Review

Self-assembled metal–organic polyhedra: An overview of various applications

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ABSTRACT

Self-assembly is a potent synthetic tool that allowed chemists to design numerous complex structures, supramolecules of various shapes from relatively simple starting materials. Metal–organic polyhedra are a rising and promising member of the self-assembled supramolecule family possessing fascinating structures and functionalities directly deriving from the precursor units. During the last two decades, research in this field has been briskly progressed and it is now objective to exemplify various applications such as biomedical, catalysis, molecular sensing, gas adsorption and separation, and synthesis of metal–organic frameworks from polyhedra. This review will be focus on each and every application with various unprecedented examples and highlight few challenges still need to be address.

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1. Introduction

Self-assembly is defined by George Whitesides as "a process where pre-designed components assembled in a determined structure without the intervention of human operators" [1]. This broad and cautiously stated definition emphasized on three indispensable characteristics for a process to be termed as self-assembly. This includes utilization of carefully designed building blocks where information encoded within the building blocks will dictate a specific way of their interactions, generating determined structure of higher complexity as compared to simpler building blocks, and finally will commensurate without the intervention of human operators. The self-assembly can be easily correlated to the concepts and tools of supramolecular chemistry. In the early 1960s, the discovery of "crown ethers", "cryptands", and "spherands" by Pedersen [2], Lehn [3], and Cram [4], respectively, led to the comprehension that the small molecules can easily recognize each other through non-covalent interactions such as hydrogen bond, van der Waals, π–π interaction, etc. Such large supramolecules formed by
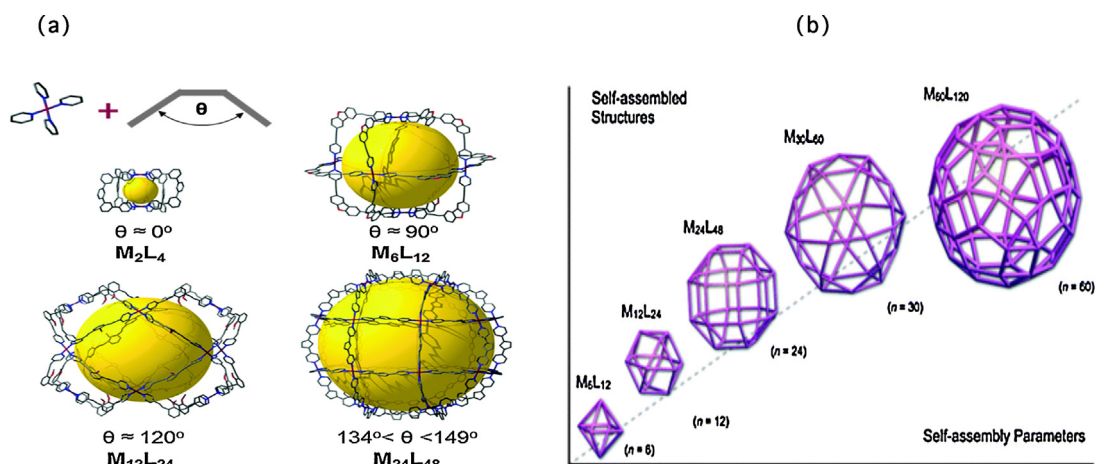
Fig. 1. (a) Illustration of the strong influence of the bent angle of the ligand on the geometry of the resulting MOP. Reproduced with permission from [45]. (b) The family of M_nL_{2n} polyhedral cages, where metals (M) and bridging bis(pyridine) ligands (L) are mapped onto the vertices and edges, respectively. Reproduced with permission from [12].

these interactions in a definite algorithm have altogether different physicochemical properties than those of the precursor units. It is indeed a proficient and an efficient pathway to synthesize complex multi-component systems. In a step-wise synthesis, the reaction intermediates are isolated and subsequently purified before doing the further extension. On the contrary, in self-assembly, the reaction intermediates are present momentarily and no isolation or purification steps are carried out. It indirectly enforces considerable challenges and restrictions on the design and construction of chemical species. The idea of intermolecular interactions along with the principle of crystal engineering will open the door for constructing such systems for demanding applications. The best example is deoxyribonucleic acid (DNA) double helix; the hydrogen bonding interactions between the base pairs implies a specific mode of binding.

Porous coordination nanocages formed between linkers such as carboxylic acid, pyridine, pyrimidine, *etc.* and metal clusters are known as metal–organic polyhedra (MOPs). The former acts as a Lewis base whereas the latter serves as a Lewis acid. Synthetic organic chemists are able to deliver a plethora of organic linkers and the presence of a set of metal ions in the periodic table gives inestimable permutations of rational reactions. However, design strategies that depend on a sensible choice of reaction conditions, parameters, *etc.* can be devised to guide the synthesis of complex structures. These discrete nano-architectures in different metal-to-ligand ratio usually are synthesized by non-solvothermal ways. The robustness, permanent porosity, appropriate cavity size, hydrophobic nature, thermal and chemical stability of these discrete structures are the backbone for various unprecedented applications.

2. Metal–organic polyhedra

Self-assembled complex structures formed by non-covalent interactions are abundant in nature such as the high-symmetry protein assemblies ferritin (*O* symmetry) and apoferritin [5,6]. However, abiological preparation of such complex structures is really a daunting task. The connectivity between the metal ions or metal clusters and organic linkers led to 0D polygons or discrete polyhedra, 1D chain or ladders, 2D sheets or bilayers, and 3D extended networks. Zero dimensional discrete polyhedra are usually prepared by the self-assembly of metal ions and linkers having hard donor atoms as binding sites. Metal–organic

polyhedra prepared by various designing strategies lies in any of the categories of the solids namely: platonic (tetrahedron, cube, octahedron, dodecahedron, and icosahedron), archimedean (truncated tetrahedron, cuboctahedron, truncated cube, truncated octahedron, rhombicuboctahedron, snub cube, icosidodecahedron, truncated cuboctahedron, truncated dodecahedron, truncated icosahedron, rhombicosidodecahedron, snub dodecahedron, and truncated icosidodecahedron), faceted (tetrahemihexahedron, octahemioctahedron, small icosihemidodecahedron, cubohemioctahedron, small rhombihexahedron, small rhombidodecahedron, small dodecahemidodecahedron, small cubicuboctahedron, and small dodecicosidodecahedron), and stellated with a different Schläfli symbol.

2.1. Design strategies

Transition metal ions in their preferred coordination geometry serve as acceptor units that can self-assemble with a range of rigid and flexible donors into predictable architectures. The metal–ligand bond coordination is a cornerstone of various designing strategies such as directional bonding, symmetry interactions, molecular paneling, weak linking, and dimetallic building blocks. These strategies are predominantly used by Atwood [7], Cotton [8,9], Fujita [10–12], Lindoy [13–16], Mirkin [17–19], Nitschke [20–22], Raymond [23–26], Stang [27–31], Saalfrank [32,33], Ward [34,35], Yaghi [36–38], Zhou [39–41], and others [42–45] in designing 2D and 3D supramolecular architectures. The directional bonding approach relies on the angular orientation (0° to 180°) of binding sites and appropriate stoichiometric ratio of the precursor units. The small variation in angular orientation among donor groups (*i.e.* nitrogen and oxygen in bis(pyridine) and dicarboxylic acid, respectively) led to a change in the geometry of self-assembled polyhedra as shown in Fig. 1a. Furthermore, coordination spheres of general formula $[M_nL_{2n}]$ (*n* is an integer and may vary from 6 to 60) are extremely susceptive to the bend angle of ligands. For instance, a small increment in bend angle from 120° to 149° completely change the cage ensemble from $M_{12}L_{24}$ cuboctahedron to $M_{24}L_{48}$ rhombicuboctahedron but, a difference of 3° in the mean bend angle (between 131° and 134°) behaves as a critical structural switch to determine the geometry of the Pd(II) cage [46]. Moreover, modification at the concave (endohedral) or convex (exohedral) position of the ligand backbone by various functionalities such as alkyl chains, azobenzene groups, saccharide units, coronene group,