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# Abiological Self-Assembly via Coordination: Formation of 2D Metallacycles and 3D Metallacages with Well-Defined Shapes and Sizes and Their Chemistry

Self-assembly is the spontaneous organization of components into well-defined ensembles based upon the recognition elements embedded in the components. Nature is the supreme and consummate master of self-assembly, adroitly exploiting a range of non-covalent interactions such as van der Waals, $\pi$–$\pi$ stacking, dipole–dipole, hydrophobic–hydrophilic, and hydrogen-bonding to carry out countless biological phenomena. All living organisms, from the simplest to humans, depend upon molecular self-assembly. Protein-folding, nucleic acid structures, phospholipid membranes, ribosomes, chromosomes, and microtubules are representative examples of self-assembly in nature that are of critical importance to living organisms. The protein coats of viruses consist of self-assembled capsids that resemble polyhedra, icosahedra, or dodecahedra.

In the past three decades, abiological (non-biological) self-assembly has emerged as a major, active, and cutting-edge area of chemistry. Many attempts to mimic nature's elegant self-assembly processes with hydrogen bonds were met with limited success, particularly in the formation of large, finite assemblies with well-defined shapes and sizes, due to lack of or little directionality of weak interactions and the necessity of accurately positioning many dozens of these interactions to obtain functional assemblies. In contrast, as a consequence of d-orbital involvement, dative metal–ligand bonds are highly directional. Moreover, third-row metal–ligand bonds have bond energies in the range of 15–25 kcal/mol, much less than covalent bonds (ca. 60–120 kcal/mol) but stronger than the weak interactions in biology (ca. 0.5–12 kcal/mol). Hence, coordination kinetics can be modulated to engage in self-repair and self-healing to achieve thermodynamic control in the formation of superstructures. Furthermore, because it is stronger than weak interactions, one dative metal–ligand bond can replace several hydrogen bonds in the self-assembly process.

Initial work using coordination in self-assembly primarily involved the formation of infinite systems such as helicates, ladders, and grids. Out of those studies evolved the use of coordination in the self-assembly of finite ensembles with well-defined shapes and sizes. Early work in this area focused on developing methods for the rational, pre-designed self-assembly of metallacycles and metallacages, their structural characterization, and establishing the scope and limitations of coordination-driven self-assembly.[1] More recent and current work, as exemplified by the score of publications in this *JACS* Select collection, is focused on more complex methods of self-assembly and assemblies as well as applications.

Until recently, the vast majority of coordination-driven self-assembly employed only two building units, a donor and an acceptor. **Schmittel** and co-workers[2] used eight different components and a self-sorting approach to self-assemble an unusual scalene triangle. Likewise, **Zheng** et al.[3] used three components involving both carboxylate and pyridyl donor units and a platinum acceptor to self-assemble both 2D and 3D metallasupramolecules. Moreover, they described new types of supramolecule-to-supramolecule transformations, whereby a square could be transformed into a rectangle and a trigonal prism into a tetragonal prism. Similarly, **Ward** and co-workers[4] observed unusual cage-to-cage interconversions of large self-assembled polyhedral coordination cages, such as the rearrangement of a $Cd_{16}L_{24}$ tetracapped, truncated, tetrahedral cage to a $Cd_6L_9$ trigonal prismatic cage. **Severin** and colleagues[5] described a modular approach involving the connection of metallamacrocycles via dynamic covalent chemistry for the formation of interesting cage structures via self-assembly.

**Wesdemiotis**, **Newkome**, and co-workers[6] reported the formation of a giant 2D, $D_{6h}$ supramolecular spoked wheel via a multicomponent, coordination-driven self-assembly process. Likewise, researchers from the **Newkome** and **Wesdemiotis** groups[7] used terpyridine ligands as donors and ruthenium(II) and iron(II) transition-metal ions as acceptors to self-assemble a heteronuclear hexamer and nonamer with alternating Ru/Ru/Fe metal centers. Moreover, they used traveling wave ion mobility mass spectrometry to characterize these new 2D metallamacrocycles. **Gao**, **Zhao**, and **Wang**[8] used a novel azacalix[8]pyridine as well as acetylide ligands and silver ions to self-assemble [2]- and [3]-pseudo-rotaxane structures that they characterized by X-ray crystallography. **Eddaoudi**, **Liu**, and co-workers[9] reported the conversion of metal–organic squares to porous zeolite-like supramolecular assemblies. A group led by **Champness** and **Schröder**[10] reported a remarkable reaction, the self-assembly of a $Cd_{66}$ ball, a high-nuclearity metal–organic nanosphere. **Liu**, **Lin**, and co-workers[11] investigated the thermodynamics and selectivity of 2D metallasupramolecular self-assembly employing tripyridyl ligands and copper or iron on a gold (111) surface using scanning tunneling microscopy.

**Yamanaka** and co-workers[12] used a preformed $C_2$-symmetrical cavitand with attached ethynylpyridine donors and *cis*-$Pd(OSO_2)_2$ as an acceptor to self-assemble hybrid supramolecular capsules that accommodate various 1,2-diarylethane, ethylene, or acetylene molecules as guests. **Severin** and colleagues[13] used a ruthenium acceptor and a tritopic trispyridyl donor unit to assemble a hexanuclear ruthenium trigonal prism cage with an adaptable cavity size, able to accommodate either two coronene or two perylene molecules as guests. **Cronin** and collaborators[14] prepared a large supramolecular heteropolyoxapalladate encapsulating a $Pd_2$ dinuclear guest. **Nitschke** and co-workers[15] reported a three-component self-assembly process to prepare face-capped $Fe_4L_4$ capsules, capable of binding a wide variety of guest species in size- and shape-selective fashion. In a related study, **Nitschke**'s group[16] examined controlling the transmission of stereochemical information through space in terphenyl-edged $Fe_4L_6$ cages and the formation of diastereomers with $T_1$, $S_4$, and $C_3$ point symmetries. **Bergman**, **Raymond**, and

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co-workers[17] reported a remarkable (1.7−2.1) × $10^6$ rate acceleration in the enzyme-like catalysis of the Nazarov cyclization of 1,4-pentadien-3-ols by encapsulation in a self-assembled gallium supramolecular cage. In a similar study, **Bergman**, **Raymond**, **Toste**, and colleagues[18] reported an 8-fold acceleration of the catalysis by $Me_3PAu^+$ of hydroalkoxylation of allenes by encapsulation in their self-assembled gallium supramolecular host with up to 67 catalytic turnovers. Similarly, **Fujita** and co-workers[19] reported a palladium cage-catalyzed Knoevenagel condensation of aromatic aldehydes in water under neutral conditions. Likewise, **Fujita**'s group[20] examined the Diels−Alder reaction of a variety of substituted naphthalenes with maleimide in a self-assembled palladium cage they call a molecular flask. Due to the tight fit of the reagents in the cage, the reaction is regio- and stereoselective.

With a view toward developing electronic and optical applications of self-assembled supramolecular metallacycles, **Goodson** and collaborators[21] investigated the ultrafast dynamics of platinum metallacycles via femtosecond fluorescence upconversion and transient absorption. It was shown that the presence of platinum influences the spin−orbit coupling and increases the rate of intersystem crossing while decreasing the lifetime of the singlet state.

As can be seen from the above-described examples, coordination-driven, abiological self-assembly of finite metallacycles and metallacages with well-defined shapes and sizes is a vibrant, active area of contemporary chemistry. In the past half-dozen years, and in particular most recently, the field has progressed from simple two-component self-assembly to more complex processes with a concomitant greater diversity of nanoscale ensembles. Likewise, ever more uses and applications are being reported. Future work will likely involve even more applications in both the material science and biochemical/biomedical areas. New optical and electronic materials, unique sensors, potential drug delivery systems, further catalytic uses, etc. will undoubtedly emerge. To facilitate these uses and applications, a better, deeper, more detailed understanding of the self-assembly process itself is also required, along with new, more sophisticated methods of assembly of rationally predesigned systems.

**Peter J. Stang**, Editor

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