



Review

Discrete metal-carboxylate self-assembled cages: Design, synthesis and applications



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ARTICLE INFO

Article history:

Received 31 March 2014

Accepted 8 July 2014

Available online 16 July 2014

Keywords:

Biomedical

Carboxylate

Metal-organic polyhedra

Nanocage

Self-organization

Sorbent

ABSTRACT

Discrete metal-carboxylate cage-like materials are an important class of metal-organic polyhedra. The designs of these self-assemblies in terms of their characteristic polygonal shape, surface area, and related properties are functions of metal centers and carboxylate bridging linkers. Thus, several combinations of different metal ions with angular, linear ditopic, or tritopic carboxylic links can be integrated to map these nanoscale materials, as well as the optional functional groups for the ligands. Synthetic protocols based on variations in the solvent, temperature, and pressure can be employed to achieve metal-carboxylate self-organization. These types of discrete polyhedral nanocages with an internal void are materials with a broad spectrum of potential future uses as substrates for extended networks and highly selective gas sorbents in catalysis and biomedical processes.

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1. Introduction

Throughout the world, material scientists are actively engaged in exploring new materials with desirable properties and functional stability [1]. Materials science has become highly useful for the design, formulation, and characterization of materials from very simple to symmetrically self-assembled molecular architectures [2]. In supramolecular science, self-assemblies with a very high degree of symmetry made of multiple subunits are very common in biological systems [3]. For example, the primary intracellular iron-storage protein (ferritin) [4] is a spherical protein complex (octahedral symmetry) made of 24 protein subunits. Icosahedral symmetry is observed in the capsid, which is the protein shell of the adenovirus. Similarly, the self-assembly of the tobacco mosaic virus is a helical structure that contains 2130 duplicate protein subunits, which are organized around an RNA strand [5]. Numerous artificial/abiological self-assembled polyhedra based on metal-organic constituents have been built by learning from these natural extremely symmetric biological self-assemblies. These polyhedra have been introduced as a new class of materials in addition to other well-known metal-organic materials [6,7].

Chemically bonded organic and inorganic hybrid materials, *i.e.*, metal coordination compounds, are a major current research area, which involves their design, synthesis, and potential applications [8–10]. Metal-organic systems such as macrocycles and polyhedral frameworks are synthesized from appropriately designed ligands and selected metal ions under specific reaction conditions. Recently, the concept of molecular nanosize containers was introduced and compounds produced from different chemical formulations such as organic [11,12] or metal-organic [13,14] were reported. Metal-organic polyhedra (MOPs) [15] are not infinite networks in the same manner as metal-organic frameworks (MOFs) [16,17], but instead they are discrete molecular entities, which are constructed from edge-sharing molecular polygons or *via* connections between molecular vertices [18]. The molecular polyhedra obtained in a spherical manner based on self-organization *via* metal to carboxylate (M–O–C(R)–O–M) links are cage-like architectures at the nanoscale size, with outer and inner surfaces. MOPs are also known as nanocages, nanospheres, nanocapsules, or nanoballs. Metal-carboxylate MOPs have flexibility in their geometrical topology, size, surface area, and porosity. MOPs have potential applications by serving as host molecules. Therefore, metal-carboxylate MOPs have become attractive for applications in catalysis, sorption, biophysical science, and as secondary building blocks/substrates for MOFs [19,20].

2. Design

Discrete metal-carboxylate cages possess various polyhedral structures, well-defined cavities, high symmetry, and stability. The design of these architectures can be controlled, including capsules, boxes, and polygonal cages. They are easily governed based on the principles of self-assembly, including organic and inorganic moieties [15,21–25]. Interestingly, the shape and size but also the function of the MOP can be pre-designed. Thus, a precise molecular host can be fabricated for certain applications [26–31]. The chemistry of MOPs can be extended broadly if required, to provide permanent porosity and chemical stability [32]. Therefore, the MOP structure for required specific properties can be developed based on the suitable design of the ligand and the selection of a metal ion in terms of nodality and/or geometry. Metal to ligand bonds can overcome weak interactions (such as H-bonds, π - π , dipole-dipole, and Van der Waals) thereby facilitating the rational design of cage-like assemblies. The control of the scale of the design and topology of the MOP can be optimized by the appropriate selection of the metal

ion and coordinating ligand. To tune that structure and functions, the design strategy focuses on the organic ligand modification and the possibility of combining with different metal ions [15,33].

2.1. Metal centers

Metal ions are used widely in the design of coordination compounds. In particular, transition metal ions are used extensively in the construction of MOPs. In the formation of the MOP periphery, the metals usually occupy positions as vertices. The metal plays an important role in achieving the requisite properties and shape of the MOP. Metals such as Cu(II), Mo(II), Fe(III), Co(II), Ni(II), Cd(II), and Pt(II) are favorable candidates. Specific designs of MOPs using Cu(II) and Mo(II) have been popular during the last decade and they are classified as a collection of dinuclear paddlewheel (PW) clusters. The general PW formula $M_2(\text{COO})_4$ (where M is a metal and “COO–” is as carboxylic functional group) distinguishes the design of these MOPs from the MOPs of other metals [34].

2.2. Organic bridging linkers

Highly directional organic ligands bridge the geometrically pre-fixed metal-containing nodes and allow the formulation of extremely symmetrical MOP architectures [15,34–36]. Novel organic linkers provide new opportunities in the field of metal-organic materials. Therefore, different types of ligands have been employed successfully to direct suitable assemblies around the given metal ion. The ligands used possess a variety of reaction centers, including carboxylate, hydroxyl, and/or nitrogen donor groups. Aromatic carboxylate-based MOP structures possess a collection of metal centers that are linked by di- or tritopic carboxylate moieties, which results in an overall polyhedral shape. Variations in the structure of the organic linkers allow the tunability of the dimensions, properties, and functionality of MOPs. An overall angular bend ($0^\circ \leq \theta < 180^\circ$) due to the aromatic spacing among two carboxylate reaction sites directs the cage-like assembly. This approach to “ligand bridging-angle-driven assembly” is well known in the design of ditopic carboxylic acids as the ligand for PW-oriented metal centers [37]. In addition, linear ditopic and tritopic carboxylic acids provide a broad range of ligands, while various metal centers can be used other than metallic PWs [33].

2.3. Angular ditopic carboxylic bridging linkers

A wide variety of polyhedra have been categorized that utilize Cu(II)/Mo(II) and benzene 1,3-dicarboxylic acid (H_2BDC) because these metal cations have a propensity for forming the PW geometry with dicarboxylates [37]. The general molecular formula of the resulting MOP is $[M_2(5-R-BDC)_2(S)_2]_{12}$, where M is Cu(II) or Mo(II), R is the substituent, as shown in Table 1, and S is the coordinated solvent, whereas this excludes uncoordinated/encapsulated guest solvent molecules. The construction of MOP assemblies with Cu(II) or Mo(II) ions and derivatives of H_2BDC involves 12 dinuclear PW units (also referred to as secondary building units (SBU)), which are interconnected *via* 24 ligands, as shown in Fig. 1 [34,38]. The internal cage cavity in the MOPs with the ligands shown in Fig. 1 has a volume of *ca* 1 nm³ [39,40].

The angular orientation of the two dicarboxylic groups in a ligand is a major driving force that determines metal-based self-assembly. The aromatic spacer group(s) among carboxylic sites can cover the planar square node for the MOP design. Most of the design practices applied to MOPs follow this strategy where the PW units are linked at an angle of 120° or less using angular bifunctional ligands like 5-R-BDC. Thus, the connecting geometry of the linker, such as the bend angle in a ditopic bridging ligand, controls the geometrical topology of the overall architecture. After the

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