

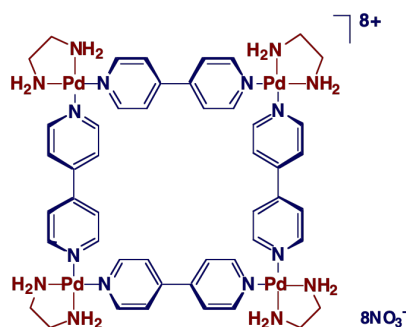
COORDINATION SELF-ASSEMBLY: PAST, PRESENT, AND FUTURE

MAKOTO FUJITA

Department of Applied Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

Short Summary: Since 1990, our group has been developing a new construction principle, featured as "coordination self-assembly", leading to the spontaneous formation of cyclic structures, catenanes, three-dimensional cages, and so on that are assembled from a large number of transition metal centers and simple coordinating organic molecules. A Pd(II)-cornered square complex served as the first example of coordination assembly that generated not only a framework but also a "space", a potential and excellent platform for creating new properties and functions. The cages can be gigantic and behave as large molecular containers, leading to new chemical properties and reactivity of the substrates entrapped in these cages. In 1994, the same principle for cavity construction was applied to the preparation of an infinite coordination network that showed molecular inclusion in the cavity. Recently, single-crystal-to-single-crystal guest-exchange observed in the porous coordination network led to a revolutionary method for determining X-ray structures of small molecules which were encapsulated in the crystalline self-assembled cages.

Over the last three decades, self-assembly based on coordination chemistry has made remarkable developments and various type of well-defined nano structures such as helices, macrocycles, cages, and so on have been constructed from a large number of transition metal centers and simple coordinating organic molecules. In 1990, our group reported a spontaneously assembled molecular square with 4 palladium(II) atoms at its corners.[1] This report served as one of the earliest examples of coordination self-assembly, a new principle of metal-guided synthesis, being antithetic to organic synthesis, of the structure of matter on the nanoscale with an enormous impact on the molecular sciences.



Even back to 1980's, a few milestone works had already existed for molecular self-assembly around metal centres: for example, Cu(I)-templated catenane (Sauvage 1983) and double helical complexes (Lehn 1987). These earlier examples however did not show any particular functions or properties, in this regard comparable to most of metal complexes formed under thermodynamic conditions. The square complex is distinctive from the others in that self-assembly generated not only frameworks but also cavities that are excellent platforms to create new properties and functions through molecular recognition therein. The square's two-dimensional (2D) framework was subsequently extended into three-dimensional (3D) frameworks like cages, capsules, bowls, tubes, spheres, and catenanes[2] (Fig. 1). Extremely simple procedures strikingly dominate over the tedious ones of previous covalent syntheses. The results enjoy its unique status for (i) the facile creation of large hydrophobic cavities, (ii) very strong binding of neutral molecules in the cavities, and (iii) unprecedented physical and chemical phenomena within the cavities. In this article, amongst many contributions from our group to this field, several key self-assembled structures are disclosed emphasizing the past, present and the future of the field.

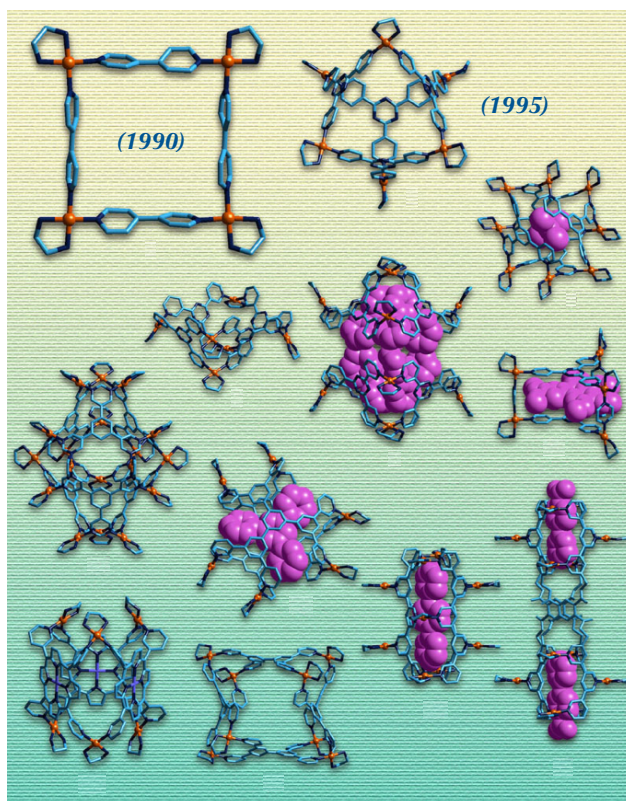


Fig 1. Coordination self-assemblies with cavities.

Molecular Confinement Effects in the Self-Assembled Cages[3]: The cavities of self-assembled cages are extraordinarily large and are capable of binding neutral guests. Unique functions are created from the self-assembled architectures. In the M_6L_4 cage, four large guests (e.g., adamantane, carborane) are encapsulated. Two different guests can be accommodated in a pairwise selective fashion, facilitating reaction design in the cavity. In the recognition of biomolecule fragments (oligopeptides or short nucleotides), their in vivo structures are reproduced in the cages in water.

Reactivity and catalysis controlled by cavities represent one of the most important functional properties of self-assembled hosts. The photodimerization of olefins as well as Diels-Alder reactions in the cage are featured by remarkable rate enhancement ($>10^2$ times), perfect regio- and stereo-selection, high pairwise selection, and even by chiral induction up to 50%ee. Notably, unreactive aromatics, even naphthalene, smoothly undergo the Diels-Alder. In a single crystalline state reaction, extremely unstable reaction intermediate generated in the cage can be examined by X-ray analysis (Fig. 2a).

Through confinement in the cavity, small molecules can be mechanically manipulated to alter their properties. For example, an over-crowded olefin in an anti-folded conformation was transformed into a twisted conformation revealing a biracial nature due to the poorer overlap of p-orbitals. An aromatic amide was bent into a non-planer conformation to be easily hydrolyzed due to the disruption of amide conjugation (Fig. 2b). Spin-crossover, stable organic mixed valent states, metal-metal bonding, spin-spin interaction, photo-induced guest-host electron/energy transfer have been observed through the accommodation of appropriately designed substrates.

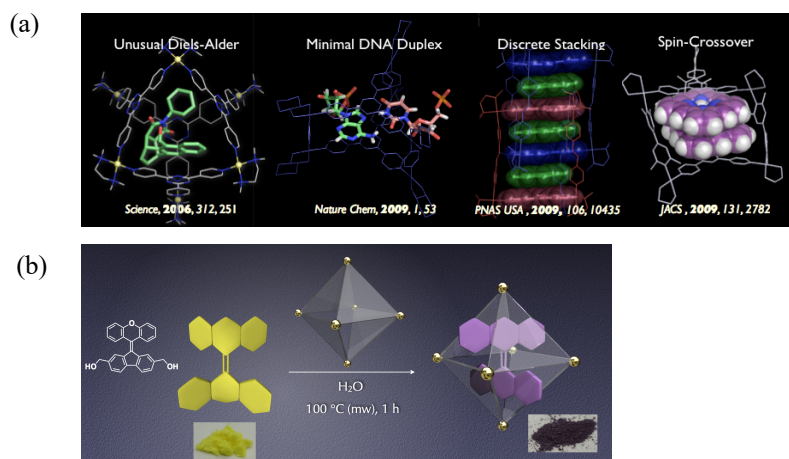


Fig. 2. (a) Examples of new reactions and properties developed in the self-assembled cavities. (b) “Twisting” manipulation of an over-crowded olefin to show biracial nature.

Polyhedrons with Protein Size Cavities[4]: Self-assembly of 5-nm sized, cubooctahedral $M_{12}L_{24}$ complexes and “EndoChemistry” at their endo-surface and inner space were developed (Fig. 3). Discrete inorganic synthesis was demonstrated by the precise endo-template synthesis of silica in the sphere. The sphere can encapsulate even a protein within the shell, providing potential methods for controlling protein functions and for protein structure determination.

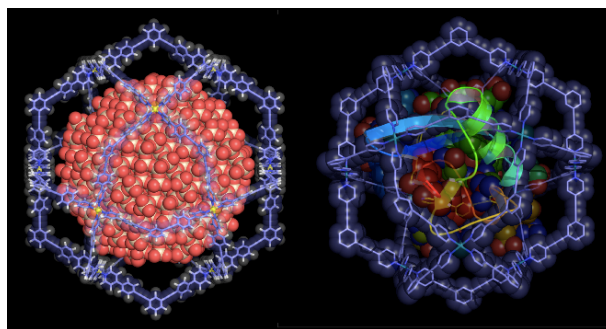


Fig. 3. Examples of Endo-Chemistry in the 5-nm sized $M_{12}L_{24}$ spheres. Left: perfectly monodisperse silica nanoparticle ($M_w/M_n = 1.004$) prepared in the sphere; Right: A protein encapsulated by the sphere.

Self-assembly of gigantic M_nL_{2n} Complexes under Mathematical Restriction[5]: We also reported $M_{24}L_{48}$ rhombicubooctahedron and $M_{30}L_{60}$ icosidodecahedron, all of which belong to Archimedean solids. Recently, a non-Archimedean $M_{30}L_{60}$ polyhedron was reported, whose topology is mathematically rationalized based on a theory of tetraivalent **Goldberg polyhedra** made up of squares and triangles. The self-assembly of $M_{48}L_{96}$ (Fig. 4) was achieved, which was predicted by the theory built by ourselves.

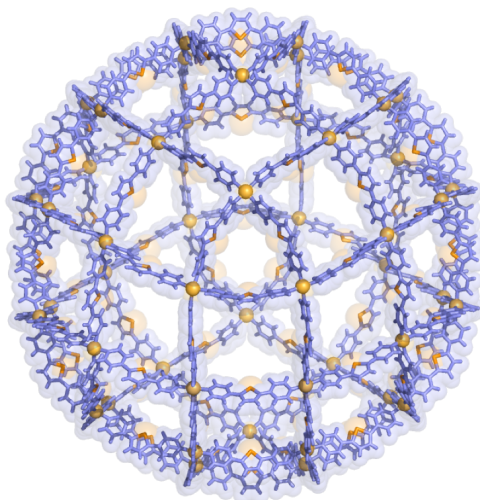


Fig. 4. X-ray structure of $M_{48}L_{96}$ complex.

Porous Coordination Network and Crystalline Sponge Method: Since 1994, coordination self-assembly has been applied to the construction of porous coordination networks[6], currently termed as MOFs. Only a few works were acknowledged in 1980's with attention to the void of the structures (Robson, 1988). Our persistent endeavor in this field is to unambiguously confirm the events in the pore by X-ray analysis, based on the single-crystal-to-single-crystal guest exchange phenomena. A variety of organic transformations and even reaction snapshots have been observed. Recently, these phenomena were led to a revolutionary method for determining X-ray structures of compounds without sample crystallization (Fig. 5).[7] The method has quickly arisen as a transformative technology and has been accelerating chemistry as well as many related disciplines not only in academia but also in industries.

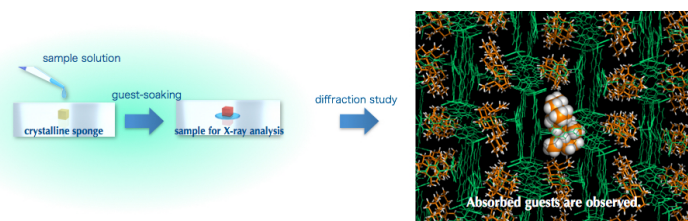


Fig. 5. Cartoon presentation of the crystalline sponge method.

Perspective In traditional disciplines, organic chemists create new “shapes” (*i. e.*, new frameworks, stereochemistries, nano structures, etc.), whereas inorganic chemists do new “states” (*i. e.*, new spin state, oxidation state, excited states, etc.). The scientific significance in coordination self-assembly is that a new interdisciplinary in chemistry has been developed, in which inorganic chemistry creates new shapes.

References

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