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Review

Construction of supramolecular hexagonal metallacycles *via* coordination-driven self-assembly: Structure, properties and application

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ABSTRACT

The formation and growth of natural objects are affected by the available space and materials. A regular hexagon is one of three regular polygons that can overlap without a plane. Among these three regular polygons (equilateral triangle, regular quadrilateral, and regular hexagon), the regular hexagon occupies the largest area with the smallest amount of material. The construction of supramolecular hexagonal architectures has been of great interest within supramolecular chemistry and materials science. Since supramolecular self-assembly enables the preparation of highly complex supramolecular systems from relatively simple building blocks, various metallosupramolecular hexagonal architectures have been successfully constructed under mild conditions by employing facile coordination-driven self-assembly strategy, and some of the architectures have exhibited wide ranges of applications in the fields of catalysis, electrochemistry, photochemistry, molecular sensing, *etc*. This review summarizes recent advances in the field of supramolecular hexagonal metallacycles. The design, self-assembly, and applications of various supramolecular hexagonal metallacycles, especially those incorporating functional moieties, will be discussed.

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1. Introduction

Since the study of science began in the ancient world, nature has intrigued and inspired man with its symmetry and beauty. While nature offers an incredibly diverse range of objects, both living and inanimate, their basic forms can be found to repeat across the natural spectrum. The hexagon is a kind of polygon with six edges and six angles. The regular hexagon, a shape featuring six sides that are often of equal length, is ubiquitous in nature, from rock formations to precipitation and even the animal kingdom, and has been considered as the nature's perfect shape. The beautiful and unique features of the hexagon can be found in numerous natural settings, including honeycomb, turtle shells, snowflakes, rocks, and even clouds on another planet. The common occurrence of hexagons in nature is not surprising given the functionality of the shape. Hexagonal shapes can fit together very efficiently without losing any space in a process known as tessellation. In 1999, mathematician Thomas C. Hales of the University of Michigan at Ann Arbor proved the "honeycomb conjecture", which confirms that hexagonal shapes infinitely fit together with the least amount of perimeter exposed. Honey bees are thought to make their honeycomb from hexagonal shapes for this reason in addition to the known strength qualities of hexagons. Meanwhile, many functional biological systems feature hexagonal shapes, such as HIV capsid, the family of ATPases and DNA hexagon helicases [1–4]. Likewise, hexagon ring-shaped structures are also found in carbon-based chemistry, from benzene to graphite, nanotubes, and fullerenes. It is also believed that the hexagonal structure is the most efficient shape in terms of space and building materials.

The natural formation of highly complex and highly symmetric superstructures is often based on a variety of noncovalent interactions, including hydrogen-bonding, van der Waals, and many other weak inter-/intra-molecular interactions. For instance, the hexagon shape of the HIV capsid is the product of nature's self-assembly processes. With their structures elucidated by the modern techniques of X-ray diffraction and cryogenic electron microscopy, nature has employed these shapes due to their close approximation of a sphere and the corresponding maximization of volume to surface area for containing viral genetic information. The aforementioned structures provide inspiration for chemists seeking to develop myriad ways of utilizing noncovalent interactions to direct the spontaneous self-assembly of supramolecular systems in a manner similar to the self-assembly processes that occur throughout nature [5–9].

Obviously, it would be a daunting endeavour to try to use an exact model of nature's process due to the inability to completely control the directionality of the multiple non-directional hydrogen-bonding, van der Waals, and other weak interactions that are responsible for biological self-assembly. Stepwise synthetic procedures are the most widely used routes for constructing a variety of compounds. Therefore, numerous large macrocyclic systems have been assembled by stepwise covalent syntheses. For instance, Tobe and Moore et al. accomplished the preparation of a series of hexagonal structures from phenylacetylene rods [10,11]. However, stepwise covalent syntheses are often time- and yield-prohibitive for large molecules, although they are powerful approaches for the synthesis of small organic molecules. Thus, a considerable amount of effort has been devoted to developing alternative synthetic strategies for preparing large complex supramolecular structures.

Coordination-driven self-assembly, which takes advantage of the spontaneous self-assembly of precursor building blocks and metals *via* coordination, has proven to be a feasible and useful strategy for constructing complex supramolecular structures [12–19], as exemplified by the pioneering work of Lehn [20,21] and Sauvage [22] in the formation of infinite helicates, grids, ladders, racks, knots, rings, catenanes, rotaxanes, and related species. Many research groups, such as those of Stang [23–26], Fujita [27–32], Raymond [33–35], Mirkin [36–38], Shionoya [39–42], Nitschke [43–46], and Newkome [47–50], have independently exploited different approaches to construct discrete metallacycles and metallacages with well-defined shapes and sizes [51–54]. In particular, by taking advantage of the merits of coordination-driven self-assembly, such as the fast and facile formation of the final architectures in fewer steps and the inherently self-correcting, defect-free assembly, numerous discrete two-dimensional (2-D) assemblies, including molecular squares, rectangles, triangles, pentagons, and hexagons as well as many other polygons of varying symmetry, have been obtained [55–68]. During the last decade, several insightful review articles about coordination-driven self-assembly have been published [69–76]. Very surprisingly, despite the rapid development of supramolecular hexagonal metallacycles constructed through coordination-driven self-assembly, there have been no reviews on the advances in discrete hexagonal metallacycles. Thus, in this review, we will present a brief overview of the recent development in the field of supramolecular hexagons and discuss some of their potential applications.

2. Construction of supramolecular hexagonal metallacycles

2.1. Synthetic strategies towards supramolecular hexagonal metallacycles

As in nature, it is the inherent information such as size, angle, and geometry, coded within the complementary building blocks determines the self-assembly process and architecture of supramolecular ensembles. In principle, coordination-driven self-assembly process can possess kinetically inert or kinetically labile metal-ligand interactions. The kinetically inert, like conventional organic covalent bonds, are kinetically stable with respect to ligand displacement, which is unfavorable for the formation of well-defined thermodynamic products. However, the ligand might be easier to be exchanged in self-assembly with kinetically labile metal-ligand interactions. So that self-assembly process through such interactions are reversible and allow facile conversion to the favorable formation of thermodynamically most stable products, in which the self-assembly plays a crucial role. Meanwhile the metal-ligand coordination is highly directional and predictable, which is very helpful to control the self-assembly of building blocks into well-defined, discrete supramolecules [12–19].

There are two basic requirements for the construction of 2-D assemblies *via* coordination-driven self-assembly: (i) rigid, complementary precursors with predefined angles and symmetry; and (ii) appropriate ratios of complementary precursors [77–80]. The symmetry of individual building units and the overall shape of the resulting assembly are the most important factors to be considered in the design of discrete metallacycles. The shape of an individual two-dimensional polygon is determined by the value of the turning angle within its angular components, and different type of ligands, such as bis-pyridyl, terpyridyl and heterotopic