

Template-controlled reactivity: Following nature's way to design and construct metal-organic polyhedra and polygons

Tamara D. Hamilton, Giannis S. Papaefstathiou, Leonard R. MacGillivray*

Department of Chemistry, University of Iowa, Iowa City, IA 52242-1294, USA

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Abstract

We show how a template-controlled reaction performed in the organic solid state can be used to construct a molecule that functions as an organic building unit of both a metal-organic polyhedron and polygon. The template is a small organic molecule that organizes two olefins via hydrogen bonds for a [2 + 2] photodimerization. The process of utilizing a molecule to build a molecule that is subsequently used for self-assembly is inspired by the general two-step process of template-directed synthesis and self-assembly of Nature that is used to construct large, functional self-assembled structures.

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1. Introduction

Metal-organic polygons and polyhedra are developing at a rapid rate owing to their applications in host-guest chemistry [1], catalysis [2], and sensing [3]. Much of the inspiration to construct such self-assembled structures has stemmed from Nature and its influence on the field of supramolecular chemistry [4]. Lehn has described supramolecular chemistry as an information science based on the principle that the instruction set for the formation of a large, complex assembly of molecules is contained within the constituent components [4]. In the case of a metal-organic, or metallo-supramolecular, assembly, it is the information contained in the ligand, coupled with the coordination geometry of the metal, that define the structure of a final self-assembled product. The program

is, therefore, molecular and the operation is supramolecular [4].

2. Organic ligands for metal-mediated self-assembly

In this context, the development of strategies to synthesize ligands that form metal-organic polygons and polyhedra is important [5]. Moreover, whereas chemists typically employ conventional approaches of organic synthesis to synthesize multidentate ligands that form self-assembled metal-organic structures, one need only look again to Nature (e.g. virus construction) to realize that a sophisticated manifestation of principles of supramolecular chemistry is at work—in the form of template-directed synthesis—to construct the covalent building units (i.e. proteins) of self-assembled biological structures [6]. Thus, intriguing questions arise: Can chemists integrate principles of template-directed synthesis and self-assembly to construct a metal-organic polygon and/or polyhedron?

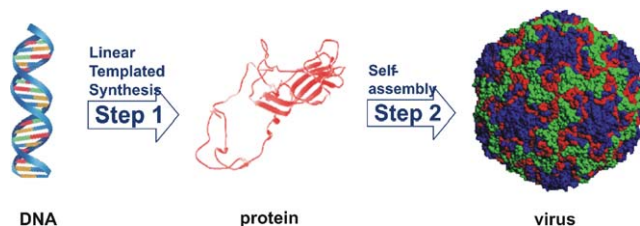
*Corresponding author. Fax: +1 319 335 1270.

E-mail address: len-macgillivray@uiowa.edu (L.R. MacGillivray).

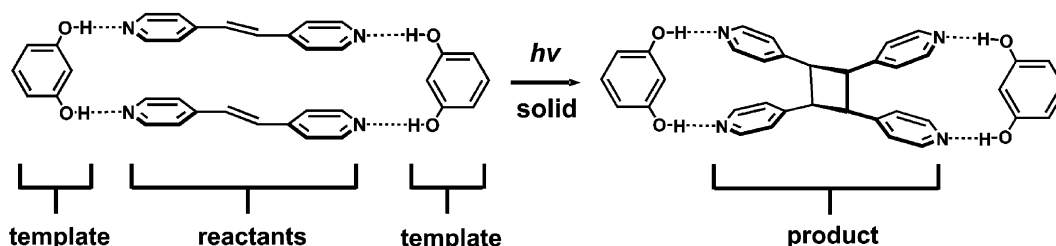
How may such ideas be developed in a purely synthetic system? What kinds of metal-organic assemblies would arise from such an approach? (for a similar question, see [7]).

3. Template-directed synthesis and self-assembly in nature

To address these questions, it is instructive to consider how Nature constructs a shell-like polyhedral assembly such as a virus (Scheme 1) [6,8]. Virus construction is achieved using viral DNA or RNA that serves as a linear template by directing the assembly and covalent synthesis of organic building units, in the form of polypeptides, via non-covalent forces. The interactions that facilitate the construction of the building units involve hydrogen bonds and π - π forces. The resulting protein subunits then fold and self-assemble, in a second step, to give a shell-like structure, or capsid. Clearly, the ‘baseline’ of this synthetic strategy is supramolecular, the information stored within the template being expressed via coding and amplification within the building units and self-assembled structure, respectively, and eventually through feedback to the template [6]. From a synthetic chemist’s point of view, the template-controlled synthesis is highly efficient, achieving an extraordinary degree of stereocontrol [9]. To date, however, approaches to construct metal-organic polygons and polyhedra have focused primarily on the second step of self-assembly (For a study involving two-level self-assembly involving organic and inorganic components, see [10]) in which the organic ligands are synthesized without assistance of a molecular template [1–3].



Scheme 1.



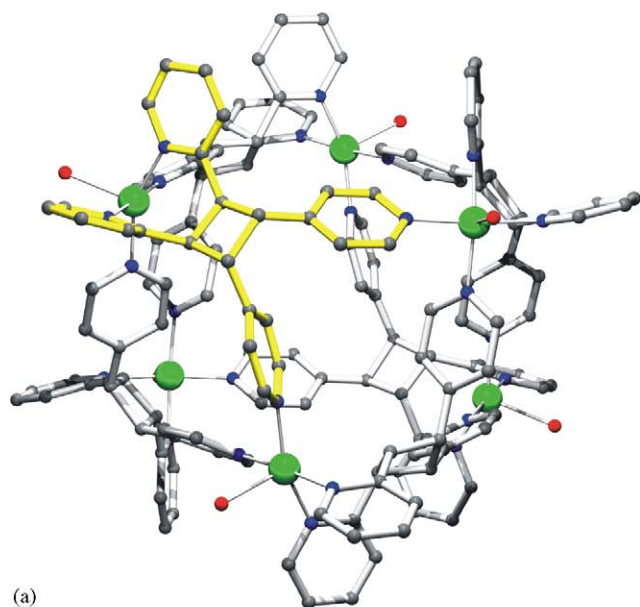
Scheme 2.

4. Template-controlled solid-state synthesis

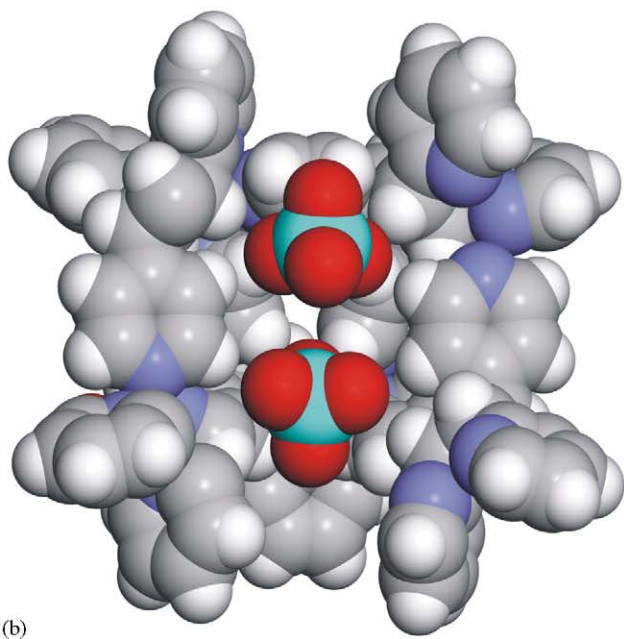
We wondered if we could apply principles of template-controlled synthesis followed by molecular self-assembly to construct shell-like metal-organic polyhedra and polygons. To address this question, we have described how U-shaped organic molecules can be used as linear templates [11] that direct the syntheses of organic molecules in the organized environment of the solid state (Scheme 2). The templates assemble olefins lined with pyridyl groups, via hydrogen bonds, in positions suitable for intermolecular [2 + 2] photodimerizations. Subsequent removal of the template yields a cyclobutane product with, in the minimal case, two exodentate pyridyl groups. Thus, co-crystallization of resorcinol (res) with *trans*-1,2-bis(4-pyridyl)ethylene (4,4'-bpe) produced a molecular assembly, of composition 2(res) · 2(4,4'-bpe), held together by four O–H...N hydrogen bonds with two molecules of 4,4'-bpe assembled for a [2 + 2] photoreaction [12]. Ultraviolet irradiation of the solid produced *rcctt*-tetrakis(4-pyridyl)cyclobutane (4,4'-tpcb) in 100% yield and gram quantities. Moreover, we hypothesized that the number and positioning of the hydrogen-bond acceptor groups, owing to the ubiquity of pyridines in coordination chemistry, could make the photoproducts potential organic building units of self-assembled metal-organic structures [1–3].

5. A metal-organic polyhedron and polygon derived from a linear template

Our hypothesis was confirmed through the demonstration that an unsymmetrical product of a template-controlled solid-state synthesis, namely 2,4'-tpcb, can serve as a building unit of a metal-organic polyhedron (Fig. 1) [13]. Specifically, upon combination with a copper(II) salt of a non-coordinating anion (e.g. perchlorate), 2,4'-tpcb formed a hexanuclear polyhedron with a geometry that conformed to a trigonal antiprism (Fig. 1a). Each copper atom of the polyhedron adopted a square pyramidal coordination environment with chelating 2-pyridyl units and monodentate 4-pyridyl



(a)



(b)

Fig. 1. X-ray crystal structure of the hexanuclear metal-organic polyhedron involving 2,4'-tpcb and copper(II) perchlorate: (a) ball-and-stick model (one 2,4'-tpcb highlighted in yellow) and (b) space-filling model depicting the perchlorates (color scheme: green = copper, cyan = chlorine, red = oxygen, blue = nitrogen, gray = carbon, white = hydrogen).

units forming the base and a water forming the apex. Thus, the 4-pyridyl groups produced the edges of the antiprism while the 2-pyridyl groups produced the corners. Two ClO_4^- anions also occupied the interior of the polyhedron (Fig. 1b) [1]. Despite being simple and primitive (for a similar question, see [7]), the 'total' supramolecular synthesis [14] of the polyhedron can be compared to the syntheses of biological polyhedral

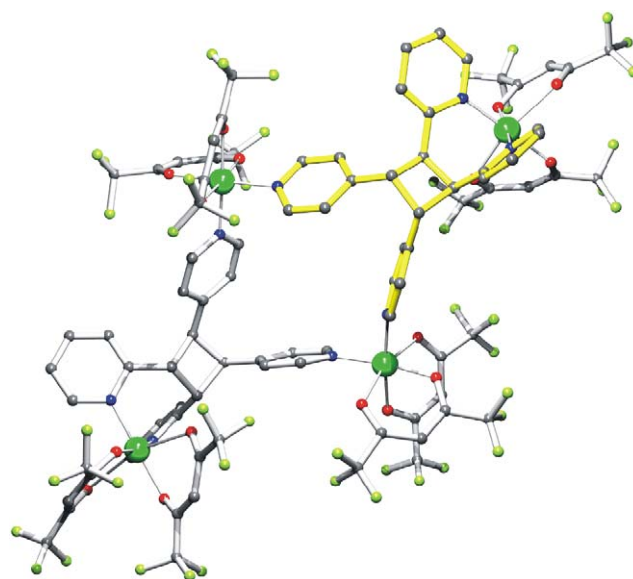
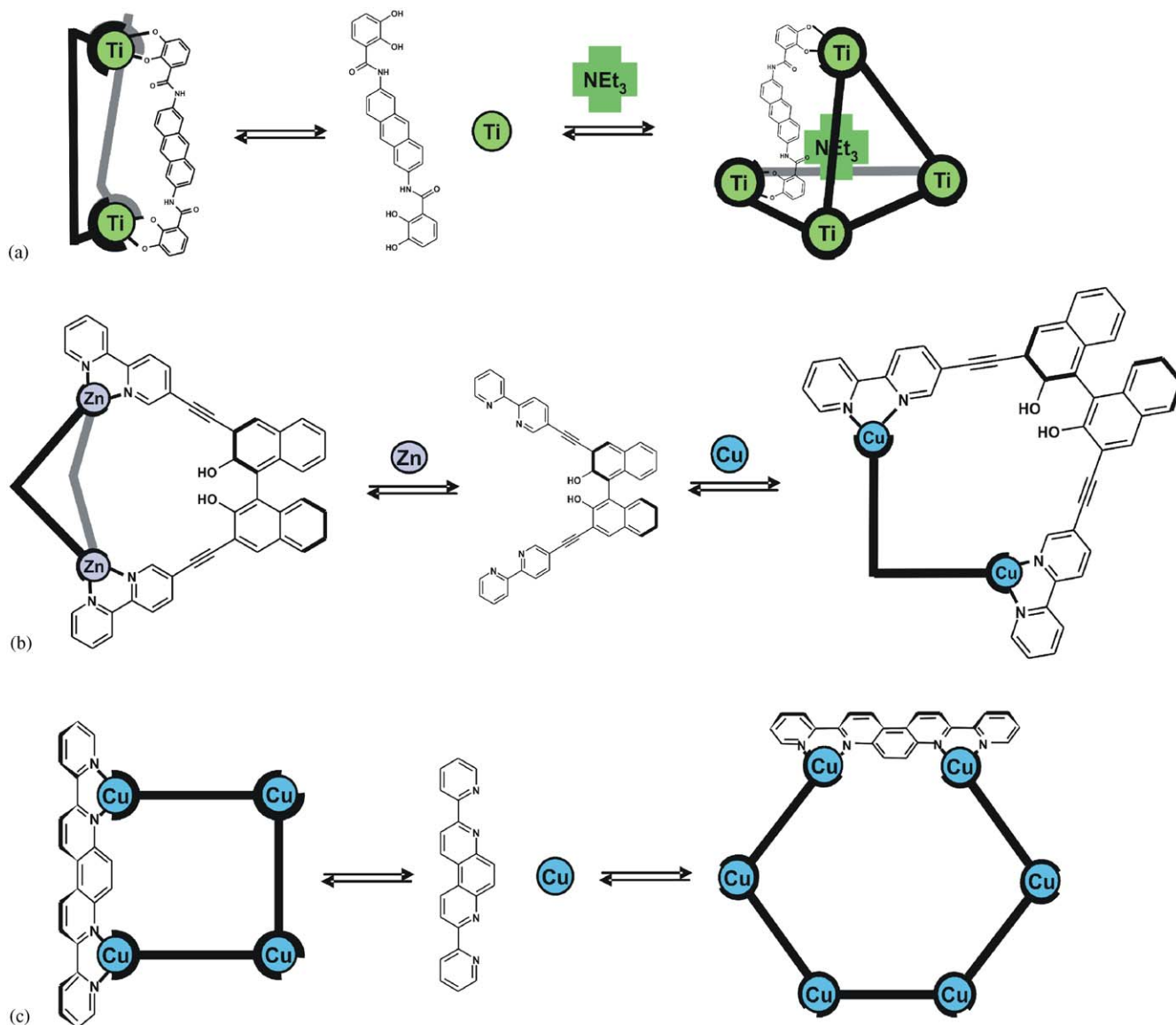


Fig. 2. X-ray crystal structure of the tetranuclear metal-organic polygon involving 2,4'-tpcb and copper(II) hfac (one 2,4'-tpcb highlighted in yellow) (color scheme: green = copper, light green = fluorine, red = oxygen, blue = nitrogen, gray = carbon, white = hydrogen).

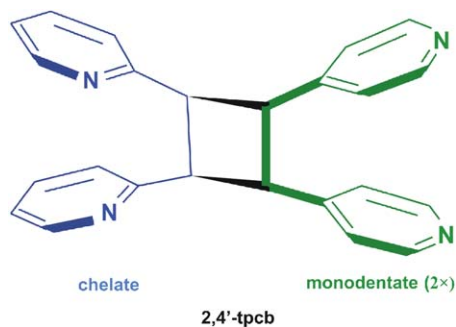
assemblies such as viruses where molecular templates and self-assembly are both at work [6].

Following our initial report, we also revealed that 2,4'-tpcb can serve as a building unit of a metal-organic polygon [15]. Specifically, upon combination with a copper(II) salt of a chelating anion [e.g. hexafluoroacetylacetonate (hfac)], 2,4'-tpcb assembled to form a tetranuclear metal-organic polygon with a geometry that conformed to a rhombus (Fig. 2). Each metal atom of the polygon adopted an octahedral coordination environment in which two metal atoms that formed opposite corners of the polygon were coordinated by two chelating hfac ions and 4-pyridyl groups and while two metal atoms that occupied the periphery were coordinated by 2-pyridyl groups and hfac ions. Thus, as with the polyhedron, each cyclobutane of the polygon bridged three metal atoms within the metal-organic structure. In contrast to the polyhedron, however, 2,4'-tpcb served as a ditopic, as opposed to a tritopic, linker owing to the chelating ability of the hfac anions. The cavity of the polygon was shown to be too small to accommodate an organic molecule as a guest [15]. The ability of an organic ligand to sustain both a polyhedral and polygonal metal-organic structure had not been encountered in the field of metallo-supramolecular chemistry, although there were reports of ligands that sustain both: (a) a helicate and a polyhedron [16], (b) a helicate and a polygon [17], and (c) two different polygons (Scheme 3) [18].

In the language of Lehn [4], 2,4'-tpcb is a ligand with two complexation subroutines that can be read upon



Scheme 3.



Scheme 4.

combination with a metal. The subroutines arise from the two functions of the ligand; namely, monodenticity and chelation (Scheme 4). Such ligands when combined

with a metal-coordination algorithm lead to a double subroutine self-assembly process [4]. The information can be expressed as either a linear combination of the different subroutines, each yielding a predetermined substructure, or as a cross-combination involving interference of the two subprograms. If the different outputs can be controlled externally then behavior such as switching may be realized [16,18]. In the case of our metal-organic polyhedron, *both* subroutines of 2,4'-tpcb were read by *each* copper(II) center, which led to a cross-product of the subroutines. On the other hand, in the case of the polygon, *each* subroutine, owing to the chelating abilities of the hfac anions, was expressed at a *separate* metal center. Thus, the polygon resulted from a linear combination of the two subroutines [4]. Importantly, the complexation abilities of 2,4'-tpcb were

programmed using a linear template in the solid state, the information being amplified during the subsequent self-assembly process.

6. Conclusion

Template-controlled synthesis performed in the organic solid state provides a means to construct molecules that serve as building units in metallo-supramolecular chemistry [1–3]. The high level of geometrical control provided by the templates [11] and the solid state [12] has afforded a means to synthesize an unsymmetrical ligand that serves as a subunit of both a metal-organic polyhedron and polygon. By utilizing a molecule derived from a linear template as a ligand to form self-assembled metal-organic structures, we have shown that it is possible to go beyond self-assembly to further harness biology as an inspiration [6] in the development of a two-step supramolecular approach to construct self-assembled metal-organic products. We anticipate that the strategy described here will be further inspired by biology [6] for the design and construction of metal-organic polygons and polyhedra of increasing structural and functional complexity [1–3].

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