Unprecedented self-assembly of precise molecular particles

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Atomic self-assembly in pure metals and metal alloys can lead to various conventional (cubic, hexagonal close-packed (hcp), and icosahedron) and non-conventional (Frank–Kasper and quasicrystal [1]) structures. The non-conventional crystalline structures often lead to unexpected physical properties. For example, the A15 (A3B type) Frank–Kasper phase of Nb3Sn, Nb3Zr and Nb3Ti are found to be superconducting. Metallic quasicrystals are hard and have low-friction, low-thermal conductivity, and special electronic properties.

Beyond the atomic self-assembly, computer simulations have predicted many complex self-assembled structures, such as Frank–Kasper phases and quasicrystals, as a function of shape, size, and interaction for nanoparticles (Fig. 1) [2]. However, it has been challenging to experimentally achieve these structures from both hard (colloidal particles and mixtures) and soft (hierarchically self-assembled surfactants, dendrimers, and micellar block copolymers) nanoparticles. This is because precise shape, size, and interaction for colloidal nanoparticles are still difficult to control.

In a recent report by Huang et al. [3], this grand challenge has been conquered by precise synthesis of rigid giant tetrahedra from molecular nanoparticles i.e. polyhedral oligomeric silsesquioxane (POSS), by using two orthogonal ‘click’ chemistry techniques, namely, the azide-alkyne [3 + 2] cycloaddition reaction and the thiol-ene reaction. In this clever way, different numbers of hydrophobic and hydrophilic POSS Legos are introduced into the targeted giant tetrahedral with precise position control. Although these ‘Click’ chemistry techniques have been proved to be quantitative, the authors demonstrated powerful capability of organic separation/purification, multidimensional molecular characterization using nuclear magnetic resonance (NMR) spectroscopy and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy.

The authors also demonstrated sophisticated structural and morphology characterization using both reciprocal and real space characterization tools, namely, small-/wide-angle X-ray diffraction (SAXS/WAXS) and transmission electron microscopy (TEM) with selected-area electron diffraction (SAED). The most striking finding is that the A3B (A and B are hydrophobic and hydrophilic POSS cages, respectively) giant tetrahedra with relatively strong hydrogen-bonding POSS cages exhibit the A15 Frank–Kasper phase with relatively strong hydrogen-bonding POSS cages. In the second step, these two-sized spherical aggregates further assemble into the A15 phase superlattice. It is still interesting to find out why these A3B giant tetrahedra with strong hydrogen-bonding self-assemble into two-sized spherical aggregates in the first place. On the contrary, switching the strong hydrogen-bonding into weak hydrogen-bonding in the hydrophilic moiety caused degeneration of the size of spherical aggregates. Consequently, a conventional body-centered cubic (BCC) structure is obtained. Finally, the Janus A2B2 giant tetrahedra self-assemble into double gyroid (space group Pm3n) and lamellar structures, and the reverse AB3 giant tetrahedra self-assemble into inverse cylindrical phase.

In short, the above elegant achievements are resulted from an excellent combination of the precise organic synthesis and delicate structural
characterization. It is pressing to further discover unexpected physical properties for these novel self-assemblies from precise giant tetrahedra. No doubt, generalization of the strategies and principles into other supermolecules will bring us the bright future in self-assembled soft materials science.

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