SELF-ASSEMBLED MATERIALS

Supramolecular lattices from tetrahedral nanobuilding blocks

The location of hydrophilic and hydrophobic regions on tetrahedral nanoparticles determines how they pack together into a variety of structures

By **Shu Yang**

The self-assembly and packing of nanoscale particles that have nonspherical shapes is only beginning to be explored. Recent computer simulations have suggested that hard, convex polyhedra can pack more densely than spheres, leading to complex structures of liquid crystals, plastic crystals, crystals, and disordered phases (1). In particular, aperiodic quasicrystalline and crystalline phases occur in the packing of tetrahedra, the simplest polyhedron (2). On page 424 of this issue, Huang et al. report the precise synthesis of rigid giant tetrahedra consisting of hydrophobic and hydrophilic polyhedral oligomeric silsesquioxane (POSS) cages (3). They assemble a diverse range of highly ordered supramolecular lattices by exploiting the location of the hydrophilic POSS cage substituent and the number of substitutions, together with the interplay of crystallization and the collective hydrogen-bonding interactions.

The A15 phase was discovered in metal alloys with A_3B composition (4). As seen on the right side of the figure, it is a cubic lattice consisting of six A units (pale red spheres) in Kasper polyhedra with 14-coordination and two B units (dark red spheres) in icosahedra with 12-coordination. Its space group is $Pm\bar{3}n$ and it exhibits a two-dimensional 4^4-square tiling pattern. Relative to other superlattices, the A15 phase is more loosely packed and can better accommodate distortion away from ideal sphere packing.

Closely packed face-centered cubic (fcc) and hexagonal close-packed (hcp) structures are common from packing of hard spheres, but soft spheres often form non–close-packed lattices, including body-centered cubic (bcc), body-centered orthorhombic (bco), and the diamond lattices. Recently, the formation of the A15 phase for soft spheres has been suggested by theory (5, 6) and demonstrated experimentally for packing of "deformable" soft spheres assembled from lyotropic lipids, conical fan-shaped dendrimers (7), and asymmetric block copolymers (8) (see the figure, top and middle left, respectively).

Typically, these building blocks have a hard core that favors lattices with maximum packing fraction and a soft corona that can be deformed to maximize entropy and minimize interfacial contact. Nonetheless, these soft spheres do not constitute a single-particle system. Often a mixture of bcc lattices, Frank-Kasper σ phases, and A15 phases is observed, because block copolymer and dendrimer particles are not identical but are polydisperse—they have a distribution of chain lengths. The large number of chain conformations and the soft nature of polymer chains also impede

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precise control of the molecular structures and their assemblies.

Molecular nanoparticles (MNPs), including fullerenes such as C_{60}, POSS derivatives, and polyoxometalates, represent a new class of nanobuilding blocks. Bridging the length scale between polymers and small molecules, MNPs can be synthesized with explicit chemical composition and precisely controlled size, shape, symmetry, and function. They are rigid, incompressible, and impenetrable. MNPs have been regarded as "nanoatoms" or "giant molecules."

Among them, POSS derivatives (9) have enjoyed rapid growth in research and applications because of their well-defined structures, high interaction parameters, and tunable chemistry of the periphery groups. Hydrolysis of $RSiX_3$ (where X is a halide and R can be alkyl, aryl, alkoxy, epoxy, hydroxyl, carboxylic acid, amine, or vinyl groups), followed by condensation, leads to the spontaneous formation of cage-like POSS,

denoted T_8R_8 (where each Si is connected with three oxygens to form a T unit). The resulting compounds have the general formula $(RSiO_{3/2})_8$.

Creating giant tetrahedra with precise partitioning of hydrophobic and hydrophilic POSS cages requires site-selective functionalization and regioselective multifunctionalization of the apex by the POSS cages. First, the hydrophobic POSS cages with seven isobutyl groups (BPOSS) and one alkyne group are coupled to tetrakis(4-azidophenyl)methane via the azide-alkyne [3+2] cycloaddition reaction. Because these "click" reactions offer near-quantitative yield, giant tetrahedra with one, two, or three unreacted azide groups are obtained by controlling the stoichiometric feed ratio of the azide versus alkyne groups. In the second step, hydrophilic POSS cages with either hydroxyl or carboxylic acid groups are coupled to the giant tetrahedron via a thiol-ene reaction. Although vinyl groups are often incompatible with hydroxyl or carboxylic groups, they possess orthogonal reactivities in click chemistry, where the reaction is site-selective.

Thus, it is possible to sequentially introduce hydrophilic POSS cages one by one on the giant tetrahedra, much like putting together Lego blocks. Such unprecedented control of shape and topology is not possible in polymer systems. Incorporation of different reactivities leads to competing interactions that drive self-assembly—that is, collective hydrogen-bonding interactions between the hydrophilic POSS cages and the crystallization of BPOSS cages. Meanwhile, replacing the BPOSS cage with a hydrophilic POSS cage on the tetrahedron lowers the molecular symmetry.

When cast from solution on mica, crystallization of BPOSS cages dominates. To minimize interfacial energy, frustrated supramolecular lamellae are formed with two layers of BPOSS and one interdigitated layer of the hydrophilic POSS cages. The preformation of lamellae is critical to the

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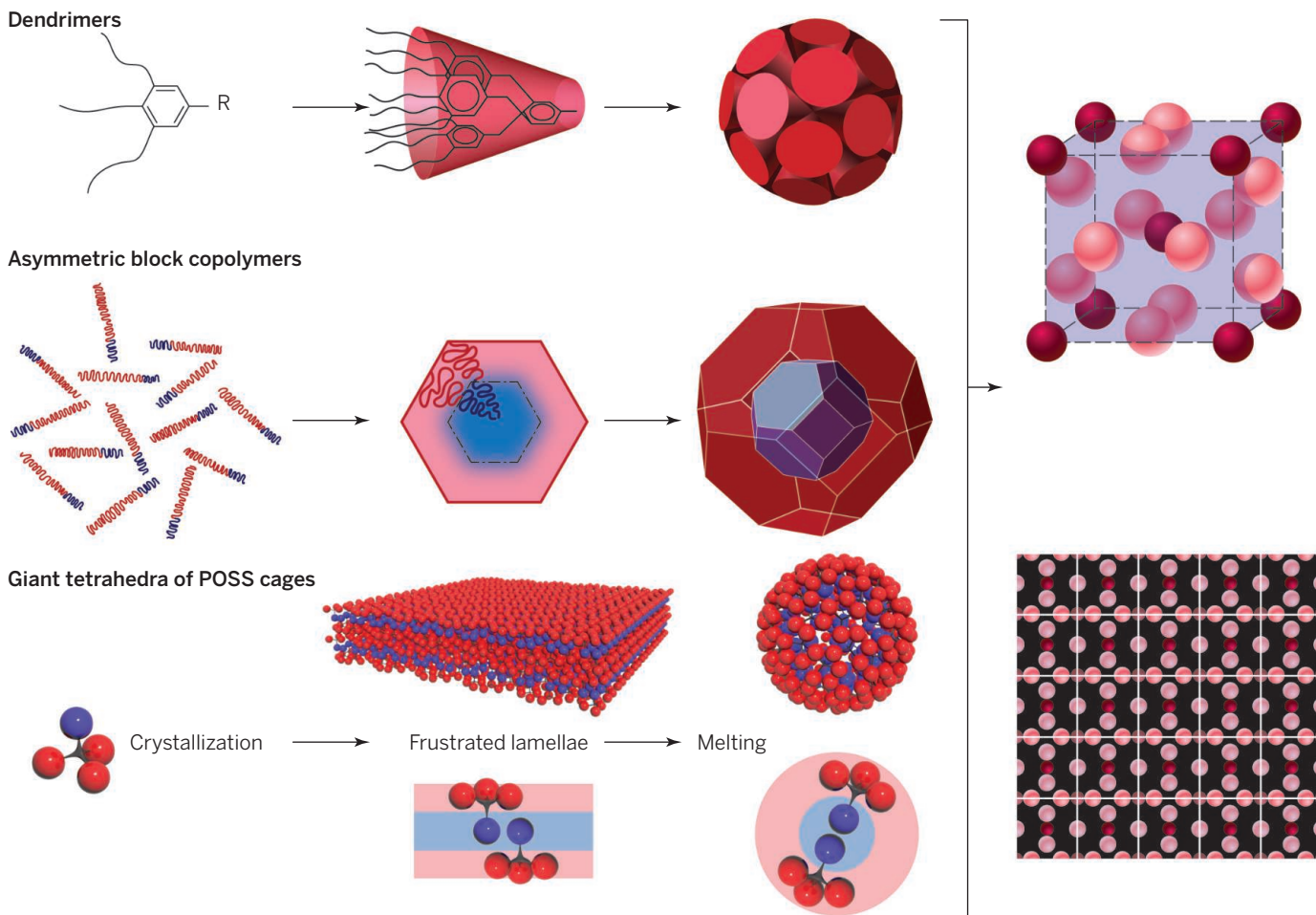
Different parts for self-assembly of A15 supramolecular lattices. On the right side of the figure, the A15 lattice, which assembles for metal alloys from two different types of atoms, is shown as a three-dimensional rendering at the top and as a 4⁴-square tiling pattern at the bottom. Different routes to this same type of lattice are shown on the left side for dendrimers at the top, asymmetric block copolymers in the middle, and giant tetrahedral POSS cages, as elaborated by Huang *et al.*, at the bottom.

latter superlattice formation. Upon melting, hydrophilic POSS cages form spherical aggregates while BPOSS layers scroll to form the shell. The core-shell spheres spontaneously pack into the A15 supramolecular lattice as a result of balancing the molecular symmetry and molecular interactions (see the figure, lower left).

Design of giant nanoatoms from precisely controlled organic and hybrid materials also has caught the eye of polymer scientists. For example, Ober and co-workers demonstrated sub–50 nm patterns using glass-forming, low-molecular-weight organic compounds as photoresists (*10*). Relative to traditional polymeric resists, molecular glass resists offer smaller feature size and line-edge roughness as well as higher dissolution contrast, which is critical to driving miniaturization of electronic devices on the sub–100 nm scale.

The precise synthesis of Lego-like POSS cages opens up an entirely new paradigm of self-assembly in which lattices can be assembled one-by-one and on demand. The rich chemistry that can be introduced on

POSS cages, the versatility and regioselectivity enabled by click chemistry, and the possible structural variations of POSS derivatives will be of great interest to materials scientists. Besides T_8-type POSS cages, there are less stable T_6, T_{10}, and T_{12} POSS cages. It will be interesting to extend the chemical strategy presented by Huang *et al.* to construct other types of giant polyhedra and investigate their self-assembly. Meanwhile, the coupling reactions and the molecular interactions can be fine-tuned to assemble other superlattices. Furthermore, small-molecule fluorophores, metal complexes, conjugated molecules, and peptides can be introduced into the nanocavity of the POSS cage or its periphery for imaging, sensing, catalysis, charge-carrier transport, and biological applications (*9*). Also, the T_8 core may not act as a traditional silica-like insulator.

Finally, it will be interesting to disperse these shape-persistent tetrahedra and their superlattices into a polymer matrix or a liquid crystal medium, or to place them on a patterned surface to create truly hierarchi-

cal assemblies. They can also be tethered to a polymer chain to construct a block copolymer analog, so as to take advantage of their rich phase separation behaviors, or to form complexation with other polyhedra to create Janus superlattices. The ability to build nano-Legos with precise geometrical factors and tunable molecular interactions offers a powerful yet versatile tool to create ever more complex functional materials. ∎

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