A breakthrough of artificial photosynthesis

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Photosynthesis in plants, algae and cyanobacteria uses light energy from the Sun to convert CO$_2$ and water into carbohydrates and oxygen, thus sustaining all aerobic life forms on Earth. Photosynthetic water splitting into oxygen, protons and electrons, is catalyzed by the oxygen-evolving center (OEC) in photosystem II (PS II), which is crucial in global bioenergetics and has shaped the atmosphere by oxygen production. Due to the broad fundamental interests and potential applications in artificial photosynthesis, the structure and mechanism of this natural catalyst have attracted extensive attentions during the last two decades. Recent X-ray structure of PSII reported by Dr Shen’s group have revealed that OEC is comprised of a unique asymmetric Mn$_4$Ca-cluster \cite{1,2} (Figure 1 left), which provides a blueprint for the development of efficient and cheap artificial catalysts for water-splitting reaction to overcome one of the bottleneck of artificial photosynthesis. However, it is of a great challenge for chemists to synthesize the whole structure of the OEC in laboratory \cite{3}.

Dr Zhang has been devoting to work on the structure and mechanism of the biological OEC in PSII since 1997 when he was my PhD student, and he succeeded in predicting the binding mode of calcium—one of key cofactors of the OEC in 1999 \cite{4}.

After more than 18 years investigation on both natural photosynthesis and artificial photosynthesis, recently, Dr Zhang and his team have reported the first artificial asymmetric Mn$_4$Ca-cluster \cite{5}. This new artificial model complex displays remarkable structural similarities as that of the OEC in nature in respects of the asymmetric Mn$_4$Ca core structure and peripheral ligands (Figure 1 right). Like the natural OEC, the artificial Mn$_4$Ca-cluster can undergo four redox transitions and display two low-temperature electron paramagnetic resonance (EPR) signals. More interestingly, Dr Zhang and his team have demonstrated that the artificial Mn$_4$Ca-cluster might be able to serve as a potential catalyst for water-splitting reaction similar to the biological OEC. However, to elucidate the catalytic properties of this artificial Mn$_4$Ca-cluster, more investigations are required in future.

Recent artificial Mn$_4$Ca-cluster reported by Dr Zhang’s team \cite{5} has mimicked the OEC of natural photosynthesis. This work should be considered as a breakthrough in the field of artificial photosynthesis. It provides a reasonable chemical model of Mn$_4$Ca-cluster to investigate and understand the structure and properties of the OEC in natural PSII. More importantly, it may promote to develop new generation of efficient and low-cost artificial catalysts for photo water-splitting, which is one of important ways to generate green fuels energy by using solar energy in future.

Figure 1. The Mn$_4$Ca-cluster in PSII (left) and in artificial complex (right).
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 (A2 type) Frank–Kasper phase of NbSn, Nb2Zr and Nb2Ti 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 tetrahedra 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. Only with these stringent steps in organic synthesis, selective supramolecular self-assembly of the giant tetrahedra with precise shape, size, and hydrophobic/hydrophilic interaction is possible.

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 A1B (A and B are hydrophobic and hydrophilic POSS cages, respectively) giant tetrahedra with relatively strong hydrogen-bonding exhibit the A15 Frank–Kasper phase (space group Pm3m), a periodic approximate of the aperiodic icosahedral quasicrystals, with hierarchical self-assembly schemes after annealing in the melt. In the first step, the hydrophobic/hydrophilic interaction drives the formation of two-sized spherical aggregates with \( \sim 38–49/50–65 \) supermolecules. 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 A1B 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 \( \text{A}_2\text{B}_2 \) giant tetrahedra self-assemble into double gyroid (space group \( 1a3d \)) and lamellar structures, and the reverse \( \text{AB}_2 \) 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

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**Figure 1.** Scheme of the effects of shape, size, and interaction of well-defined nanoparticles on their self-assembled structures.