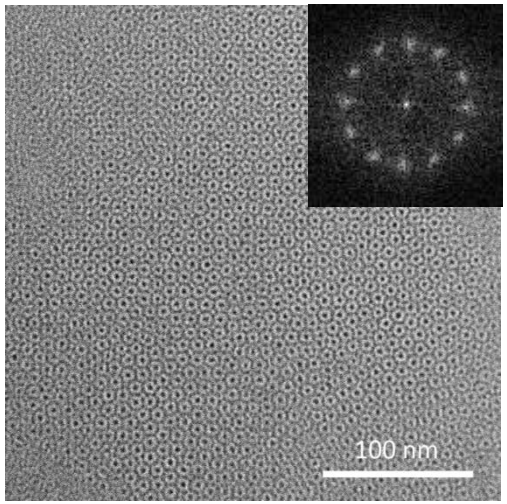
Dodecagonal Quasicrystal with 12 Folds

- **DPOSS-4PS$_{11}$ samples show 2D quasicrystalline structure.**

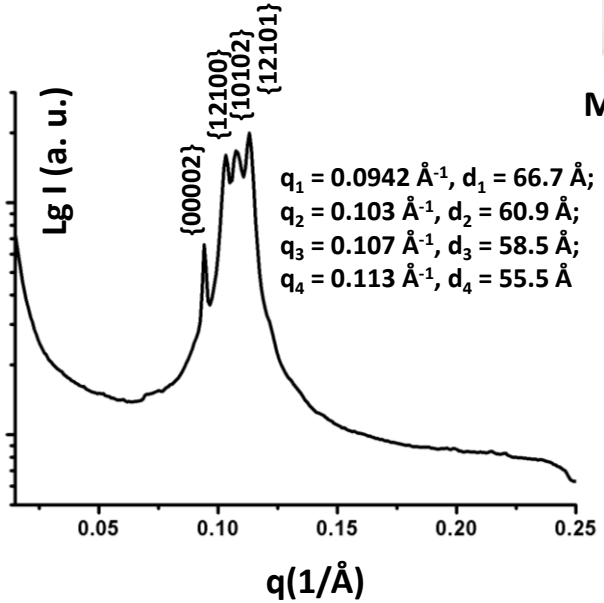


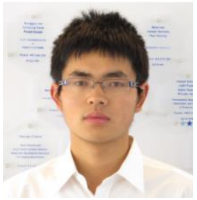
Tiling $3^2.4.3.4$, 3^6, $3^2 4^2$, and 4^4

TEM

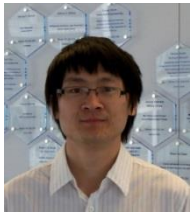


SAXS





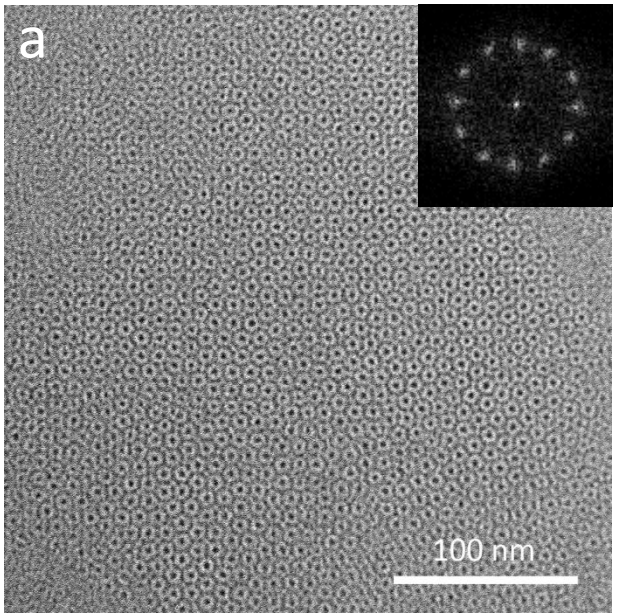
Mingjun Huang



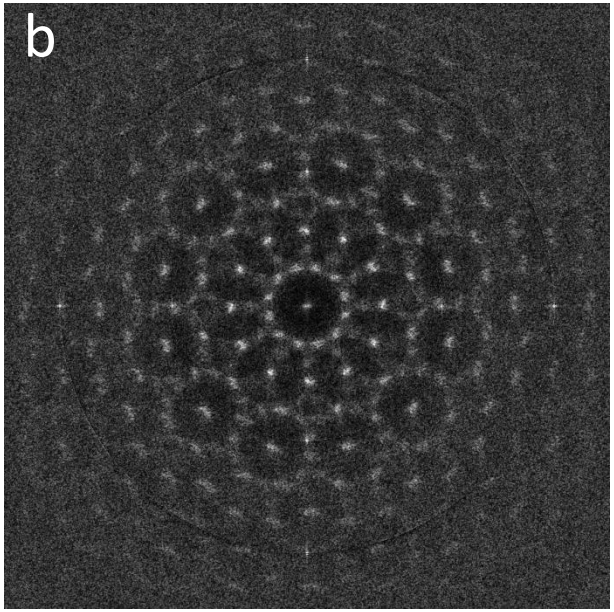
Dr. Kan Yue

TEM image and SAXS pattern of dodecagonal quasicrystalline structure from DPOSS-4PS$_{11}$. The FFT of the TEM image clearly shows the 12 fold symmetry.

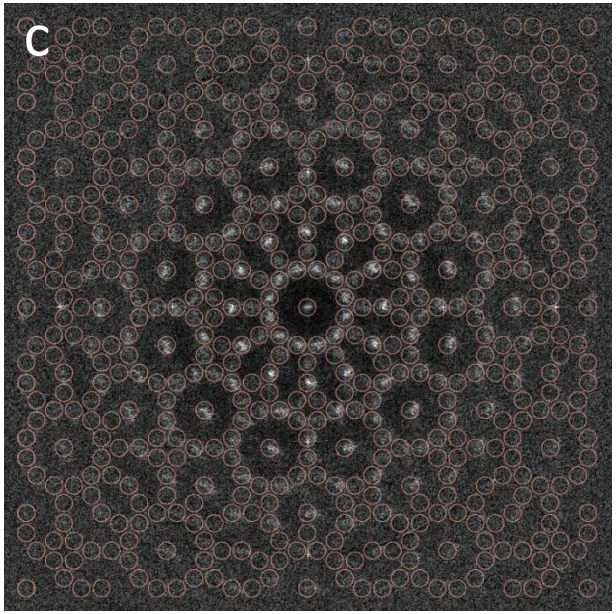
Mathematic Prove of a 2D Dodecagonal Quasicrystal



Experimentally observed



After a FT of the lattice from experimental data



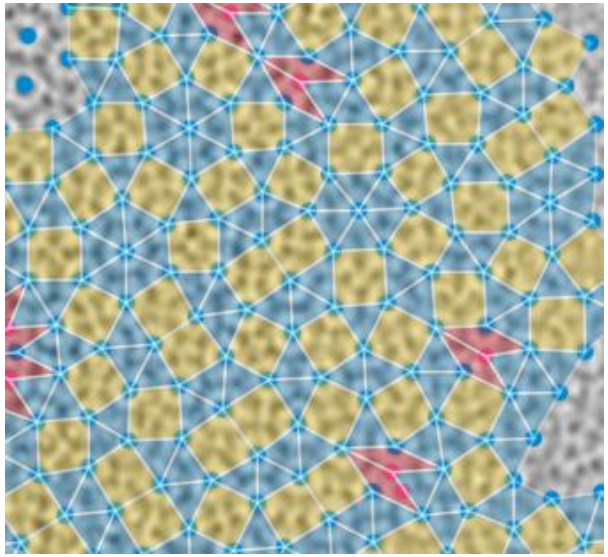
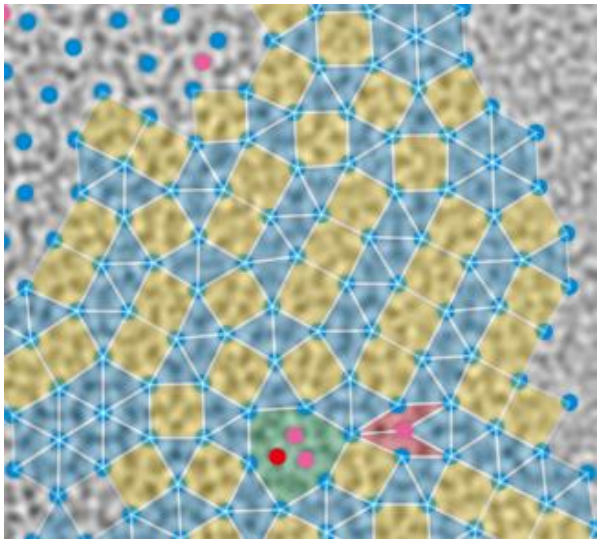
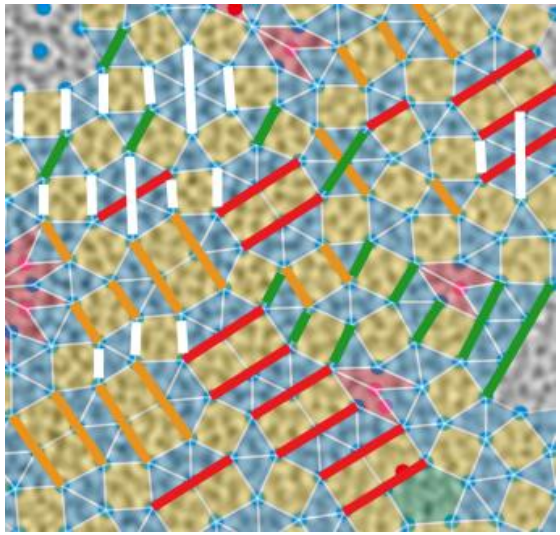
Match with the theoretical dodecagonal quasicrystal

- a) Taking all the dark points of TEM observations to construct a lattice;
- b) Taking a FT of the a) to obtain the diffraction pattern in the reciprocal lattice;
- c) Constructing a 12 folded dodecagonal quasicrystal lattice in the 4-dimension and projecting to the 2D reciprocal lattice and comparing with the b).

All experimentally observed diffractions can be matched by the calculated data.

Missing and diffuse diffractions in b) indicates some degree of random tiling packing.

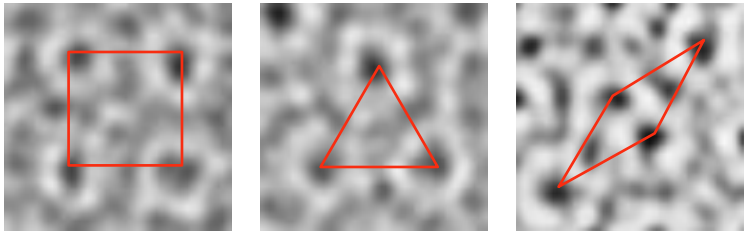
Detailed Evidence for Random Tiling

- In addition to squares and triangles, we do see rhombus;
- Some small ordered lattices;
- The linear combination of 4 sets of reciprocal vectors (yellow-white-green-rad, the angle between neighboring vectors) gives rise to the 12-fold symmetric pattern.

Tile Elements and Phason Flips

Tile Elements:

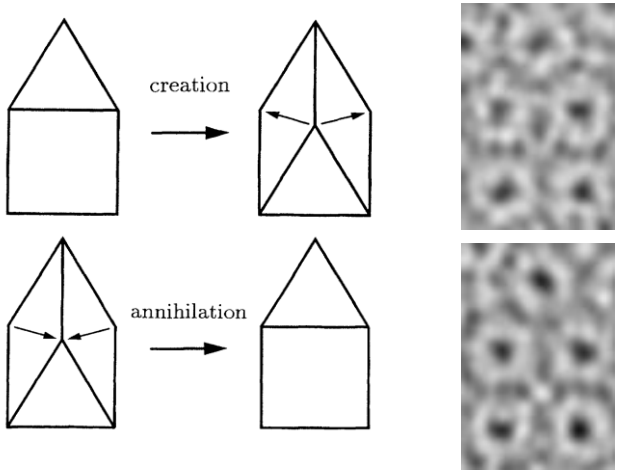


Square Triangle Rhombus

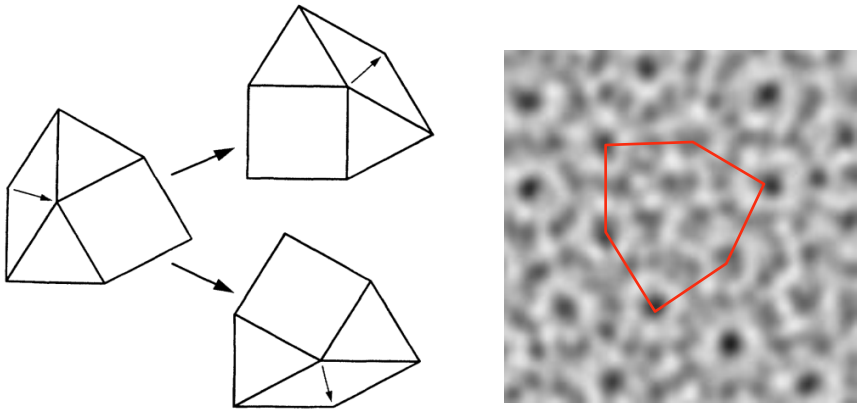
System stability: At a fixed ratio of core radius over shell thickness, the energy of the system will depend on **the relative number of squares and triangles** but not the lattice configuration, thus random tiling is favored to maximize the system entropy.

Phason Flips:

- Energy state changes:

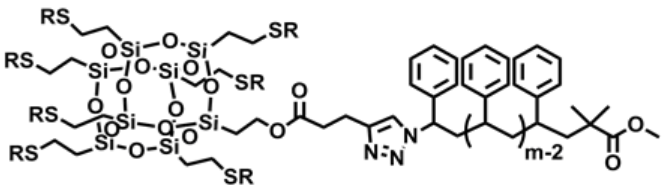


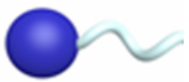
- Energy remains unchanged:



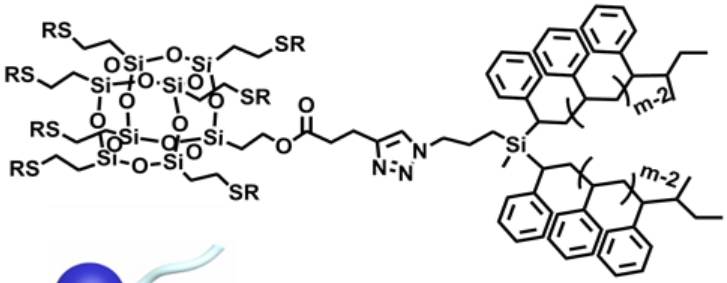
Ref: Oxborrow, M. and Henley, C. L. *Phys. Rev. B* **1993**, *48*, 6966.

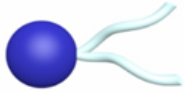
Samples for Studying Topology-Induced Evolution



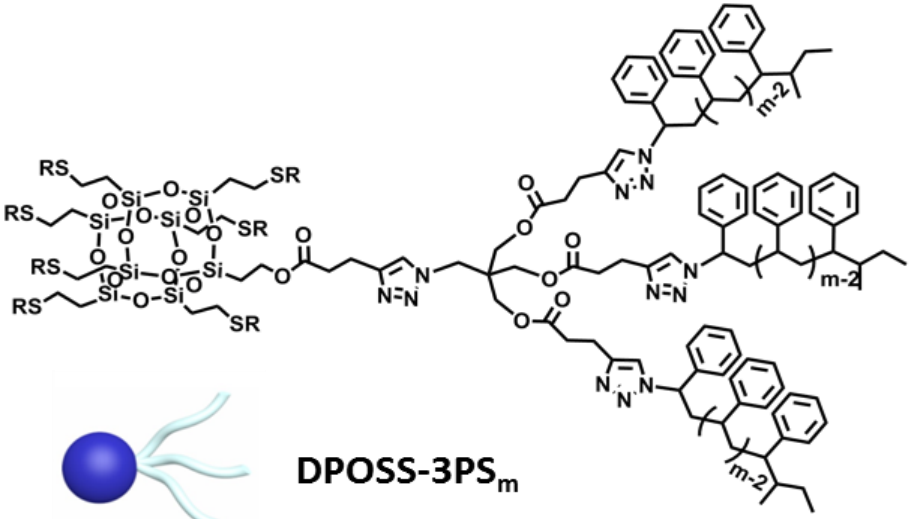


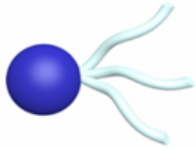
DPOSS-PS$_m$



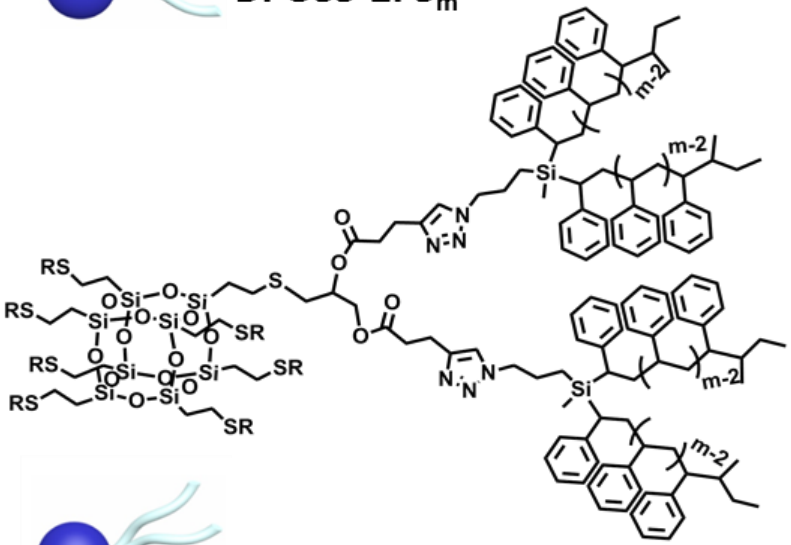


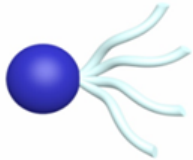
DPOSS-2PS$_m$





DPOSS-3PS$_m$

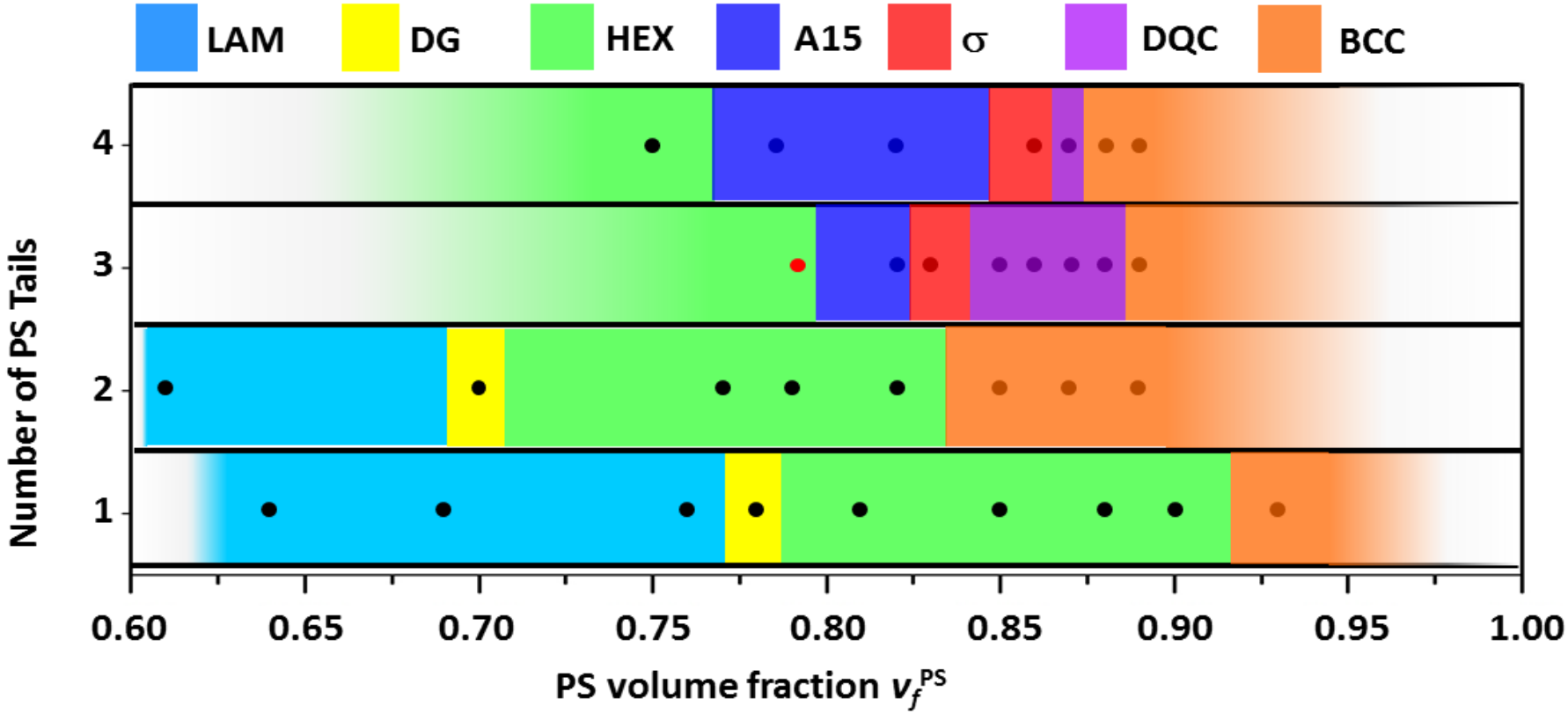




DPOSS-4PS$_m$

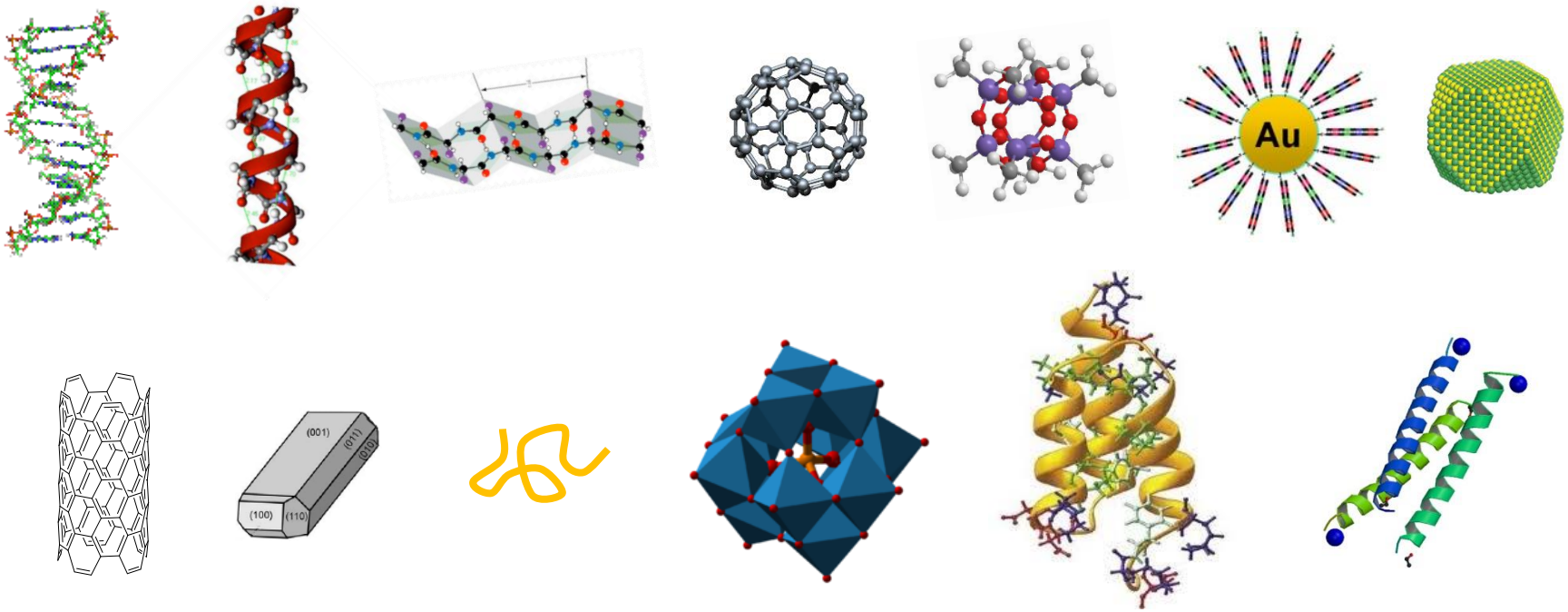
Phase Boundary Diagram for Topology-Induced Evolution on the F-K and DQC phases

- Tilted phase boundaries;
- Four conventional phase structures (LAM, DG, HEX and Spherical phase);
- Within the spherical phase for N = 3 and 4, a window is opened for the F-K and DQC phases);
- Phase sequence is HEX ➞ A15 ➞ σ ➞ DQC ➞ BCC phases.



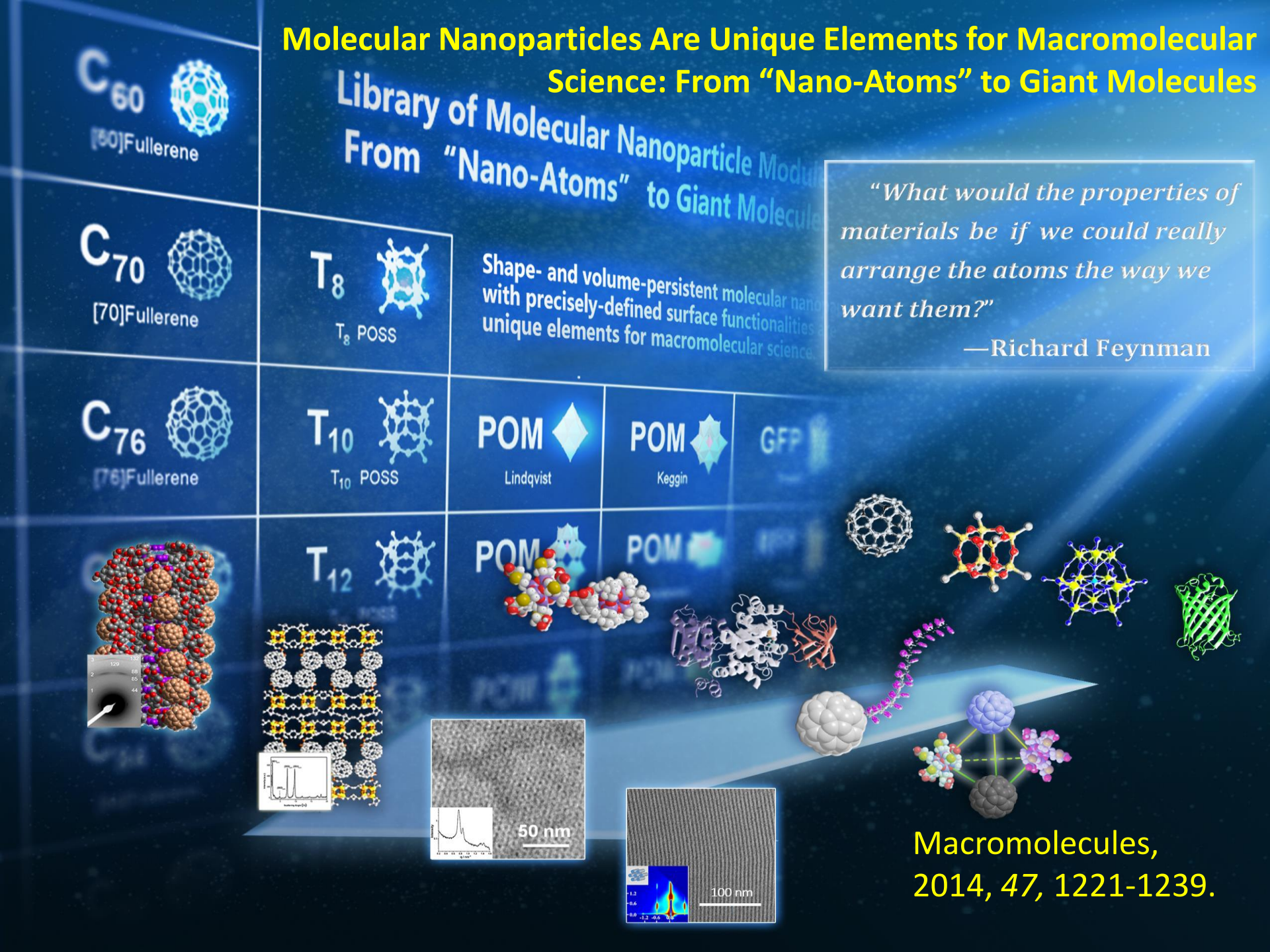
Expanding the Table of Nano-Atoms

- **Giant molecules are constructed from "nano-atoms" that possess independent, well-defined 3D structures and specific functions.**



"Nano-atoms" are synthons at the nanometer scale from a structural perspective and may also serve a specific functional role.

Molecular Nanoparticles Are Unique Elements for Macromolecular Science: From "Nano-Atoms" to Giant Molecules

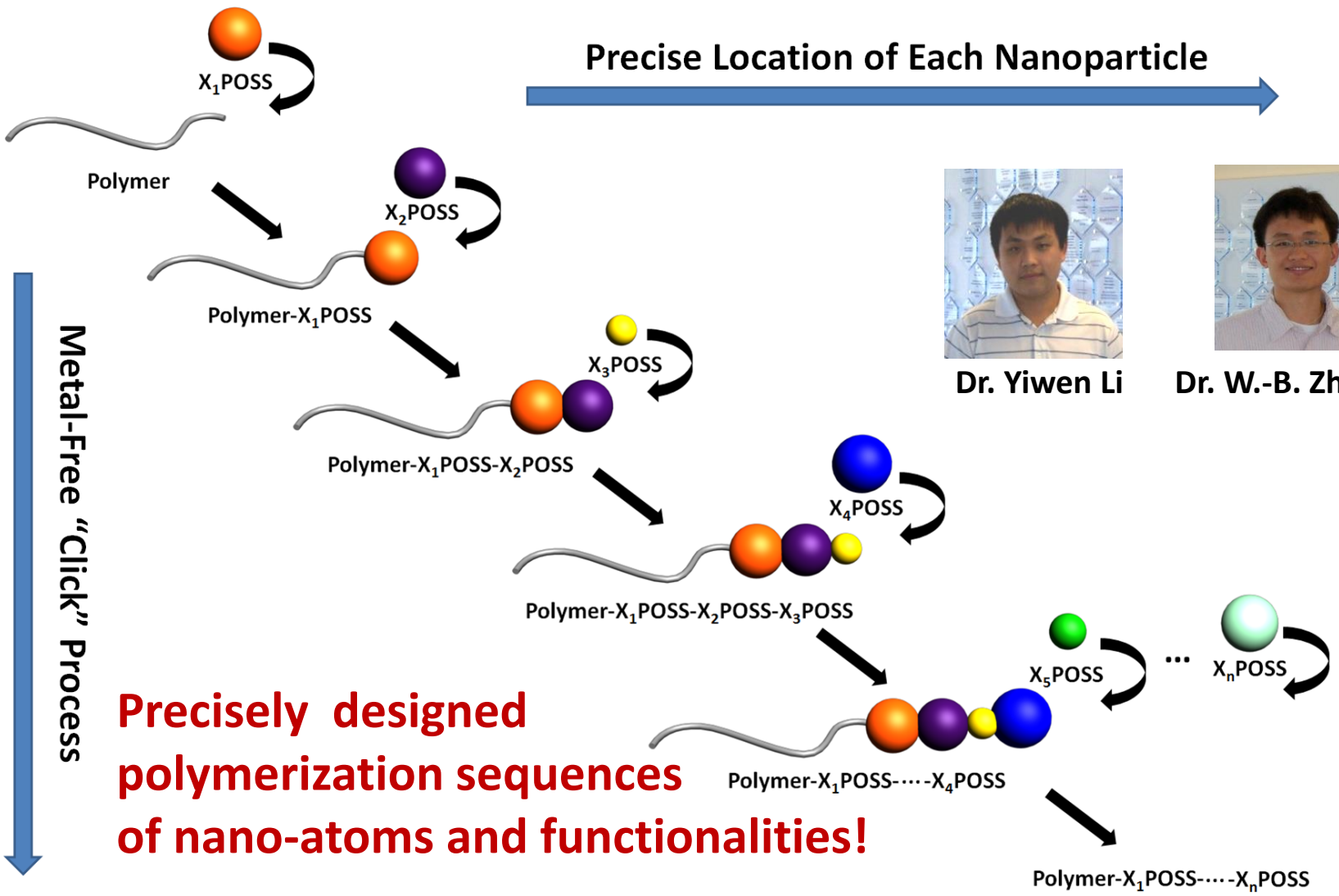


"What would the properties of materials be if we could really arrange the atoms the way we want them?"

—Richard Feynman

Macromolecules, 2014, *47*, 1221-1239.

"Nano-Atomic" Polymerization: A Materials Genome Approach



Dr. Yiwen Li

Dr. W.-B. Zhang

Precisely designed polymerization sequences of nano-atoms and functionalities!

Summary and Perspectives

The principles of physics and chemistry should be integrated in the design and synthesis of advanced functional materials.

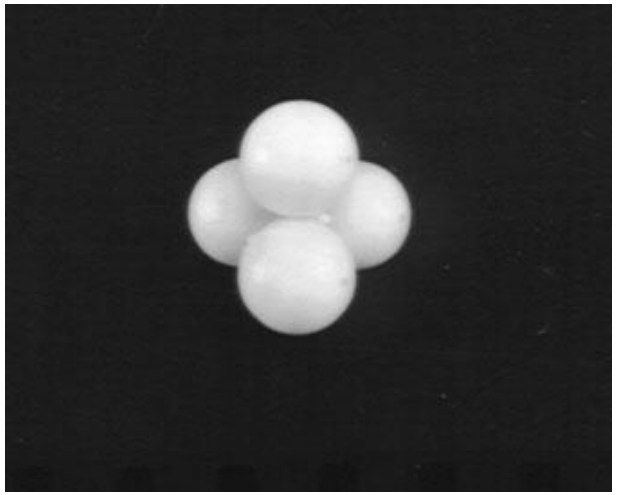
- ***Functional Synthons***: Design and synthesize building blocks with optimal functionality via precise and effective chemistry;
- ***Structural Synthons***: Design and construct hierarchical structures via supramolecular engineering to transfer and amplify the functionality;
- Materials can achieve maximized and combined macroscopic functionalities – **BEYOND NATURE!**

Future: Giant molecules based on "Nano-atoms" ? –
A Materials Genome Approach
where chemistry, physics and bioscience meet!

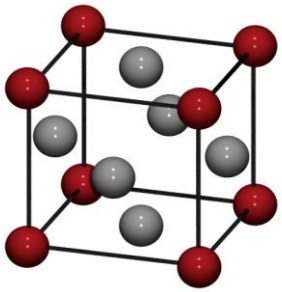
Crystals with Tetrahedral packing

Crystal: All constituent atoms, molecules, or ions are arranged in an periodic ordered pattern extending in all three spatial dimensions.

Symmetric Tetrahedron: The basic unit is sphere with one geometrical and chemical size. The CN = 12. – Most efficient packing



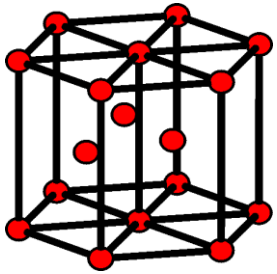
FCC



Along the [111] zone, It is an ABC packing

Cuboctahedron

HCP



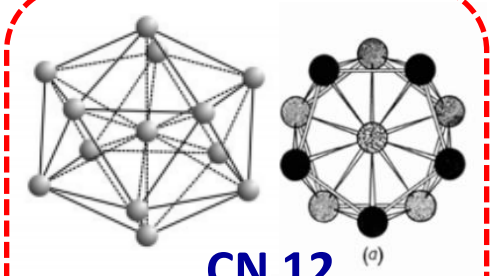
Along the [0001]zone, it is an AB packing

Twined Cubctahedron

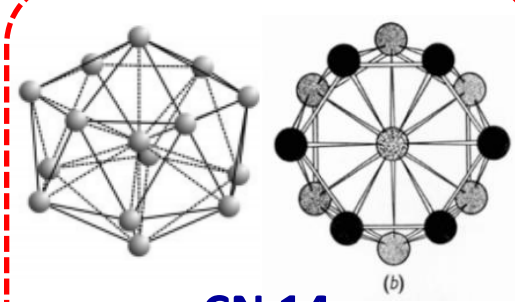
There is another possibility of packing: icosahedral that is topological close packing (*TCP*).

Frank-Kasper Phases

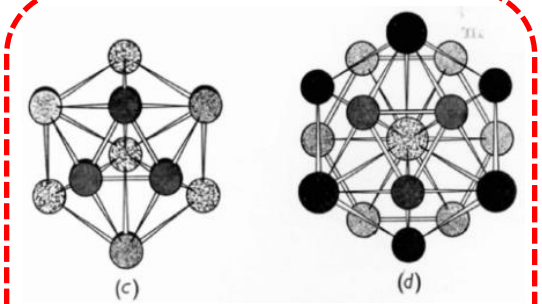
Frank-Kasper polyhedrons: **Metal alloy phases in which distorted icosahedrons can be accommodated in crystals by packing with other polyhedrons that have larger CN and atoms.**



CN 12 (Icosahedron)

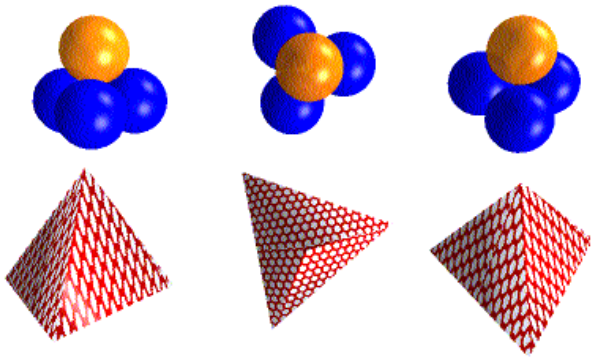


CN 14



CN 15 **CN 16**

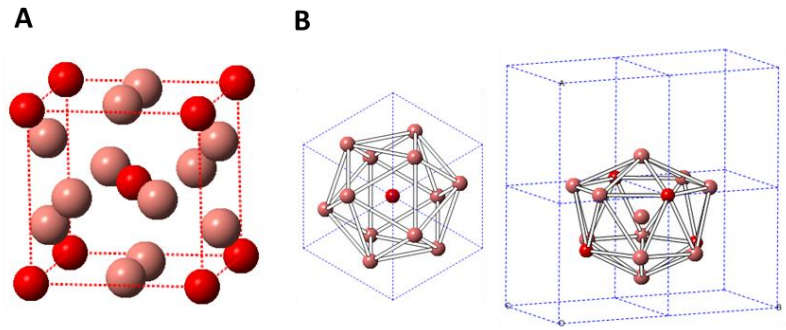
A class of *TCP* structures to pack asymmetric icosahedra into crystals using other polyhedra with a larger coordination number of 12, 14,15 or 16 and having all triangular face – called "Frank-Kasper phases".



Ref. Frank, F. C. et al. *Acta Crystallogr* **1958**, *11*, 184.

Two Typical Frank-Kasper Phases

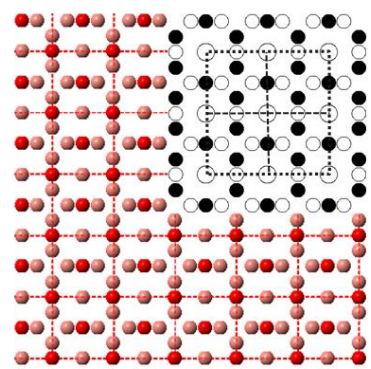
A_3B



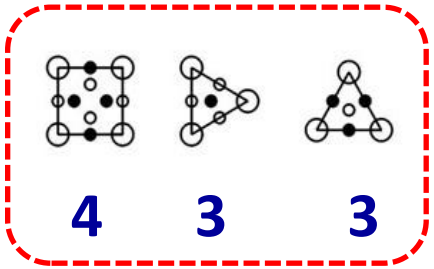
A15($Pm\bar{3}n$)

B: 12 folds-Frank Lattice

A: 14 folds-Kasper Lattice



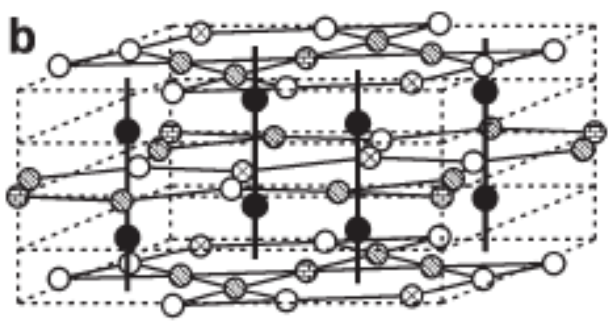
[001] Titling 4^4



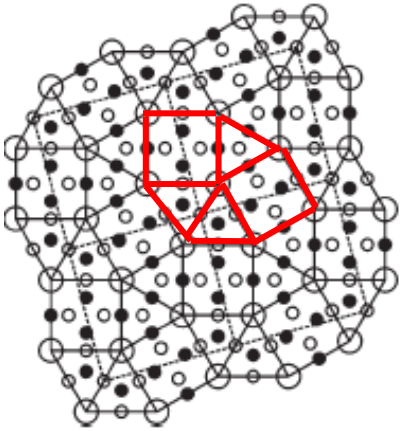
Tiling units

Two *B*: CN 12, Six *A*: CN 14

AB



Sigma, $P4_2/mmm$



[001] Tiling $3^2.4.3.4$

Five atomic special positions (1 to 5) can be recognized. The CN of 12 for icosahedrons are centered at atoms 1 and 4, the CN of 14 of a Kasper polyhedron are centered at 3 and 5, and the CN of 15 of a Kasper polyhedron are centered at 2.

Ref. Frank, F. C. et al. *Acta Crystallogr* **1958**, *11*, 184.