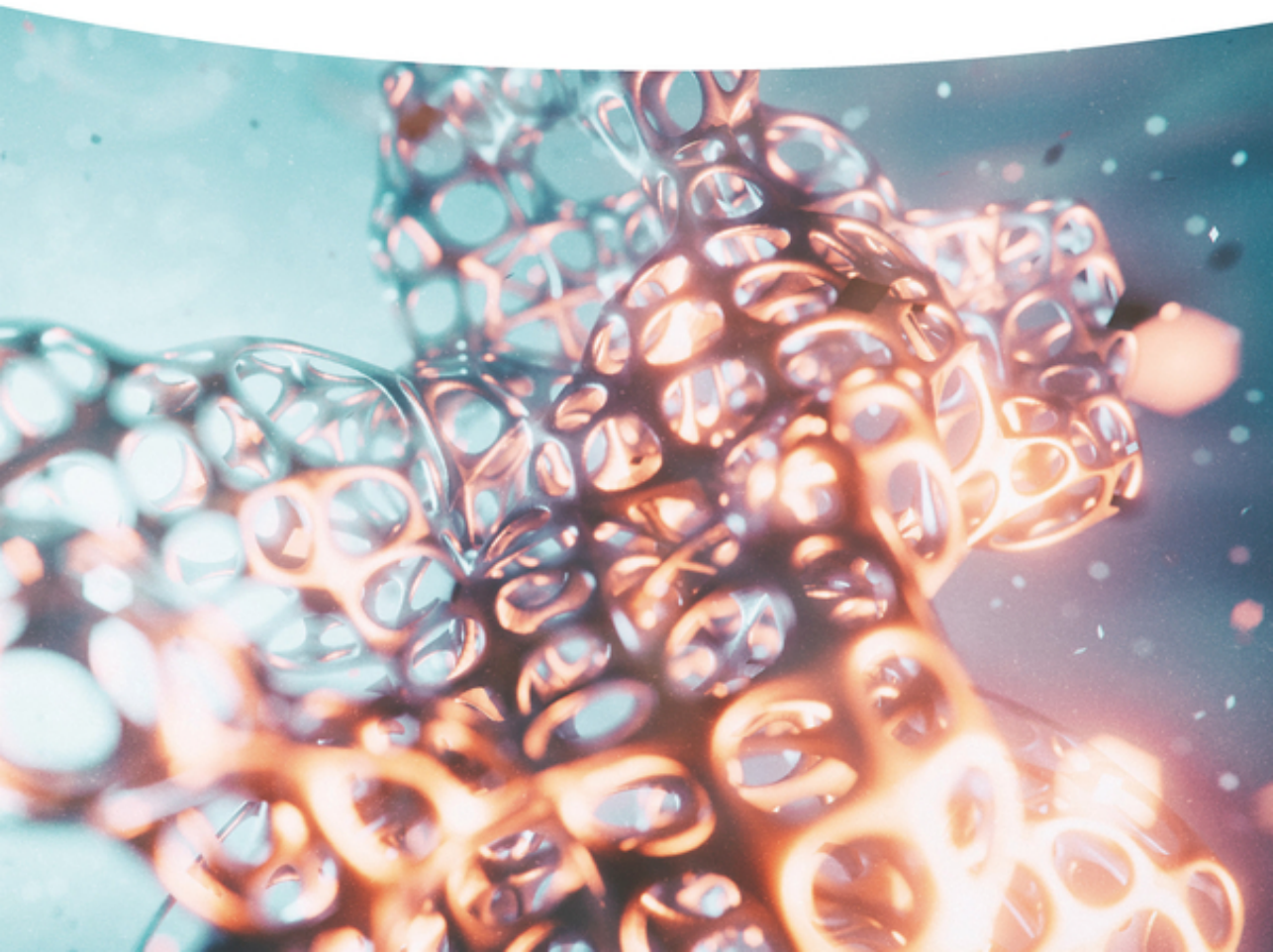


Edited by Rong Cao

Advanced Structural Chemistry

Tailoring Properties of Inorganic Materials
and their Applications



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Volume 1

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Volume 2

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Volume 3

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Editor

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Introduction

Jian Zhang, Guo-Cong Guo, Rong Cao, and Xin-Tao Wu

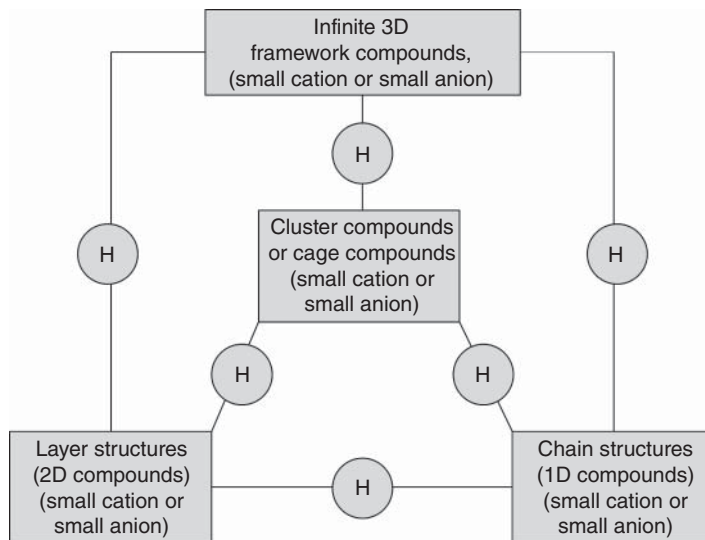
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The syntheses of new substances with specific functions are fundamental to the modern civilization, providing an inherent impetus for social, economic, scientific, and technological advancements. Worldwide governments and scientists are devoted to the discovery of new substances with specific functions and structures. The creation of new functional substances, which is the strategic highland for an innovative country, represents the core competency of this country. The creation of new substances belongs to major basic research. So far, there are still many important scientific issues unsolved at this stage, and we are far away from the key goal, that is, to develop the substances with desired properties. Structural chemistry fabricates this aim and leads the creation of new substances.

Structural chemistry is a discipline focusing on the bonding of atoms, molecules, and crystal packing as well as the correlations between the structure and the macroscopic chemical and physical properties. Therefore, structural chemistry serves as a source of the innovation of materials sciences. Although more than 23 million of substances have been synthesized or separated in the past century, only a small portion has found real-world applications. Currently, it remains a grand challenge for the scientific community to produce new substances with desired functions on a rational basis. One of the core tasks in the field of structural chemistry is to reveal the relationship between composition structure–function for creating new substances with expected properties through better molecular or structural design. In fact, the quantitative relationship between the structure and the property of a substance represents one of the challenges in chemistry in the twenty-first century. On the other hand, the synthetic processes must be economical, safe, resource-efficient, energy-saving, and environmentally benign. Chemists should strive for developing “perfect reaction chemistry,” i.e. synthesizing target compounds with a 100% yield and 100% selectivity without producing any waste. To create the new substances with desired functions, it is highly desirable to carry out function-directed structural design and structure-directed precise synthesis. That is the new developing direction of structural chemistry.

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The classification of the ionic-covalent compounds

According to the bonding characteristics and structural dimensions, chemical substances may be divided into four categories. The first category includes the molecules, cluster compounds, or cage compounds with discrete structures, and such compounds can be assembled into chain structures (one-dimension = 1D, the second category), layer structures (2D, the third category), and framework structures (3D, the fourth category) through ionic or covalent bonding modes.

One of the main bottlenecks lies in the inadequacy of the original designing, methods, and theories for the creation of new functional substances with different structures. Therefore, by strengthening the research on the structure- and function-guided creation of new substances, this situation could be drastically changed. However, two key issues should be considered in the area of structural chemistry: (i) how to accomplish the oriented synthesis for the specific structure of matter? (ii) How to design the matter's structure with specific function? In this book, we intend to reveal the relationship between the structure and function of matter and develop efficient and precise synthetic methodologies and theoretical tools for new functional substances.

This book is written by the experts engaged in structural chemistry research of Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences. It aims to reflect the recent research progress of structural chemistry in China and abroad. The book mainly includes two parts: synthesis and structure, and structure and property. It focuses on the structural design and properties of clusters, porous materials for gas sorption, separation and catalysis, and photoelectric or magnetic materials. This book clarifies the scientific connotation and subject development direction of structural chemistry.

In the first chapter, the metal–organic macrocycles containing regular/irregular polygons, including multilayered cyclic structures are discussed. In addition, helicates, tetrahedrons, triangular prisms, cubes, octahedrons, hendecahedrons, dodecahedrons, cuboctahedrons, hexadecahedrons, and barrel- and ball-shaped cages are reviewed. Discrete metal-organic metallasupramolecular structures have drawn increasing attention due to their special esthetic 2D or 3D structures and potential applications in molecular recognition, sensing, separation, and biomimetic catalysis. In general, metallasupramolecular structures can be defined as metallacycles and metallacages, while many borderline cases exist concerning the complexity of geometry of the ligands and shape of the internal cavity. To facilitate discussion, herein the metal centers are taken as vertices and the organic ligands as edges or faces in the polygons and polyhedra to define these metallasupramolecular structures as macrocycles and cages, respectively.

In Chapter 2, we summarize the development of synthetic strategies, analytical techniques, fundamental structure characteristics, and the typical applications of the metal-oxo clusters, which have been divided into three families of the transition metal-, main group metal-, and lanthanide-oxo clusters. The metal-oxo clusters with atomical precise structures are of importance in several disciplines relevant to synthetic chemistry, analytical chemistry, catalysis, biology, medicine, magnetism, and materials science. In the oxo clusters of transition metal part, structural fundamentals and novelties of the crystalline transition metal-oxo clusters, including Ti, V, Nb, Mo, Pd, W, and Ta, will be introduced. Besides, their tunable properties and potential applications related to the enormous structural diversities will also be briefly covered. In the oxo clusters of main group metal part, an overview on the main group borates, geminates, and aluminum elements will be presented. Both inorganic and organic ligand-supported oxo cluster structures will be introduced. Finally, in the oxo clusters of lanthanides part, we will present the recent advances in the high-nuclearity lanthanide clusters, which are classified by the protecting ligands including O-donor ligands, N-donor ligands, multiple N,O-donor ligands, calix[*n*]arenes, and other donor ligands such as Se- or C-donor ligands. Based upon these sufficient discussions, the dependence of the synthetic strategy of lanthanide-oxo clusters on the ligands, anions, and templating effects will also be summarized. We believe that these structurally well-defined metal-oxo clusters can provide models for decoding the mechanistic insight of the metal-based materials at the molecular level. In turn, the performance of these clusters could further feedback to the guidance of designing materials in a more controllable way.

Chapter 3 focuses on the synthetic and structural studies on the transition metal sulfide clusters, in particular, the heterometallic Mo–Fe–S and Mo(W)–Cu(Ag)–S clusters. Benefitting from the proposed structural models of FeMoco and inspired by the versatility of the unit construction concept, we synthesized a range of metal sulfide clusters exhibiting various structural types. Special attention has been paid to the designed synthesis of the molybdenum and tungsten heterometallic thioclusters with one or more cuboidal cluster units, as well as some novel mixed-metal sulfide coordination polymers. These results demonstrate how flexible the unit construction

method can be when it comes to making cluster compounds with desired structures based on the diverse coordination modes of the sulfur atom and the knowledge of structural chemistry. The ideas behind these syntheses are of significant value not only to the structural modeling of the biological catalytic active sites but also to the creation of novel molecular functional materials.

Chapter 4 summarizes the syntheses, crystal structures, and selected properties of a number of group 11–15 metal chalcogenides that are mainly obtained by Huang et al. Metal chalcogenides are a class of compounds characteristic of the covalent bonding between metal cations and chalcogen Q ($Q = \text{S, Se, Te}$) anions. Metal chalcogenides are important materials showing excellent properties in ion exchange, semiconductor optoelectronics/thermoelectric, nonlinear optics, photocatalysis, etc. Neutral amine molecules have been successfully incorporated into the group 12 metal chalcogenides, say II–VI semiconductors, forming a novel class of organic–inorganic hybrid nanostructures with a general formula of $[(MQ)_n(L)_x]$ ($MQ = \text{ZnS, ZnSe, ZnTe, CdS, CdSe, etc.}$; $L = \text{mono- or di- amines or hydrazine}$; $n = 1, 2$; $x = 0.5, 1, 2$). The hybrid materials exhibit strong quantum confinement effects and outstanding properties such as largely modified optic absorptions, white light emission, and nearly zero/negative thermal expansion. Some of the obtained chalcogenidometalates demonstrate superior ion-exchange properties of selectively capturing hazardous metal ions such as radioactive Cs^+ , Sr^{2+} , UO_2^{2+} , and Ln^{3+} ions from complex solutions.

In Chapter 5, various metal–organic frameworks (MOFs) are categorically highlighted on the basis of their dimensions, with a focus on the construction and structural analysis, which provides an introduction of recent achievements in MOFs not only for novices but also for experienced researchers. It is expected to guide the design and preparation of more novel and advanced functional MOF materials. MOFs possess the unique features over traditional inorganic or organic materials, including structural tunability, ultrahigh porosity, large surface areas, etc., which make them being widely applied in various areas such as storage and separation, energy transfer, catalysis, enzyme inhibitor, sensing, drug delivery, and so on. MOFs have received great attention in the last two decades, and in a short time, they have matured and grown to a huge system. According to the extended manner, the structures of MOFs can be described as one-, two-, or three-dimensional infinite networks.

In Chapter 6, we give a brief survey of recent advances in the rational assembly of polyoxometalate (POM)/chalcogenidometalate-based clusters and superlattices, polyhedral coordination supermolecules, and MOFs to show the knowledge on their synthesis mechanism and procedures. First, we present the synthetic and design approaches to the many POM types encompassing iso-POMs, hetero-POMs, organically derived POMs by alkylation or coordination, and POM–MOF hybrids. Next, we summarize the design and synthesis of crystallographically defined chalcogenidometalate clusters, including supertetrahedral series of Tn , Pn , Cn , Tm,n , and oxychalcogenide types, most of which are allowed to be fabricated by the mixed-metal and cationic-template strategies to deal with the local and the global charge issues. Then, we outline the recent developments of coordination-driven

self-assembly, with a focus on discrete architectures, viz metallacages of polyhedral shapes through well-defined directional-bonding assembly strategies (e.g. edge-directed, face-directed, and symmetry-adapted approaches) including diverse linking modes. Finally, we provide an overview of secondary building units (SBUs) mainly of metal carboxylates (classified by their geometry and the number of metal atoms), and the linkers bearing other binding groups, such as pyridyls, azoles, phenols, and their representative network examples, also highlight some synthetic strategies, including modulated synthesis, isorecticular expansion, topology-guided design, and multivariate chemistry.

In Chapter 7, we summarize the typical topological networks of MOFs with some prominent examples. Over the past decade, great progress of coordination polymers including MOFs has been made and tens of thousands of new compounds have been synthesized. Topological analysis supplies a convenient tool to understand and simplify a large number of complicated compounds at the early stage. With the development of new concept “reticular synthesis,” the design and synthesis MOFs have gradually tended to be practical and theoretical. The so-called “reticular synthesis” refers to the process of assembling well-designed rigid molecular building units into predetermined regular structures (or networks) through strong bonding. “Reticular synthesis” provides a reasonable way to synthesize solid materials with high stability, extended structure, predesigned molecular building units, and special properties. Two important aspects of “reticular synthesis” are the rational design of SBUs and framework topologies. Numerous MOFs constructed by various SBUs and organic ligands but with same underlying topological networks can be designed and synthesized. Therefore, topological analysis has become a powerful tool to design and predict new MOFs.

In Chapter 8, about 60 classical examples selected from the literature on a wide range of inorganic chalcogenide classes are presented, including centrosymmetric (CS) and non-centrosymmetric (NCS) crystal structures. These chalcogenides display a rich structure diversity based on the BBUs and can be divided into five classes according to the dimensional features: (i) the zero-dimensional (0D) discrete clusters; (ii) one-dimensional (1D) chains; (iii) two-dimensional (2D) layers; (iv) three-dimensional (3D) frameworks; and (v) mixed-dimensional (MD) structures. In this chapter, we focus on the unit cell, space group, and dimensional change as well as the structural assembly of selected chalcogenides. This work gives some exploring strategies for novel chalcogenides with diverse dimensions.

In Chapter 9, we wish to present advances in the past 10 years for three kinds of optical materials: electroluminescent materials, photochromic materials, and second-order nonlinear optical (NLO) materials. Optical materials refer to materials that may modify parameters of input light (such as phase, intensity, and frequency) or switch reciprocally optical and nonoptical signals (such as electric, heat, and sound). Electroluminescent materials are materials that can be excited to excited states and then return to ground state with the release of light. They have been widely applied to LEDs or OLEDs, which have brought revolution of both lighting and display fields. Photochromic materials are bistable materials that may be switched between two ground states with at least one direction being excited

by light. They have been used for glassware (such as sun glasses, automobile rearview mirror, building window, etc.) and chromic ink (for anti-fake, cloth decorating, etc.) in the market. Other applications, such as switching, memory, bioimaging, and radiation monitoring, have also been demonstrated in laboratory. Second-order NLO materials are usually crystals without inversion symmetry that are capable of generating a second harmonic. They play a significant role in the field of laser-related science and technology, such as semiconductor manufacturing, photolithography, optical storage, and high-capacity communication networks. This chapter emphasizes the description of relations between structures and electroluminescent properties for d^8/d^{10} heteronuclear metal complexes, photochromic properties for viologen compounds and their analogs, and second-order NLO properties for the KBBF, SBBO, AB_4O_6 , apatite-like borates, $ABCO_3$, $A_3VO(O_2)_2CO_3$, and $AX^{II}_4X^{III}_5Se_{12}$ families' derivatives.

Chapter 10 will discuss the relationship between the symmetry-breaking crystal structures and ferroelectric properties, and the recent advances of molecular ferroelectrics are also systematically summarized. As an important family of electroactive materials, ferroelectrics with the polar structures are characterized by spontaneous polarization, of which the direction can be reversibly switched under external electric field. Ferroelectrics demonstrate diverse physical attributes including piezoelectricity, pyroelectricity, NLO effect, mechanical functions, and dielectric properties, occupying an indispensable position in the field of condensed matter physics. All these fascinating properties and wide applications of ferroelectric materials are closely related to their unique structural characteristics. Essentially, spontaneous polarization of ferroelectrics can only exist below the Curie temperature point (T_c), coupling with the remarkable symmetry breaking during the paraelectric-to-ferroelectric transitions. Various physical properties for ferroelectric materials exhibit giant anomalies in the vicinity of T_c , stemming from their structural changes. Compared with traditional inorganic ferroelectrics, the counterpart of molecular ferroelectrics displays many distinct characteristics, such as light weight, easy processing, mechanical flexibility, tunable structure, biocompatibility, etc. Therefore, molecular ferroelectrics are currently becoming one of the research hotspots.

In Chapter 11, three series of inorganic, organic, and inorganic–organic hybrid conductive materials were selected from the literature. An overview of some representative fantastic advancement in terms of crystal growth methods, inorganic/organic crystalline conductors, and semiconductors is presented along with current challenges and future research directions provided finally. Crystalline conductive materials have been receiving increasing attention in recent years, not only for their unique physical properties and their potential applications in future electronics. They can be divided into inorganic conductive materials, organic conductive materials, and inorganic–organic hybrid conductive materials. Inorganic conductive materials are the earliest emerging conductive materials and now becoming one of the most crucial functional materials. Organic conductive material is an interdisciplinary research field concerning the design, synthesis,

characterization, and application of organic small molecules or polymers that show desirable electronic properties such as conductivity, semiconductivity, and even superconductivity. Organic–inorganic hybrid conductive material is a crystalline hybrid material composed of organic linker bridged metal ions or inorganic clusters. The deepened study of structure–property relationships is necessary to help guide the design and synthesis of novel functional conductive materials.

In Chapter 12, we will give a comprehensive overview of magnetostructural correlations that have been illustrated in the field of molecular magnets, in particular those reported by our institute. We will examine the environments of spin carriers, low-dimensional magnets, the magnetic exchanges between nearest-neighbor spin carriers, and the diversity of topologies of magnetic frameworks. The correlations between these structural features and the seemingly complex magnetic behaviors including spin crossover, magnetic slow relaxation, magnetic ordering, and spin frustration will be discussed.

In Chapter 13, we present a comprehensive and detailed introduction of gas uptake properties of MOFs. First, we provide the basic concepts of gas adsorption, such as physical adsorption, chemical adsorption, Langmuir monolayer adsorption, and BET multilayer adsorption, and expound the correlation between the type of adsorption isotherms and MOF structures. Second, we classify the pore sizes of MOFs into three kinds based on IUPAC definition and discuss the relationship between pore size and sorption isotherms. Third, we describe the defects in MOFs and their measuring technologies and further expatiate on the connection between defects and adsorption capacities. Fourth, we summarize some representative MOFs with high surface area and discuss four universal factors and their influence on the surface area of MOFs. Finally, we introduce the concept of adsorption enthalpy and elaborate three methods to calculate adsorption enthalpy based on the experiments. Besides, we distinguish the difference between adsorption amount and usable adsorption amount and discuss the factors influencing adsorption enthalpy of materials and the influence of adsorption enthalpy on adsorption capacities and work capacities in practical application. We expect this chapter can deliver significant guidance for researchers to design/discover novel MOFs with excellent properties of gas storage and separation and therefore expand their practical application.

In Chapter 14, we introduce the CO₂ capture and separation, separation of hydrocarbons, noble gases, hydrogen isotopes, and the enantioselective separation based on MOFs. Meanwhile, the relationship between structure and separation during these processes will be discussed in details.

In Chapter 15, we review and summarize the typical strategies and examples in MOF catalysis to give a brief but broad scope overview of the MOF catalysis area. We will first discuss catalysis with different active sites: (i) open metal nodes (SBUs) and modified SBUs for Lewis acid catalysis, oxidation reaction, Suzuki–Miyaura coupling reaction, and so on; (ii) linkers functionalized by Brønsted acids, unsaturated metal complexes, or organic bases; and (iii) pore-encapsulated guest species such as metal nanoparticles, POMs, metal complexes, and enzymes. Three major approaches are discussed next to show the unique advantage of MOFs compared

to traditional heterogeneous and homogeneous catalytic systems: heterogeneous asymmetric catalysis based on privileged ligands or chiral pore structure; cooperative or sequential catalysis that involves more than one active sites; and synergistic photocatalysis for CO₂ reduction, water splitting, and organic reactions.

This book is dedicated to the 60th anniversary of Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, and its founder director, Professor Jiaxi Lu, on the memory of his 105th birthday.

2

Coordination-Assembled Metal–Organic Macrocycles and Cages

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2.1 Introduction

Metal–organic supramolecular macrocycles and cages have attracted considerable attention due to the ease of preorganization self-assembly and unique physicochemical properties, such as host–guest chemistry, molecular recognition, etc. Similarly with the construction of highly complex supramolecular assemblies with biological importance using simple and identical subunit in nature, coordination-driven self-assembly provides a facile way for the construction of highly organized supramolecular architectures, assembling different components into predesigned assemblies with well-defined sizes and shapes. Since the early exploration of two-component complexes involving Pt– or Pd–pyridine interactions, transition metals, lanthanides, and massive donor units are subsequently adopted, generating multicomponent macrocycles and cages with diverse structures and functionalities. Herein, this chapter reviews the recent developments in metal–organic coordination macrocycles and cages, with a focus on the construction and functionalities. It is organized based on the configuration of the structures and key design principles, and their functionalizations will be discussed particularly.

2.2 Metallacycles

Metallacycles stand for one unique class of discrete two-dimensional (2D) structures, which can be constructed by using metal centers (such as Pt, Zn, Cu, Au, Ag, Pd, Ru, Rh, Ir, etc.) assembled with suitable ligands. Ever since the first report on the tetranuclear Bpy₄(enPd)₄ “molecular square” by the Fujita group in 1990, overwhelming examples of beautiful metallacycles have been documented in the

literature. Representative reports from Chinese researchers in the past two decades are summarized below.

2.2.1 Dinuclear Metallamacrocycles

In 2012, Yu and coworkers reported a bistable self-assembled M_2L_2 metal–organic macrocycle synthesized from Pd(II) with di(1*H*-naphtho[2,3-*d*]imidazol-1-yl)methane (L) (Figure 2.1) [1]. The macrocycle undergoes intramolecular conformational motion switched reversibly with anions by multiple hydrogen-bonding interactions. When employing nitrate precursor, two ligands adopt the *cis*-conformation and form a bowl-shaped structure which is locked by the nitrate anion through quadruple hydrogen bonds between the oxygen atom of the nitrate and the hydrogen atoms from the naphthanoimidazolium moieties. When the counter-anion is changed to tetraphenylborate, all ligands switch to the *trans*-conformation and a chair complex is obtained. Remarkably, two acetonitrile molecules are located along the central axis of the complex with C–H $\cdots \pi$ interactions. Interestingly, the platinum analog of this complex retains a fixed bowl-shaped conformation, and no conformation change is observed regardless of the anions owing to the inert Pt–N bonds.

2.2.2 Triangles

In 2018, Huang's group constructed supramolecular triangles with excellent luminescent properties by using bodipy-based bridging ligands assembled with Pt(II) (Figure 2.2) [2]. These triangles exhibit outstanding anticancer activity due to the presence of the vertical Pt(II) ions. Simultaneously, its transportation into cancer cells can be visualized because of the fluorescence property of bodipy cores. This study demonstrates that the formation of triangles can improve their anticancer efficacy compared to their metal precursors.

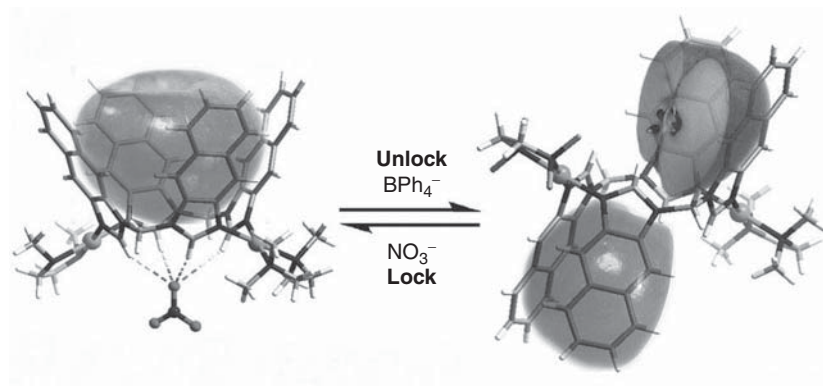


Figure 2.1 Fine-tuning conformational motion of a self-assembled metal–organic macrocycle by multiple C–H $\cdots$ anion hydrogen bonds. *Source:* Reproduced with permission Xie et al. [1]. © 2012, Wiley-VCH.

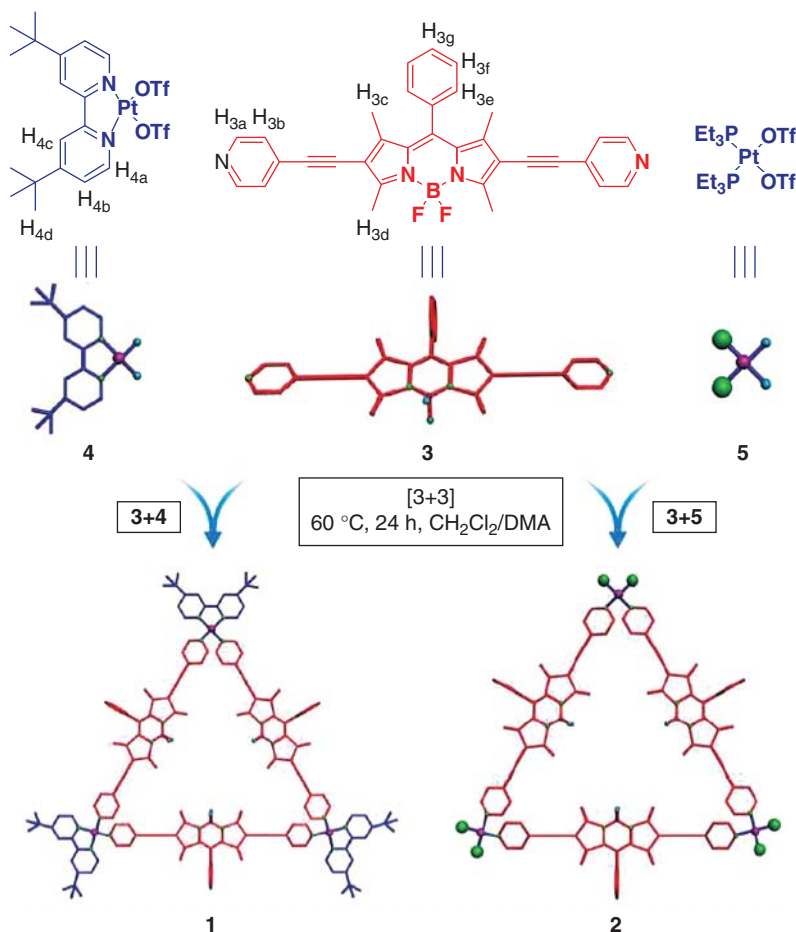


Figure 2.2 Supramolecular triangles for cancer cells transportation. *Source:* Zhou et al. [2]. © 2018, American Chemical Society.

In 2015, Chan's group reported a series of triangular metallacycles using three unsymmetrical bisterpyridine ligands with different lateral lengths assembled with Zn²⁺ [3]. The self-assembly processes are strongly geometry dependent. A ligand with the largest geometrical difference between two coordinating moieties has higher degree of cross-ligand self-selection compared with the complexation reaction of other ligands, giving the single head-to-tail (HT) triangular species. The isomeric mixtures are characterized and readily differentiated by gradient MS/MS coupled with TWIM-MS in the gas phase. HT isomers are found to be more stable than the head-to-head (HH) isomers, which are confirmed by DTD shift toward a longer drift time with increasing trap voltage and their corresponding CCSs agree reasonably with the computational values. Li and coworkers prepared a triangular Cu₃ and its extended framework [Cu₃]_n by using pyrazole-based ligands [4]. Two luminescent coordination compounds, [Cu(Pz)]₃ and [Cu₂(Bpz)]_n, were isolated

from solvothermal reactions of $\text{Cu}(\text{NO}_3)_2$ with 3,5-dimethylpyrazole (HPz) and 3,3',5,5'-tetramethyl-4,4'-bipyrazole (H_2Bpz), respectively, in the presence of NH_3 .

2.2.3 Rectangle

In 2019, Han's group demonstrated that new supramolecular metallacycles were capable of undergoing photochemical reactions in solution utilizing metal-carbene as templates [5]. These new rectangular metallacycles are generated by employing dinuclear metal-carbene organometallic clips and olefin-functionalized bridging ligands through coordination-driven self-assembly. Photolysis of these molecular metallacycles in situ leads to structural interconversion and release of the cyclobutane products quantitatively (Figure 2.3). This supramolecular-assisted synthetic methodology enables the preparation of new types of functionalized cyclobutanes.

Jin's group had also a long-standing interest in the self-assembly of two preorganized binuclear half-sandwich metal (Rh or Ir) molecular clips and pyridyl ligands. They reported two molecular organometallic box (**3a**, **3b**) compounds by applying 6,11-dihydroxy-5,12-naphthacenedione (H_2dhnq) and pyrazine spacing ligands assembled with half-sandwich iridium/rhodium (Figure 2.4) [6]. Tetranuclear complexes $[\text{Cp}^* \text{M}_4(m\text{-pyrazine})_2(m\text{-L})_2](\text{OTf})_4$ ($\text{M} = \text{Ir}$ (**3a**), Rh (**3b**); $\text{L} = \text{dhnq2}$) were obtained in high yields from **1a** or **1b** by reacting with pyrazine in the presence of AgOTf ($\text{Tf} = \text{O}_2\text{SCF}_3$), respectively. The highly symmetrical structure of this rectangle, composed of four Ir/Rh clusters as the four vertices and two pyridines and two dhnq2 as edges, was confirmed by NMR spectroscopy and

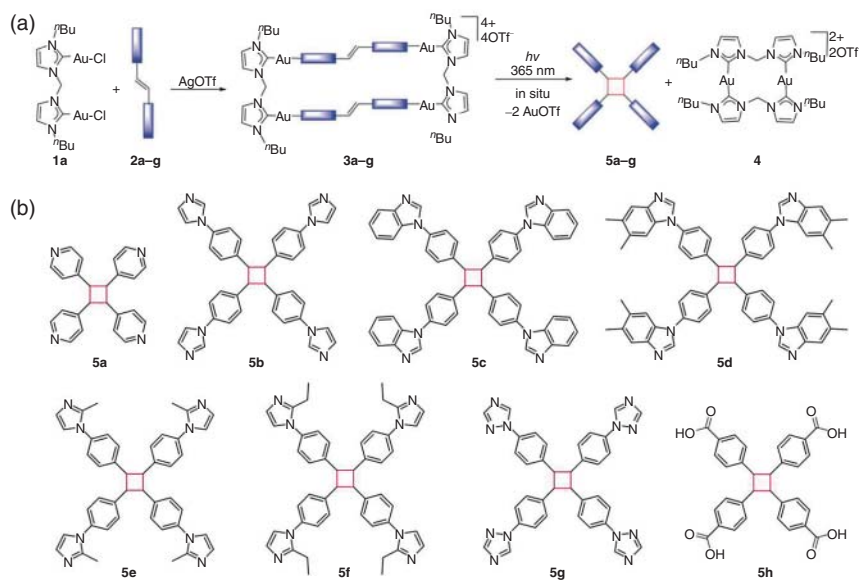


Figure 2.3 (a) Coordination-driven self-assembly of organometallic metallacycles **3a–g** and their photolytic transformation to afford cyclobutane derivatives **5a–g**. (b) The structures of cyclobutane derivatives **5a–h**. Source: Ma et al. [5]. © 2019, Wiley-VCH.

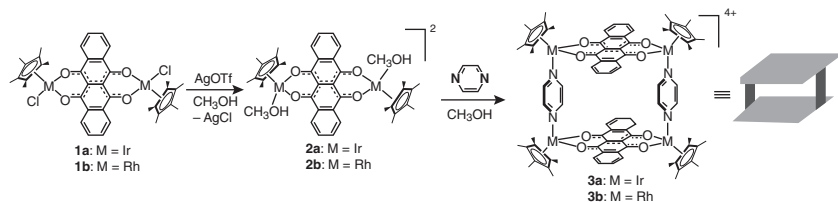
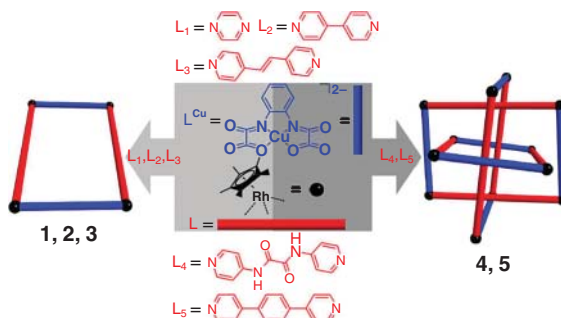


Figure 2.4 Stepwise formation of **3a** and **3b**. Source: Han et al. [6]. © 2009, Wiley-VCH.

Figure 2.5 Size-dependent formation of Borromean link structures. Source: Huang et al. [7]. © 2013, American Chemical Society.



single-crystal structure analyses. More interestingly, organometallic molecules display face-to-face π - π interactions between the planes of adjacent dhmq2 ligands, generating one-dimensional (1D) coordination frameworks, and the Cl₂C=CCl₂ guests are shown to drive the transformation of the 1D assemblies to a 2D framework through CH $\cdots$ Cl interactions. The 1D rows are perfectly aligned to form the 2D framework, in which the face-to-face π - π interactions between the planes of the monomeric complexes are remained.

Because of the openness of coordinated metal centers, aromatic D-A- π interactions, guest-induced interactions, etc., the metallacycles can form Borromean rings (BRs) through adjusting their arm length (Figure 2.5) [7]. Arising from the combination of open Cu centers and favorable cavity space, [(Cp^{*}Rh)₄(bpe)₂][Cu(opba)·2MeOH]₂·4(OTf)·6MeOH shows extraordinary catalytic abilities with high efficiency and wide substrate selectivity in the acyl-transfer reaction.

When longer linear pyridine ligand (**L2**) was used to react with dirhodium precursor **1a**, a tetranuclear metallarectangle **5a** was achieved, as confirmed by NMR, ESI-MS, and single-crystal X-ray crystallographic analyses (Figure 2.6) [8]. However, when diiridium precursor **2a** and **L2** used to build the metallarectangles, quantitative self-assembly of molecular rectangle **6a** was noticed. Similarly, interlocked BRs (**6a**-BRs) complexes were produced when halogenated diiridium precursors **2b**, **3**, **4** were used. Halogen atoms are proposed to play an important role in forming BRs structure. It is worth to note that formation of BRs is concentration-dependent, and reversible conversion of the two structures has been achieved by adjusting the solvent conditions. By using an elongated Cp^{*}Rh-based dynamic conformational binuclear building block, a class of tetranuclear rectangles with multiple aromatic stacks was achieved by a guest-induced constitutional rearrangement [9].

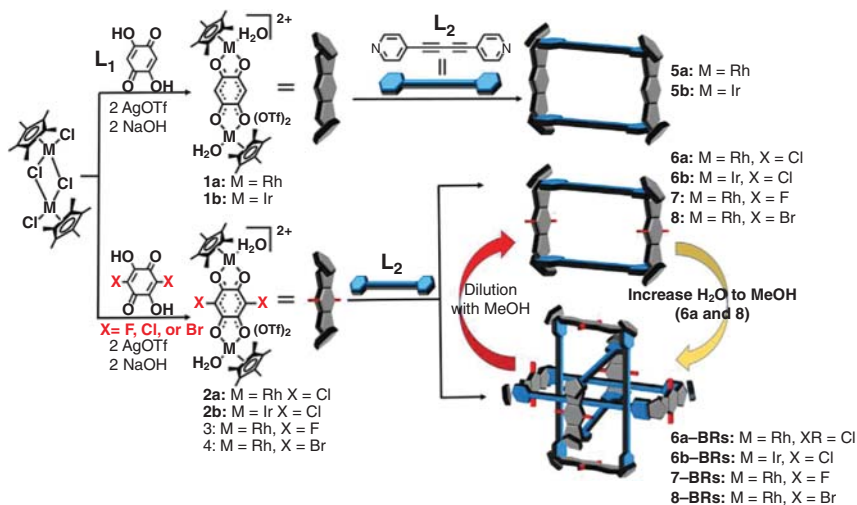


Figure 2.6 Synthesis of interconvertible metallarectangles and Borromean rings based on different dinuclear precursors. Source: Lu et al. [8]. © 2017, Cell Press.

Owing to the often-similar physical and chemical properties of structural isomers of organic molecules, facile separation of regioisomeric compounds remains difficult. An organometallic capsule was synthesized based on binuclear half-sandwich metal (Rh or Ir) molecular clips, in which two silver centers are rigidly separated from each other by two tetranuclear $[Rh_4]$ pyramidal frustums. Due to the shape and size matching, the heterometallic capsule could wrap a series of aromatic compounds [10]. This research provides an important solution for the separation of aromatic isomer molecules in industry.

Air- and moisture-stable coordinatively unsaturated organometallic complexes were synthesized based on $Cp-M-S$ fragments [11]. A series of 16-electron M_2L_2 -type metallacycles were more inclined to bind with small ligands such as $MeCN$, Cl^- , CO , pyridine, and so on (Figure 2.7). The coordination geometry around the metal center displays a two-legged piano stool, and the $S-M-S$ bond angle is approximately 90° . More interestingly, $[(Cp^*M)_2(\mu-L)_2](OTf)_4$ can reversibly convert into $[(Cp^*M)_2(\mu-L)_3](OTf)_4$, along with $[(Cp^*M)_2H_3](OTf)_4$ and $[(Cp^*M)_2(\mu-L)_3](OTf)_4$ becoming 18-electron M_2L_3 -typed cylinders. The authors propose a mechanism that once hydride iridium species are formed, the released free ligands can coordinate to coordinatively unsaturated metal centers, rapidly leading to 18-electron M_2L_3 -typed complexes.

2.2.4 Hexagons

Chiral NH functionalities play a key role in controlling the homochirality in nature's chemical armory, such as the fabrication of DNA, RNA, and enzymes. In 2017, Cui and coworkers reported the design and synthesis of a series of chiral NH-functionalized cyclic structures through introducing partially reduced analogs of zinc-salen complexes as building blocks (Figure 2.8) [12]. In the asymmetric unit,

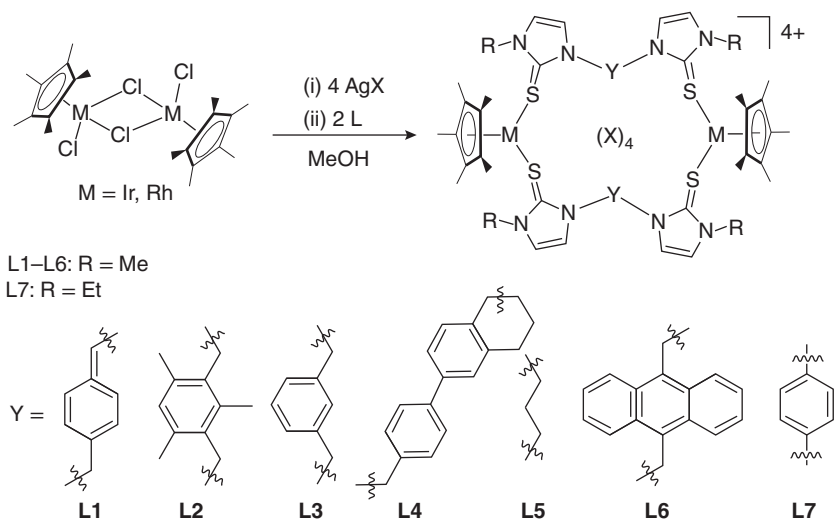


Figure 2.7 Synthesis of coordinatively unsaturated 16-electron organometallic metallacycles. *Source:* Han et al. [11]. © 2014, American Chemical Society.

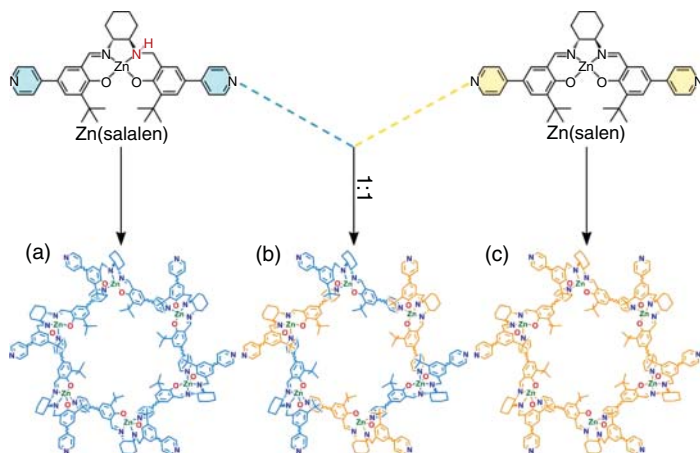


Figure 2.8 Self-assembly of chiral NH-controlled supramolecular metallacycles **(R)-1** (a) from Zn(salalen) and **(R)-3** (c) from Zn(salen). **(R)-2** (b) was achieved by Zn(salalen) and Zn(salen) with 1 : 1 ratio. *Source:* Dong et al. [12]. © 2017, American Chemical Society.

the Zn ions adopt a distorted square pyramidal geometry coordination environment and adjacent Zn ions are bridged by peripheral pyridyl groups, resulting in a hexameric metallacyclic complex. Moreover, the metallacycles are packed through multiple supramolecular interactions and form an interlocking structure via strong hydrophobic interactions between cyclohexyl groups.

Some functional metallacycles were reported by Huang's group. As shown in Figure 2.9, model **2a** solution exhibits clear-to-opaque transformation above 80 °C and model **2** shows no lower critical solution temperature (LCST) behavior. A thermosensitive amphiphilic hexagonal metallacycle (**1**) with good LCST behavior

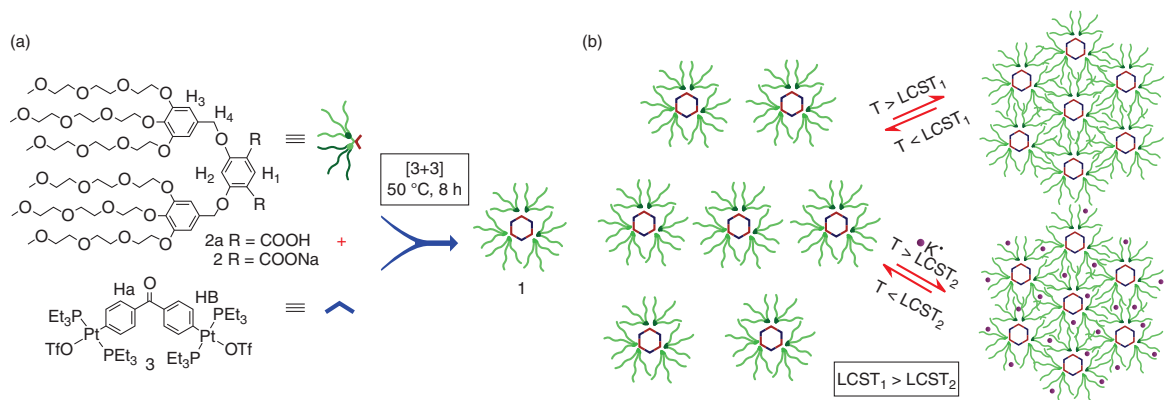


Figure 2.9 (a) Self-assembly of **2** and **3** to give an amphiphilic discrete organoplatinum(II) metallacycle. (b) Cartoon illustration of its thermosensitivity and potassium cation responsiveness. *Source:* Wei et al. [13]. © 2014, American Chemical Society.

is fabricated by introducing hydrophilic and thermal-responsive tri(ethylene glycol) (Tg) around the hydrophobic core and then self-assembling in D_2O /acetone- d_6 mixed solution. Tg chains of **1** that form H-bonding interactions with solvent molecules below clouding point (T_{cloud}) become nonpolar and intermolecular H-bonding interactions above T_{cloud} , which is an extremely important reason why **1** solution exhibits LCST behavior. Moreover, the LCST of **1** solution degrades with the increase of the concentration and the addition of K^+ . The K^+ could bind to the Tg chains, which disrupts the H-bonding interactions between Tg chains and water molecule and thus decreases T_{cloud} . Opaque **1** solution is clear upon cooling below T_{cloud} , which shows the excellent thermal reversibility of metallacycle solution [13].

Tetraphenylethylene (TPE) has excellent aggregation-induced emission (AIE) property and is a good building block for the construction of functional metallacycles. Multiple TPE units were used to construct rhomboid metallacycle **7** or different sized hexagons **8–11** based on coordination-driven self-assembly between 60° (**2**), 120° (**3**, **4**), and 180° (**5**, **6**) organoplatinum(II) acceptors with 120° TPE-based dipyrpyridyl ligand (Figure 2.10a) [14]. Figure 2.10b,c shows that TPE-based 2D hexagonal metallacycles and three-dimensional (3D) drumlike metallacages with three different counter-anions are prepared by coordination-driven self-assembly, respectively [15]. Compared with TPE molecule, these multi-TPE metallacycles and metallacages display novel AIE property and higher quantum yields, due to the rotatable external pendant phenyl rings on the metallacycles and the locked TPE-based ligands, respectively, which are beneficial to eliminate the nonradiative decay pathways. Moreover, these metallacycles can be used as sensors due to the optical changes when interacting with electron-deficient substrates, such as picric acid.

In 2012, a series of light-responsive multi-bisthiénylene (BTE) hexagons were reported by Yang's group, with precise control over the structural shapes, sizes,

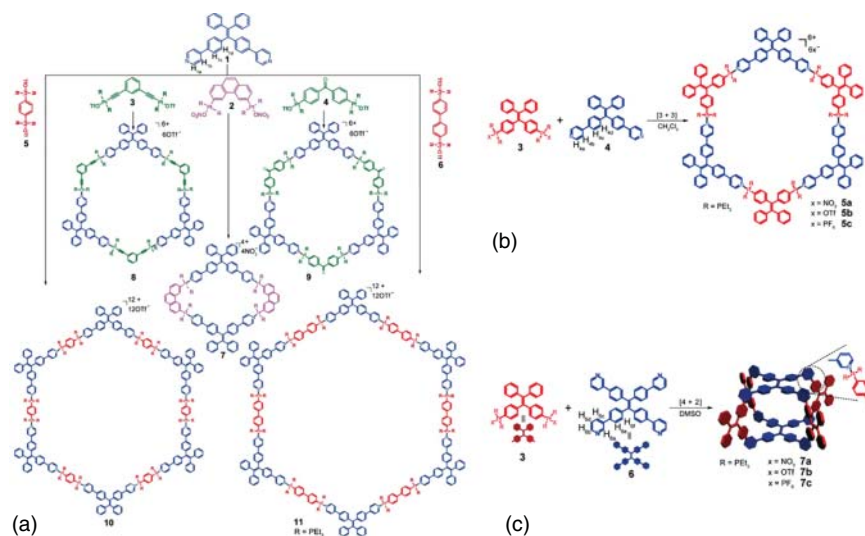


Figure 2.10 (a) Self-assembly of **1** with **2–6** to give rhomboid **7** and hexagons **8–11**. (b) Self-assembly of **3** with **4** to give **5**. (c) Self-assembly of **3** with **6** to give **7**. Source: Yan et al. [14, 15]. © 2015, 2016, American Chemical Society.

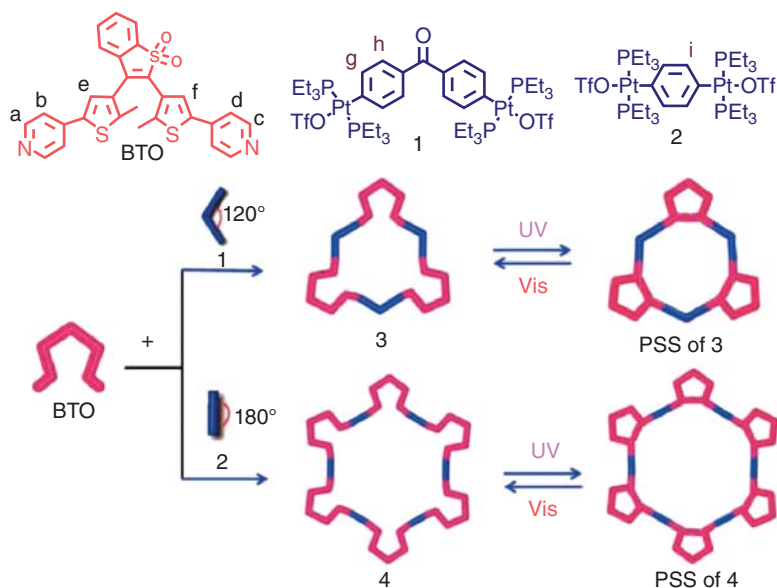


Figure 2.11 Graphical representation of self-assembled multi-bisthiénylene hexagons and their structural transformations. *Source:* Chen et al. [16]. © 2012, American Chemical Society.

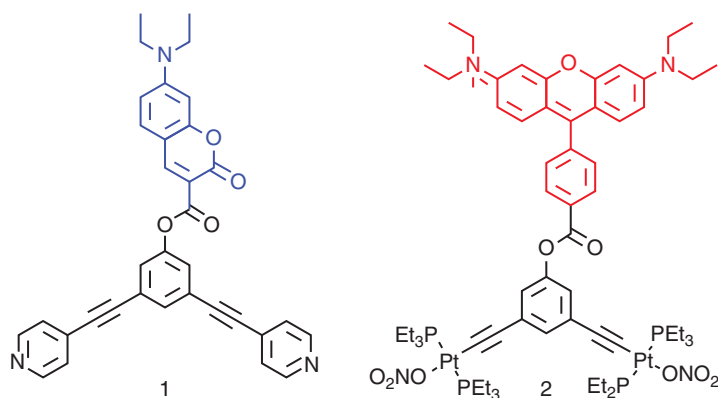
and the number of photochromic units [16]. The 120° BTE-based donor and 120° or 180° diplatinum (II) acceptors are used as building blocks, generating [3+3] hexagon **3** and [6+6] hexagon **4**, containing different numbers of photochromic units (Figure 2.11). These multi-BTE hexagons are highly sensitive and responsive to photo-stimuli as a result of the photoinduced switchable property and good fatigue resistance of the photochromic BTE system. Quantitative reversible conversions from the ring-open forms (**3**, **4**) to the ring-closed forms (PSS of **3**, **4**) have been realized by alternating UV (365 nm) and visible-light (>510 nm) irradiation in degassed CH₂Cl₂, with higher conversion yields (99%) than that of the free photochromic BTE units (88%) due to the coordination-induced preference for the antiparallel configuration of the BTE moieties in metallacycle structures.

The 2D or 3D metal–organic assemblies provide excellent scaffold for the construction of functional materials attributing to the enhanced intermolecular interactions. Reaction of alkynylplatinum(II)-containing donor ligand with diplatinum(II) acceptor yielded a vapochromic metallacycle, which exhibits highly selective color change toward CH₂Cl₂ vapor [17]. Upon exposure to CH₂Cl₂ vapor, the color of the metallacycle changes from yellow to red and retains in air for several months at room temperature, which is quite different from the behaviors of many known vapochromic materials. The chair conformation of the metallacycle in the solid state is crucial to its vapochromic behavior. It favors the close molecular stacking through intermolecular Pt...Pt and π – π stacking interactions triggered by CH₂Cl₂ vapor molecules. The stacking mode affects the Pt...Pt distance and the HOMO-LUMO energy gap of the supramolecule and further results in the vapochromic phenomena. Moreover, mechanically grinding provides sufficient energy to disrupt the close molecular stacking, enabling a reversible color change.

In 2014, they further designed three different kinds of peripherally functionalized 120° dendritic donor ligands to construct a series of metallodendrimers featuring a well-defined hexagonal metallacycle at the cores through coordination-driven self-assembly with 120° diplatinum (II) acceptor [18]. The multiple intermolecular interactions (e.g. π - π stacking, CH- π interactions, and hydrogen bonds) imposed by the peripherally DMIP-functionalized poly(benzyl ether) dendrons in hexagonal metallodendrimers facilitate the further formation of monodisperse vesicle-like nanostructures. Based on the dynamic nature of metal-ligand bonds, disassembly and reassembly of the hexagonal core are observed by the addition and removal of bromide anions. Therefore, well-controlled encapsulation and release of fluorescent dye have been successfully realized, which may be used as smart nanocapsules for guest capsulation and controlled release.

Based on the high sensitivity and efficiency of fluorescence-resonance energy transfer (FRET) technique, 7-(diethylamino)-coumarin (donor)-decorated dipyrindyl ligand **1** and rhodamine (acceptor)-functionalized diplatinum (II) unit **2** were employed to construct supramolecular metallacycles for real-time monitoring of the process and dynamics of coordination-driven self-assembly (Figure 2.12) [19].

(a)



(b)

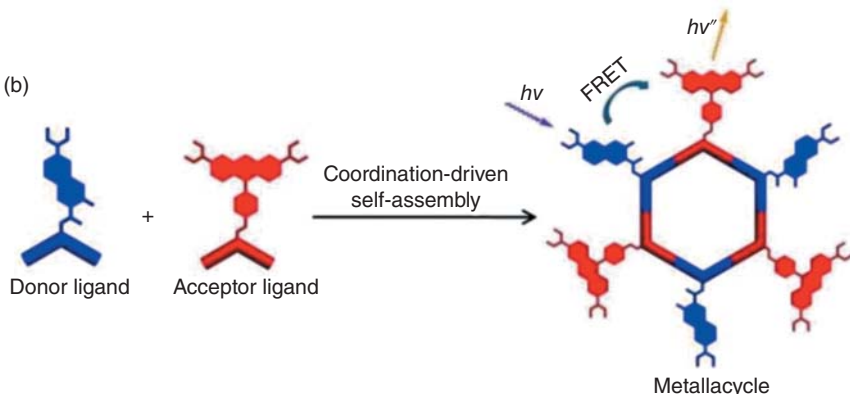


Figure 2.12 (a) Structure of building blocks **1** and **2**. (b) Cartoon presentation of coordination-driven self-assembly of the donor ligand and the acceptor ligand. Source: Huang et al. [19]. © 2017, American Chemical Society.

Shorter distance between the coumarin and rhodamine moieties facilitates the FRET process, which further results in higher Forster energy transfer efficiency (Φ_{ET}) in the system. The FRET phenomenon allows for further investigation of solvent effects in the self-assembly process, the dynamic ligand exchange between metallasupramolecular architectures, the anion-induced disassembly and reassembly of metallacycles, and the stability of metallasupramolecular structures in different solvents. FRET is capable of providing much more information about the process and dynamics of the supramolecular metallacycles and is quite helpful for the understanding of the coordination-driven self-assembly process.

2.2.5 Irregular Metallacycles

Duan's group combined biomimetic hydrogenation with in situ regeneration of the active site in a one-pot transformation using light as a clean energy source for enzyme-like catalysis [20]. By modulating the active site of a nicotinamide adenine dinucleotide (NADH) model, this redox-active molecular flask facilitates the encapsulation of benzoxazinones for biomimetic hydrogenation within the inner space of the flask. The redox-active metal centers provide an active hydrogen source by light-driven proton reduction outside the pocket and further allow the in situ regeneration of the NADH models under irradiation, exhibiting high efficiency in the light-driven hydrogenation of benzoxazinones and quinoxalinones (Figure 2.13).

In 2005, Yu et al. reported a luminescent supramolecular chiral Au_{16} ring that self-assembled from a tetrameric array of achiral $\{[(\text{dppm})\text{Au}_2]_2(\text{pipzdtc})\}$ (**1**; dppm = bis(diphenylphosphino)-methane, pipzdtc = piperazine-1,4-dicarbodithiolate) subunits based on $\text{Au(I)}\dots\text{Au(I)}$ interactions [21]. Each monomer **1** is linked by a bridging pipzdtc^{2-} ligand with an average intramolecular $\text{Au(I)}\dots\text{Au(I)}$ separation of 2.90 Å. Alternatively, the tetramer **1**₄ can be viewed as made up of two halves, namely, a dimer-to-dimer coupling. The two monomers, $[(\text{dppm})\text{Au(15)}\text{Au(16)}\text{-pipzdtc-Au(3)}\text{Au(4)}(\text{dppm})]$ and $[(\text{dppm})\text{Au(1)}\text{Au(2)}\text{-pipzdtc-Au(5)}\text{Au(6)}(\text{dppm})]$, spanned each other in space and are linked together by three intermolecular $\text{Au(I)}\dots\text{Au(I)}$ interactions ($\text{Au(16)}\dots\text{Au(1)}$, $\text{Au(2)}\dots\text{Au(3)}$, and $\text{Au(4)}\dots\text{Au(5)}$), affording a chiral dimer, although the monomer itself is achiral. Similarly, the other two monomers formed another dimer. The two dimers with the same chirality were further coupled by two intermolecular $\text{Au(I)}\dots\text{Au(I)}$ interactions ($\text{Au(6)}\dots\text{Au(7)}$ and $\text{Au(14)}\dots\text{Au(15)}$) to form a closed chiral macrocycle with a framework of 16 Au(I) centers, directly linked via short $\text{Au}\dots\text{Au}$ contacts, with a perimeter of up to 4.822 nm. The average intermolecular $\text{Au(I)}\dots\text{Au(I)}$ separation in the ring is 3.12 Å, about 0.22 Å longer than the intramolecular ones. Both are significantly shorter than the sum of van der Waals radii for gold (3.32 Å), showing that $\text{Au(I)}\dots\text{Au(I)}$ interactions exist in the molecule. On the basis of UV-vis and crystal structure studies, Yu speculated that upon an increase in the concentration, two monomers **1** which exist mainly in dilute solutions pair up to adopt a “cross-shaped” structure and result in chirality under driving of the intermolecular

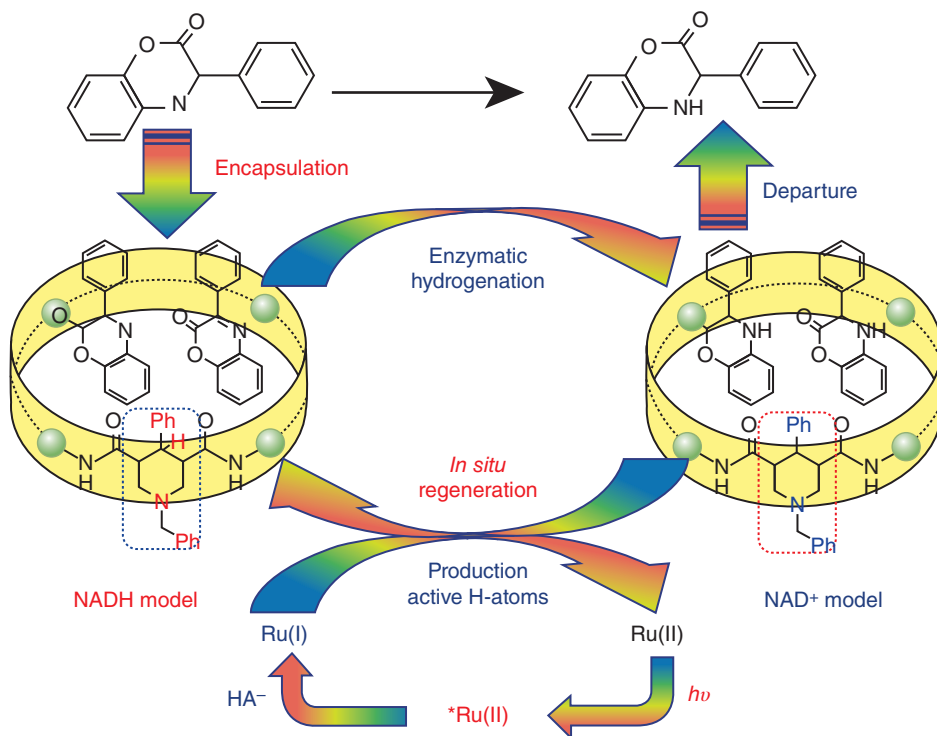


Figure 2.13 Schematic of the redox-active macrocycle with NADH mimics. Source: Zhao et al. [20]. © 2017, John Wiley & Sons.

aurophilic interactions. Then two dimers with the same handedness aggregate further with better packing to afford the chiral tetramer, probably induced and facilitated by the presence of Au(I)⋯Au(I) interactions. This unusual aggregate also provided a nice example of homochiral and aurophilicity-directed self-assembly.

A crown-like Au₃₆ ring was further developed through a spontaneous hierarchical hetero-chiral self-assembly as directed by strong Au^I⋯Au^I bonding interactions from achiral components (Figure 2.14) [22]. In a first step, three bidentate dithiocarbamate units coordinate to six Au^I centers in a HT cyclic manner to form a three-bladed propeller-shaped monomer **1** with *D*₃ symmetry in dilute solution. **1** is equimolarly formed in the form of Δ or Λ. These six Au^I centers are coplanar and form two homocentric parallel equilateral gold triangles with outer sides averaging 7.84 Å and inner sides averaging 3.05 Å. Upon increasing the concentration, three alternating Δ-Au₆ and Λ-Au₆ units then crystallize into a racemic cyclic hexamer to afford a giant crown of Au₃₆ with a diameter of 2.25 nm and a perimeter of 6.88 nm, analogous to Pedersen's [18]crown-6, with three monomers above and three below the mean plane of the gold atoms in the driving of strong intermonomer Au^I⋯Au^I bonding interactions (average: 2.890 Å).

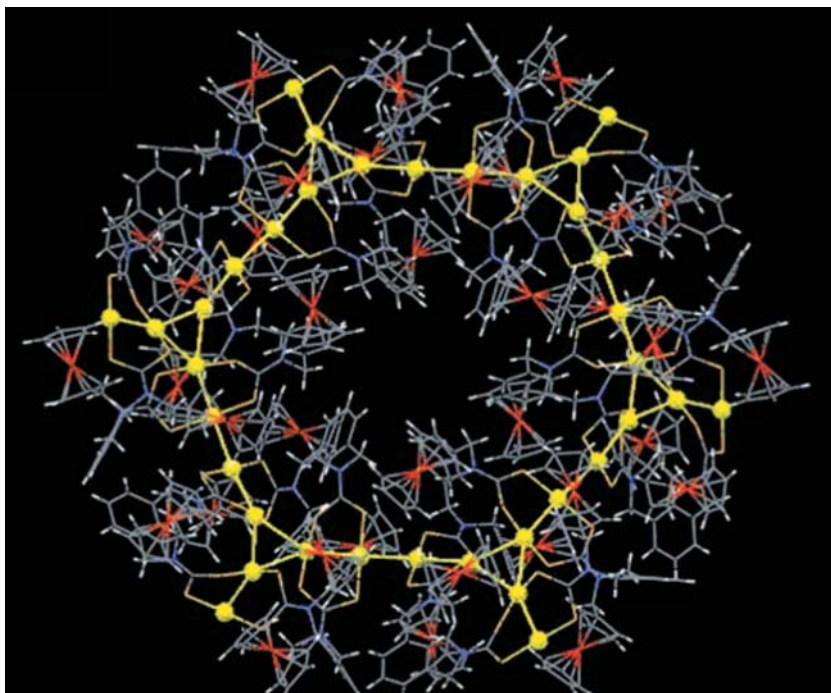


Figure 2.14 Au_{36} crown: a macrocyclization directed by metal–metal bonding. *Source:* Yu et al. [22]. © 2008, John Wiley & Sons.

2.2.6 Multilayered Metallacycles

A series of metallasupramolecular multilayered rings derived from multivalent 2,2':6',2''-terpyridine (tpy) ligands were reported by Chan's group and allowed the fundamental understanding of self-assembly behavior of sophisticated and functional supramolecular architectures (Figure 2.15) [23]. The flexible linker was found to be the key factor for controlling the architecture and stability of resulted assemblies. As a result of the geometrical constraint caused by the short C4 linker, complexation of $\mathbf{L}^1$ with Cd^{II} ions gave the complex $[\text{Cd}_6\mathbf{L}^1_2]$ with a dimer inner ring. No expected $[\text{Cd}_9\mathbf{L}^1_3]$ was formed (Figure 2.15a). With the C6 and C8 linkers, ligands $\mathbf{L}^2$ and $\mathbf{L}^3$ afforded the desired ring-in-ring structures $[\text{Cd}_9\mathbf{L}^2_3]$ and $[\text{Cd}_9\mathbf{L}^3_3]$ (Figure 2.15b), respectively. However, the self-assembly composition derived from $\mathbf{L}^2$ with Cd^{II} was found to be concentration- and temperature-dependent, and the proportion of $[\text{Cd}_{12}\mathbf{L}^2_4]$ was observed to increase with either increasing concentration or decreasing temperature. When extending the scaffold of $\mathbf{L}^3$ horizontally along the linker axis, the multivalent ligand $\mathbf{L}^5$ was synthesized and achieved a spiderweb structure unambiguously when treated with Cd^{II} ions (Figure 2.15c).

Self-selective ligation provides an efficient strategy for the preparation of more elaborate and diverse self-assembled structures. A pair of complementary tpy-based ligands selectively complexate with Cd^{II} ions into enlarged triangle and bilayered ditrigon structures (Figure 2.16) [24]. The auxiliary ion–dipole interactions between

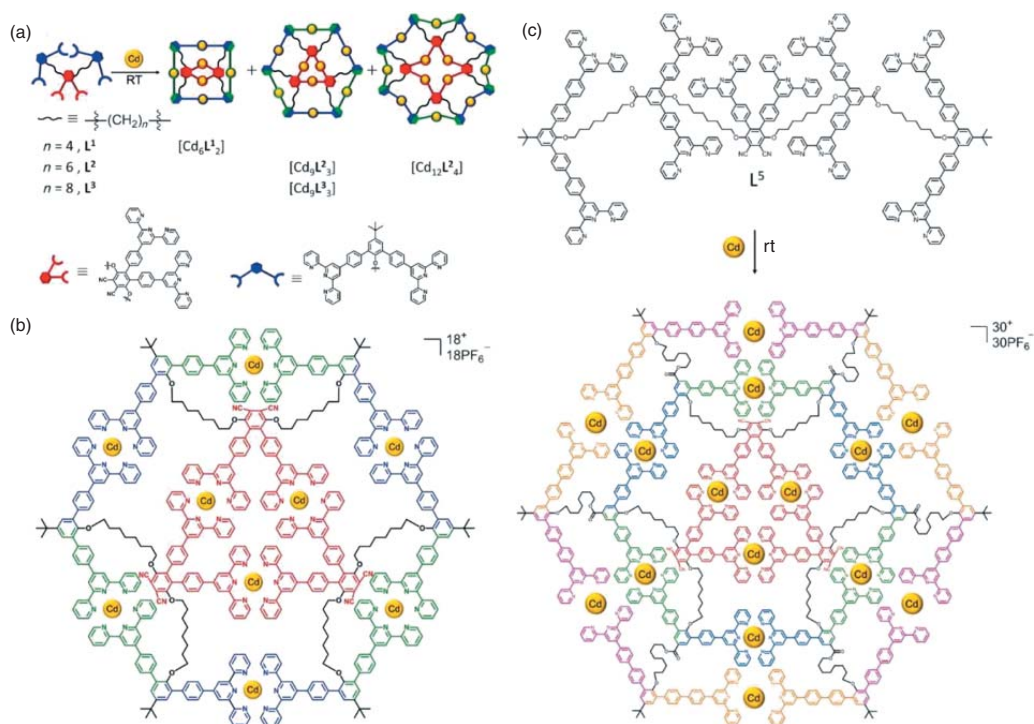


Figure 2.15 (a) Self-assembly of ring-in-ring structures from L^1 , L^2 , and L^3 . (b) The molecular structure of $[Cd_9L^3_3]$. (c) Self-assembly of spiderweb $[Cd_{15}L^3_3]$. Source: Fu et al. [23]. © 2015, John Wiley & Sons.

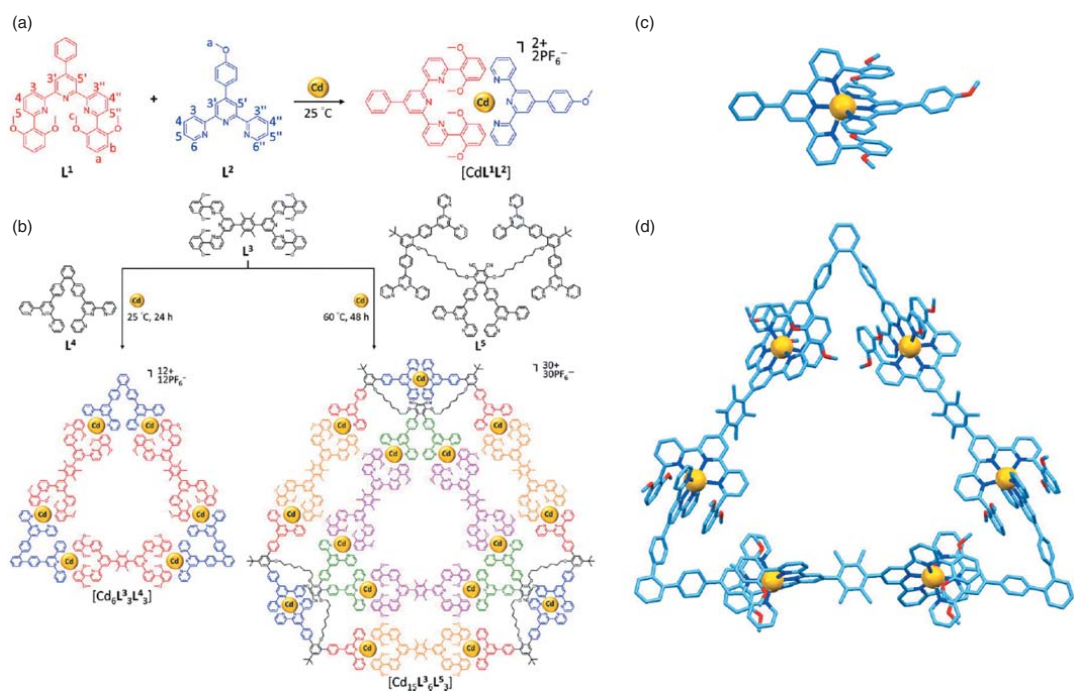


Figure 2.16 (a) Self-selective coordination of **L**¹ and **L**² with Cd^{II} ions and (b) the crystal structure of **[CdL¹L²]**. (c) Self-assembly of Ttriangle **[Cd₆L³₃L⁴₃]**, ditrigrion **[Cd₁₅L³₆L⁵₃]**, and (d) crystal structure of **[Cd₆L³₃L⁴₃]**. Source: Wang et al. [24]. © 2016, American Chemical Society.

the methoxy groups and the Cd^{II} center make **L**¹ serve as a pseudo-pentadentate ligand to facilitate the heteroleptic complexation. The X-ray crystallographic analysis displays that two dimethoxyphenyl substituents and the central pyridine unit of **L**² are parallel to each other with an average π - π stacking distance of 3.6 Å, and this donor-acceptor-donor stacking provides the additional thermodynamic stabilization for the heteroleptic structure (Figure 2.16b). The reaction of ditopic ligands **L**³ and **L**⁴ with two molar equivalents of Cd^{II} yields a multicomponent trigonal structure (Figure 2.16c). The crystal structure shows that each pseudo-octahedral Cd^{II} center is coordinated by two respective tpy units from **L**³ and **L**⁴, resulting in an alternating ligand arrangement in the metallomacrocyclic (Figure 2.16d). A more sophisticated ditrigon architecture is obtained through the self-assembly of Cd^{II} ions with ligands **L**³ and **L**⁵.

In 2014, Li's group employed tritopic and tetratopic terpyridine ligands reacting with Zn(II) ions to produce two supramolecular hexagon wreaths [Zn₉LA₆] and [Zn₁₂LB₆], respectively [25]. Compared with conventional macrocycles that use more flexible ditopic building blocks and thus leading to a mixture of multiple structures, multitopic ligands with high density of coordination sites (DOCSs) provide more geometric constraints to form single thermodynamically stable architectures. The shapes, sizes, and structures of these stable assemblies were confirmed by NMR, ESI-MS, TWIM-MS, and TEM. Actually, such hexagon wreaths are constructed by small subunit of the dimer hexagons in a recursion process around a central hexagon, exhibiting the self-similarity of the fractal geometry. By applying this approach, more sophisticated 2D supramolecular architectures can be precisely designed.

Based on AIE property of TPE, luminescent materials with similarly sophisticated structures were attained employing the third-generation AIE-active ligands with full conjugation of TPE with tpy. TPE-tpy ligands were assembled with Cd(II) to construct rosette-like metallosupramolecules ranging from **G1** to **G3** (Figure 2.17). A mixture of macrocycles was obtained by using ditopic ligand, while discrete double-layered hexameric and triple-layered heptameric rosettes were assembled from tetratopic and hexatopic ligands because such multitopic building blocks provided more geometric constraints in self-assembly processes to reach the most thermodynamically favorable structures. Additionally, because the intramolecular rotation around the TPE groups was further restricted after coordination, the assemblies exhibited high emission efficiency in both aggregation and solution states and displayed tunable emissive properties, especially, pure white-light emission for **G2**. This study provides an efficient strategy to construct various complexes and functional supramolecular architectures [26].

To increase the overall DOCS of macrocycles, a series of tetratopic ligands based on 2,2':6',2''-terpyridine (tpy) were used to design and assemble a concentric hexagon system, namely, hexagon in hexagon. Hybrid concentric hexagons could also be obtained by combining different tetratopic ligands. Furthermore, these supramolecules were utilized as building blocks to hierarchically self-assemble supramolecular metal-organic nanoribbons (SMON) at highly oriented pyrolytic graphite (HOPG) surface through the stronger π - π interaction [27].

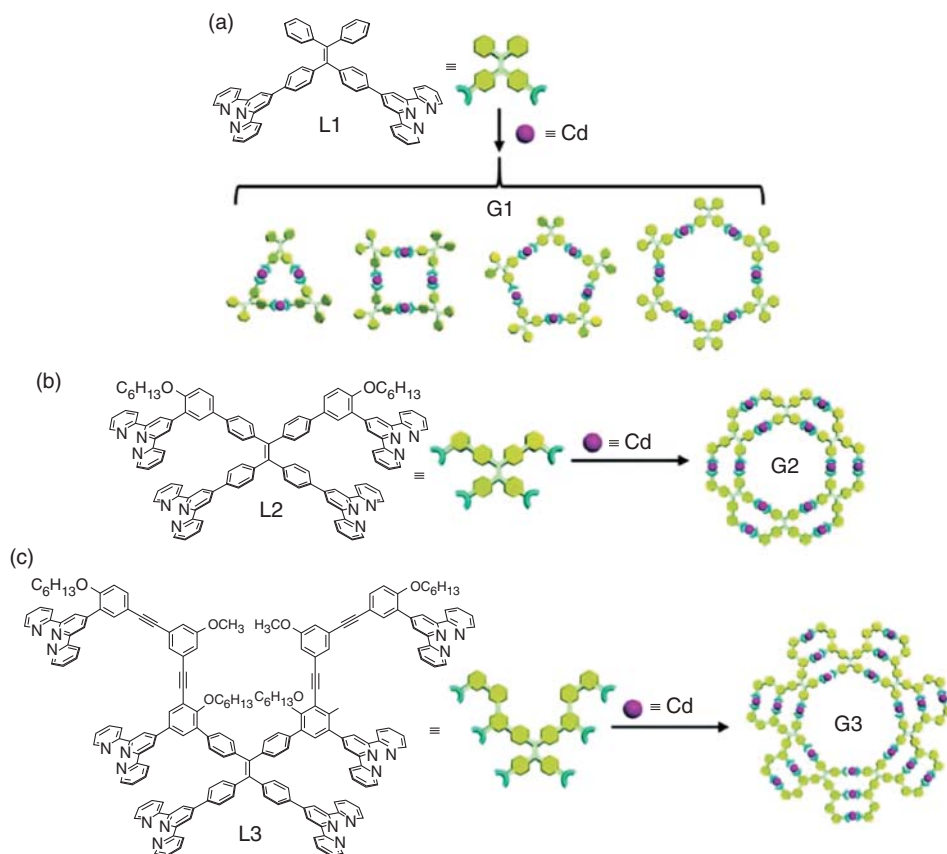


Figure 2.17 Self-assembly of supramolecular rosettes of (a) **G1**, (b) **G2** and (c) **G3**. Source: Yin et al. [26]. Licensed under CC BY 4.0.

Inspired by Kandinsky circles, three generations of giant nested supramolecules were designed and assembled by Li's group [28]. They overcome the challenge of the synthesis of multitopic ligands by using modular pyrylium salts followed by consecutive condensation reaction with primary amines. Furthermore, the nested supramolecules display high antimicrobial activity against Gram-positive bacteria MRSA and negligible toxicity to eukaryotic cells. This work paves a new avenue into the development and application of antimicrobial agents.

To create more complex artificial nanostructures, two giant rigid 2D rhombus star-shaped supramolecules were designed and assembled by stepwise multicomponent self-assembly. The super snowflakes complexes encompass three types of tpy ligands and two metal ions, Ru(II) and Zn(II), in each individual structure. Additionally, dynamic ligand exchange of two preassembled architectures **S2** and **S1** is observed to form a series of hybrid snowflakes (Figure 2.18) [29].

The Star of David, a historical Hebrew symbol known as the Shield of David or Magen David, is a fascinating structure. But the construction of this topology always is a challenge in supramolecular chemistry fields. Due to the predictability

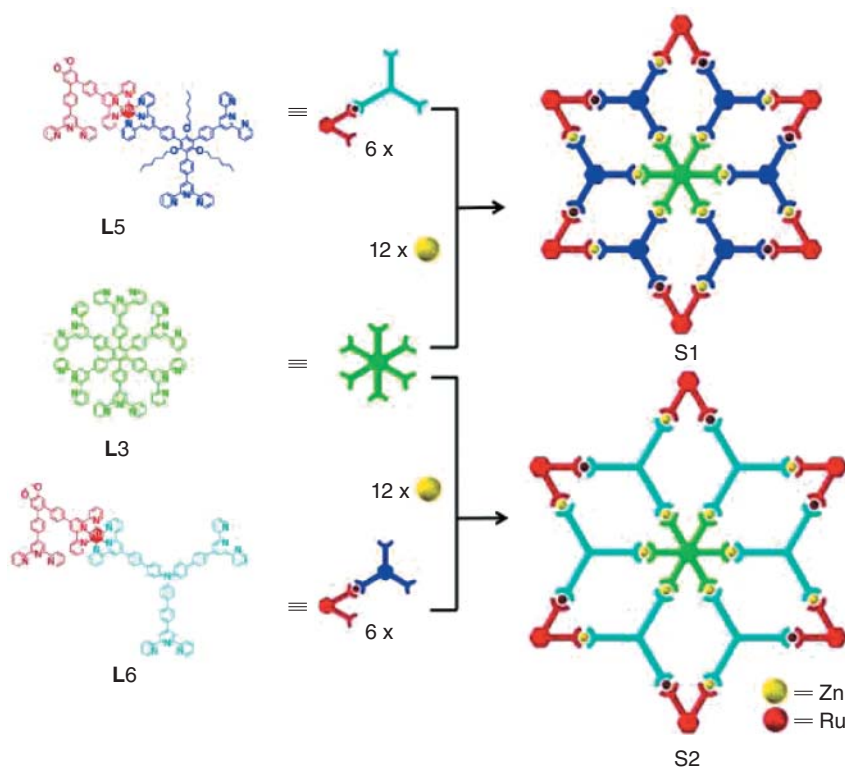


Figure 2.18 Self-assembly of snowflakes **S1** and **S2**. Source: Zhang et al. [29]. © 2017, American Chemical Society.

of coordination geometry among the coordination-driven self-assembly, not only effective synthetic strategies but also appropriate ligand designs play critical roles in the formation of highly ordered architectures. In 2017, Li and Wang's groups constructed a supramolecular pentagram and a supramolecular hexagram by carefully designing metalloorganic ligands through a stepwise synthesis approach. By introducing robust Ru-polyterpyridyl moieties to ligand LA (VRu^{2+}X , V = bisterpyridine, X = tetraterpyridine, Ru = ruthenium) or LB [$\text{V}(\text{Ru}^{2+}\text{X})_2$], the multi-nuclear pentagonal and hexagonal architectures were achieved, respectively [30]. In the same year, they successfully synthesized 2D and 3D Star of David structures by one step self-assembly of a tetratopic pyridyl ligand with a 180° diplatinum-(II) motif and Pd^{II} ions. The 3D structure shows remarkable stability owing to its high DOCS analyzing by gradient tandem mass spectrometry (gMS²) [31]. A nut-like hexagonal bismetallo-architecture with a central hollowed Star of David was further synthesized by stepwise self-assembly. The expected hexagonal metallostructure $\text{T}_{12}\text{K}_6\text{Fe}_{30}$ could not be obtained by one-pot self-assembly of **T** and **K** with Fe^{2+} directly. However, a higher ordered superstructure [T_2Ru]₆**K**₆ Fe_{24} could be prepared by the reaction of Ru-dimer metalloorganic ligand (T_2Ru) with tetrakis terpyridine (**K**) and Fe^{2+} [32].

Sierpiński triangle, a fractal geometry, has attracted increasing attention in many fields including science, technology, engineering, math, and art. In 2017, Li and Wang's groups reported the construction of different generations (**G1** to **G3**) of Sierpiński triangles using the <tpy-Ru(II)-tpy> based metalloorganic ligands as the building blocks to assemble with Zn(II) or Cd(II) in a stepwise strategy (Figure 2.19). Because of the structural and conformational complementarity of building blocks, or molecular puzzling, as well as highly reversible coordination, the stepwise self-assembly approaches were employed to overcome the formation of undesirable metallosupramolecules and coordination polymers [30].

Compared to the low generation (≤ 3) of Sierpiński metallasupramolecular fractals, it still remains a formidable challenge to assemble high generation of fractal geometries due to the challenges of design synthesis and separation. In 2018, Li's group used well-documented 2,2':6',2''-terpyridine (tpy)-based coordination-driven self-assembly to construct discrete supramolecular fractals ranging from generation **1** (**G1**) to **5** (**G5**) in high yields (Figure 2.20). Except for **G1** and **G4**, all other fractals were constructed using a series of Ru(II)-organic building blocks (ROBBs) to assemble with weak coordination metal, i.e. Zn(II). Those structures contain the same repeating shape unit, **G1**, but display at different scales, leading to different molecular geometry and symmetry. Moreover, all the geometry of **G1** to **G4** can be found as a proportion in **G5**, so they demonstrate the concept of "supramolecular fractal" [33]. Subsequently, they designed different generations of discrete polycyclic supramolecules using the same strategy, which were obtained in high yields by precise coordination of organic or ROBBs with Cd(II), Fe(II), or Zn(II) ions. Such 2D supramolecules with precisely controlled shapes and size have attracted considerable attention in materials science based on their hierarchical self-assembly behaviors both in solution and on the liquid–solid surface [34].

2.2.7 Polygon-Based Polymers

Coordination-driven hierarchical self-assembly provides an efficient way for the construction of dendronized polymers (DPs), which exhibit promising applications as electronic materials, liquid crystals, and siRNA delivery. In 2013, Yang's group reported the dendronized rhomboidal organoplatinum(II) metallacyclic polymers constructed through hierarchical self-assembly of 60° organo-Pt(II) acceptors decorated with [G1]–[G3] Frechet-type dendrons (**1a–c**) with 2-ureido-4-pyrimidinone (UPy)-functionalized 120° dipyridyl ligand **2** (Figure 2.21) [35]. PM6 semi-empirical molecular orbital analysis indicates that the rhomboidal metallacycle has planar rhomboidal backbones with exohedral functionalization by the pendant UPy motifs and dendronized subunits. The highly directional and well-defined quadruple H-bonding of UPy facilitates the polymerization of the rhomboids into dendronized organoplatinum(II) metallacyclic polymers, which possess the structural features of conventional DPs as well as the dynamic reversibility of supramolecular polymers. The size of the polymers is highly dependent on the generation number of the attached dendrons, as confirmed by DOSY and DLS experiments. TEM morphological studies suggest that [G3]-metallodendrimer **3c** aggregates to form single

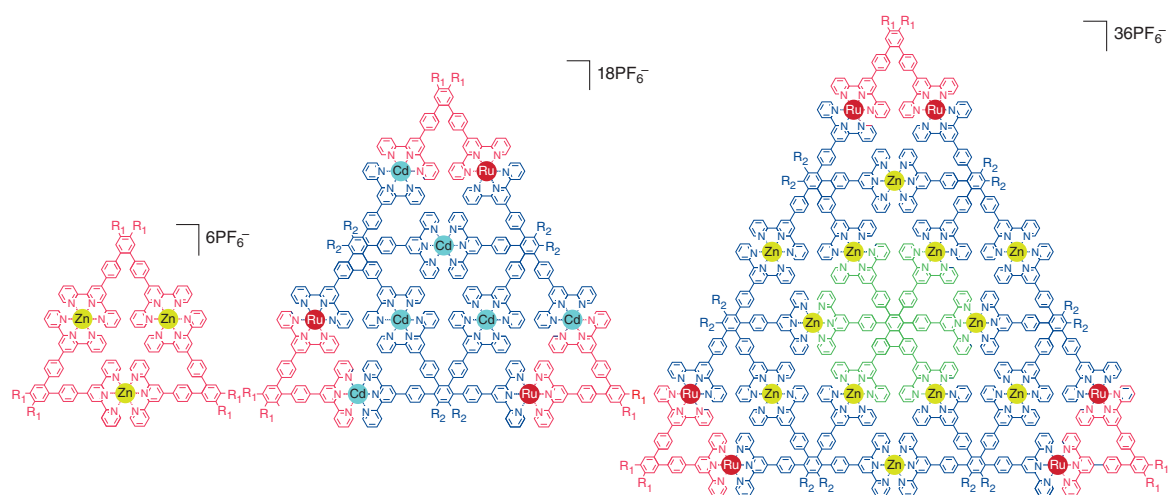


Figure 2.19 Chemical illustration of three Sierpiński triangles **G1**, **G2**, and **G3**. *Source:* Jiang et al. [30]. © 2017, John Wiley & Sons.

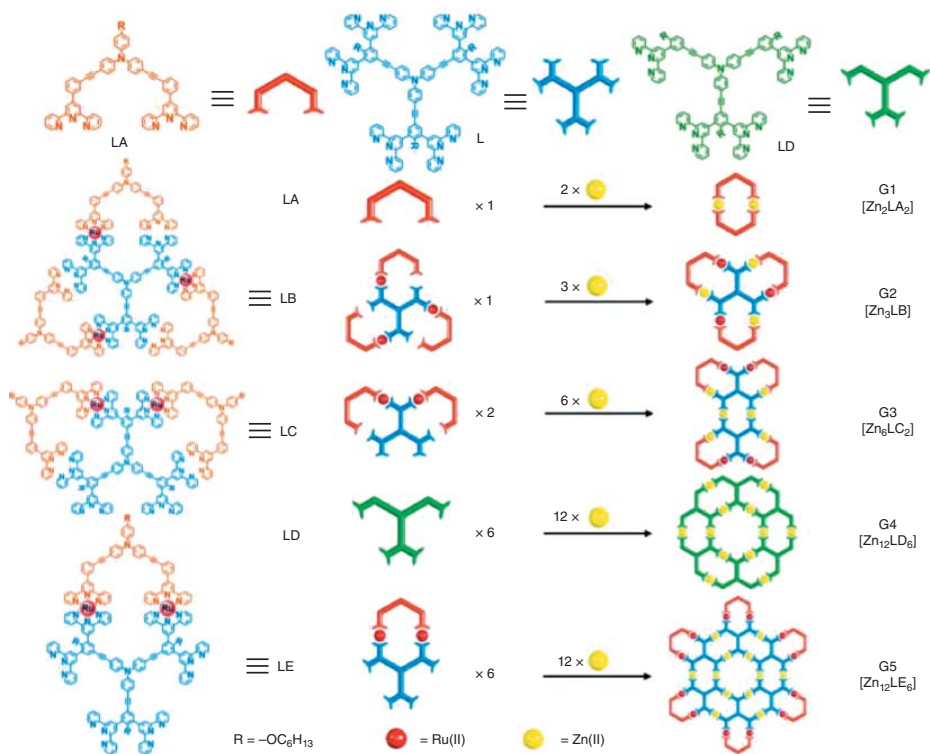


Figure 2.20 Different approaches to prepare the ligands and fractal structures. *Source:* Wang et al. [33]. © 2018, American Chemical Society.

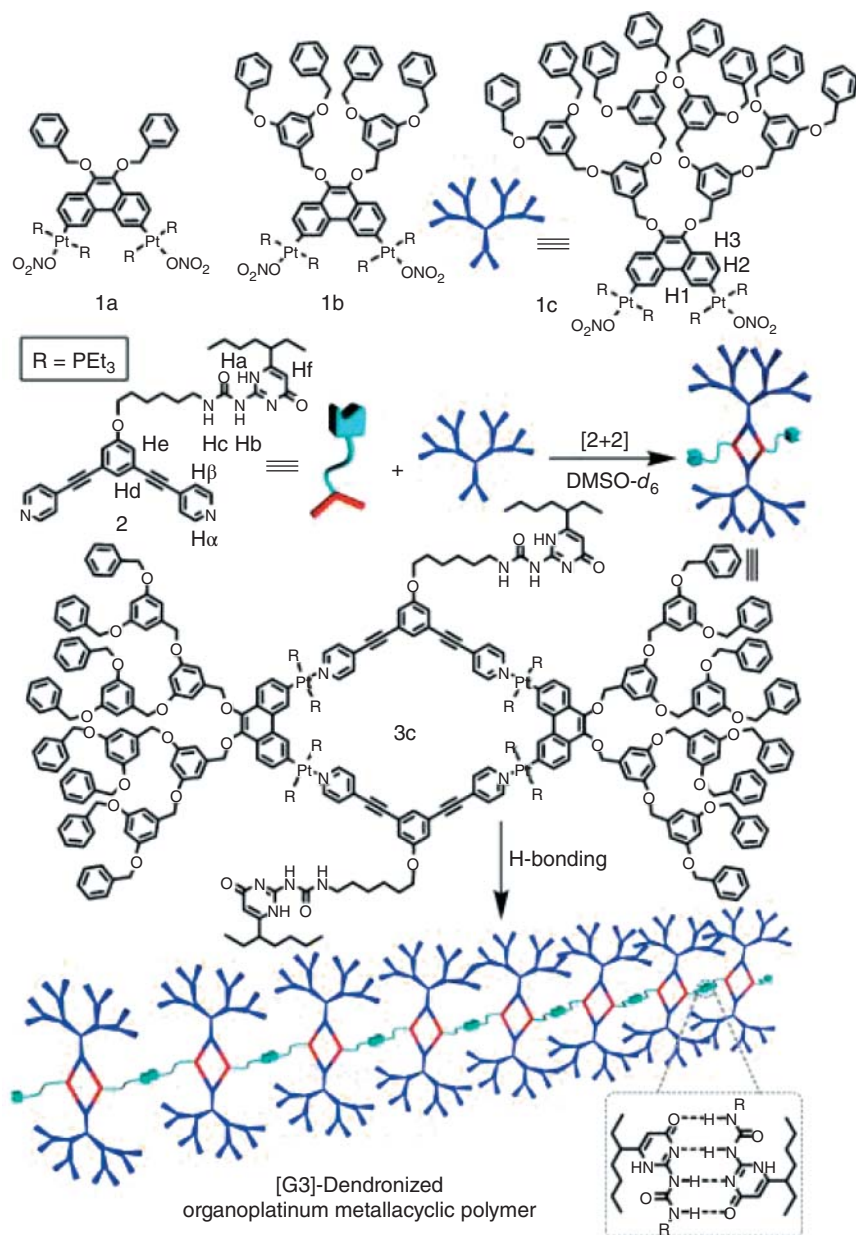


Figure 2.21 Formation of [G3]-DOMPs by hierarchical self-assembly of 60° [G3]-dendronized organo-Pt(II) acceptor **1c** and 120° UPy-functionalized ligand **2**. Source: Yan et al. [35]. © 2013, American Chemical Society.

polymeric chain nanofibers, and these fibers subsequently form laterally associated bundles containing several like strands, giving rise to widths of 6.0–50 nm.

A new class of multiple stimuli-responsive polymer gels based on hexagonal metallacycles were also prepared through hierarchical self-assembly and host–guest interactions. The reaction of a new 120° pillar [5] arene containing dipyriddy donor ligand with complementary 180° di-Pt(II) acceptors with different lengths resulted in the formation of hexakis-pillar [5] arene metallacycles of different sizes [36]. PM6 semi-empirical molecular orbital calculations revealed a structure of roughly planar hexagonal ring at the core surrounded by six rigid pillar [5] arenes with the internal diameters of 5.0 (**H2**) and 5.8 nm (**H3**). Host–guest complexations of **H2** and **H3** with neutral ditopic guests were observed which led to the formation of analogous concentration-dependent cross-linked supramolecular polymers **H2** ⊃ (G5)₃ and **H3** ⊃ (G5)₃. When the concentrations were increased to 22–23 mM, the cross-linked supramolecular polymers transformed into stable supramolecular gels with different colors. By taking advantages of the dynamic nature of the host–guest interactions and Pt–N coordination bonds, reversible multiple stimuli-responsive gel–sol phase transition of the polymer gels was realized through temperature control, the addition and removal of competitive guests and halide.

In 2015, the Yang's group further presented an example of counter polyanion-induced hierarchical self-assembly of discrete metallacycle [37]. Heparin, a sulfated glycosaminoglycan polymer with multiple negative charges that has been widely used as an anticoagulant drug, was selected to induce hierarchical self-assembly. The introduction of AIE active moiety, TPE, endowed the resultant metallacycle with interesting sensing functionality. The aggregation between the metallacycle and heparin, induced by multiple electrostatic interactions, resulted in dramatic fluorescence enhancement. Entangled pearl-necklace networks were obtained by multiple electrostatic interactions. Obvious emission intensity changes accompanied by the hierarchical self-assembly process with a linear relationship demonstrated that the functionalized metallacycle could work as a turn-on sensing probe for heparin. The metallacycle displayed high selectivity and sensitivity to heparin in comparison with structurally similar analogs such as chondroitin-4-sulfate (ChS) and hyaluronic acid (HA).

Hexagonal metallacycles decorated with three CTAs at alternative vertexes were also synthesized through the coordination-driven self-assembly of 120° dipyriddy building block **1** and the corresponding complementary 120° di-Pt(II) acceptors **2** or **3** (Figure 2.22) [38]. The tris-CTAs metallacycles were further used as RAFT agent for the preparation of stimuli-responsive and self-healing supramolecular star polymers through the controlled radical polymerization of *N*-isopropylacrylamide (NIPAAM). The resultant star polymers exhibited LCST behavior in water because of the introduction of PNIPAAM moieties. Moreover, the supramolecular polymer hydrogels cross-linked by discrete metallacycles were obtained from the star polymers at room temperature without heating–cooling process, and the existence of metallacyclic scaffold endowed the obtained hydrogels with bromide anion stimuli-responsive and self-healing properties by taking advantage of the dynamic nature of the Pt–N coordination bonds. This study opens a

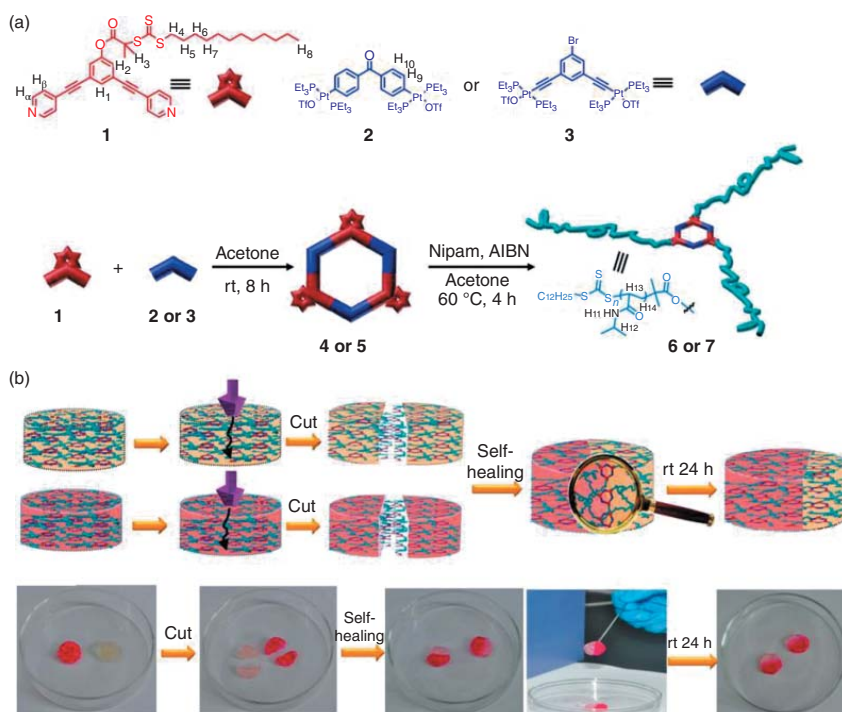


Figure 2.22 (a) Graphical representation of synthesis of organoplatinum(II) metallacycles and star supramolecular polymers. (b) Rapid macroscopic self-healing experiments of the supramolecular polymeric hydrogel. *Source:* Zheng et al. [38]. © 2016, American Chemical Society.

new avenue to the construction of novel functional materials based on well-defined metallasupramolecular assemblies, in particular “smart” soft matters.

Supramolecular hydrogels containing discrete organoplatinum(II) metallacycles are also promising candidates as biomaterials [39]. *N,N*-dimethylaminoethyl methacrylate (DMAEMA) and NIPAAM were selected as block segments due to the typical LSCT behavior of PNIPAAM and the CO₂-responsiveness and low cytotoxicity of PDMAEMA. The star-shaped supramolecular copolymers with well-defined hexagonal metallacycles as cores were prepared through coordination-driven self-assembly and stepwise polymerizing DMAEMA and NIPAAM. The resultant copolymers featured CO₂ stimuli-responsive properties including CO₂-triggered morphology transition and CO₂-induced thermoresponsive behavior. Reversible gel-to-sol transition of the supramolecular hydrogels with metal–organic macrocycles as junctions near physiological temperature can be realized through the removal and addition of CO₂. Control experiments show that both block copolymers and well-defined metallacycles are key factors in the realization of the CO₂-promoted hydrogel formation. The resultant polymeric hydrogel also displays injectable and cytocompatible properties.

2.2.8 Responsive Dynamic Metallacycles

In 2017, Sun’s group reported an artificial assembly system that features adaptive self-assembly and induced-fit transformation properties in the presence of anionic guests (Figure 2.23) [40]. Five metal–organic macrocycles with empirical formula

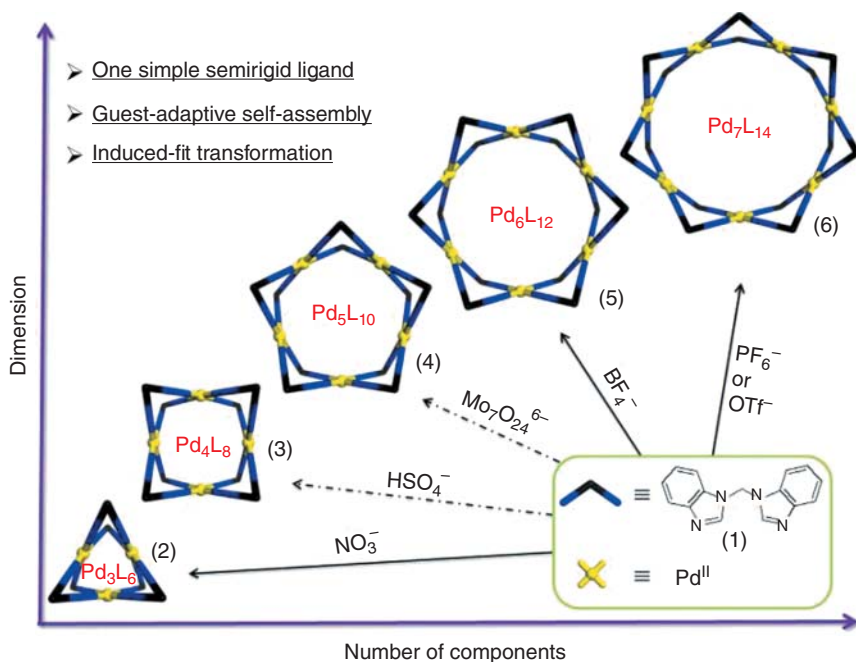


Figure 2.23 Self-assembly of anion-binding metal–organic macrocycles. Source: Zhang et al. [40]. © 2017, Nature Publishing Group.

of M_nL_{2n} ($n = 3, 4, 5, 6, 7$) were selectively obtained starting from one simple benzimidazole-based ligand and square-planar palladium(II) ions, either by direct anion-adaptive self-assembly or induced-fit transformations. Hydrogen bonding between the inner surface of the macrocycles and the bound guests, different anions in this case, dictated the shape and size of the final product. Moreover, a comprehensive map showing all the transformations across the macrocyclic species was drawn, with a representative reconstitution process from Pd_7L_{14} to Pd_3L_6 traced in detail by titration experiments, revealing a gradual ring-shrinking mechanism. Moreover, this new class of donut-shaped assemblies could provide unique tunable hydrogen-binding pockets, where molecular sensing/catalysis may be possible to take place.

2.3 Metallacages

Metallacages that are one class of discrete 3D structures have achieved magnificent attention in recent 20 years, not only for their esthetic attributes but also because of their wide applications in host–guest chemistry, supramolecular polymers, catalysis, biomedicine, and so on. Many domestic researchers have already developed a series of rationally designed metallacages with various shapes via coordination-driven self-assembly.

2.3.1 Helicates

In 2015, Sun's group succeeded in designing a cationic M_2L_4 cage by quantitative self-assembly of four anthracene-bridged benzimidazole ligands and two Pd^{II} ions [41]. The cage showed a D_4 symmetry but exhibited excellent capability in the selective encapsulation of nitrate. Solid structural confirmation of Pd_2L_4 was provided by X-ray crystallographic analysis. Crystallographic data show that four ligands in Pd_2L_4 arrange in a quadruple helicate conformation due to the steric repulsion between the anthracene panels, resulting in a D_4 symmetry of the host framework with inherent P or M helicity (Figure 2.24). More interestingly, the four anthracene walls of the ligand wrap up a very concise hydrophobic cavity where all the benzimidazole protons are pointing inward, forming a perfect bind pocket that is occupied by a nitrate anion. The binding constant (K^+ anion) for the inclusion of NO_3^- is at least 2 orders of magnitude higher than all the other anions screened. Such a big difference can be attributed to the presence of maximal hydrogen-bonding interactions between the nitrate and the host cage in spite of the mismatching on symmetry. On the contrary, the lack of hydrogen bonding weakens this binding between anions and host even if their symmetries are better matching when single-atom halide anions are placed in the D_4 symmetrical host. Similarly, little exchange for NO_2^- was observed.

The constitutional control of structural interconversions of supramolecular architectures via molecular recognition or templating effects is of fundamental and high applicative interest. In 2016, Su's group reported fully structural interconversions between monomeric Pd_2L_4 and interlocked dimeric Pd_4L_8 cages [42]. They discussed the origin of the thermodynamic stability and the driving force for

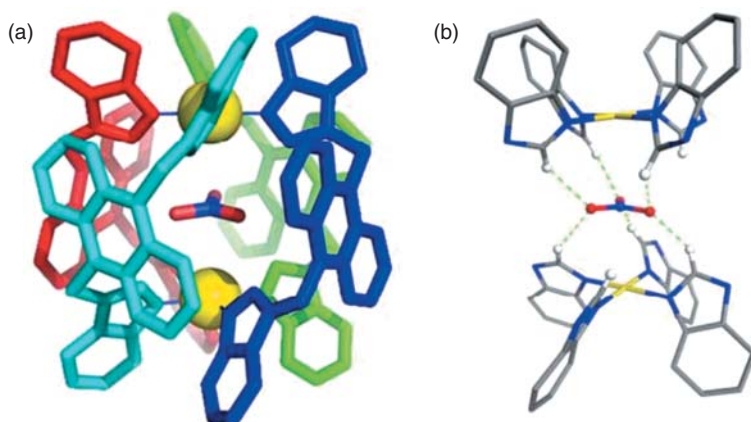


Figure 2.24 (a) The crystal structure of Pd₂L₄ with one encapsulated NO₃⁻ anion. (b) Hydrogen-bonding interactions between the NO₃⁻ and the benzimidazole ligands. *Source:* Zhou et al. [41]. © 2015, The Royal Society of Chemistry.

structural transformations via thorough investigations on anion exchange behaviors, anion-bonding affinities, kinetics, and thermodynamics in monomerization and dimerization processes, which revealed the unstable nature of the interlocked structure itself but subject to modulation through variable host–guest interactions dictated by the anion-templating effect.

Among the chiral lanthanide assemblies, triple-stranded dimetallic helicates Ln₂L₃ possessing two opposite helical senses (P or M helicity) have been widely investigated. Stereocontrolled self-assembly of dinuclear triple-stranded europium helicate (Eu₂L₃) based on DTE-functionalized ligands has been achieved via the chiral-induction strategy (Figure 2.25) [43]. The point chirality of the ligands is transferred to give either Δ or Λ metal-centers and hence leads to an overall P or M helical senses. Moreover, the helicates in solution feature a reversible photocyclization and cycloreversion, offering an opportunity to develop as chiroptical switches. Reversible photochromism has been revealed for both ligands and helicates, with distinct change observed on the circular dichroism (CD) signals for the latter.

A pair of enantiopure pyrene-functionalized C₂ symmetrical bis(tridentate) ligands [(R,R)-/(S,S)-L] were also synthesized, which led to the diastereoselective formation of P- and M-type Ln₂L₃ helicates [44]. The self-assembly process was followed by NMR and ESI-Q-TOF-MS. Moreover, commercially available Δ-TRISPHAT proved to be an effective NMR chiral resolving agent to differentiate between the two enantiomers of the helicate.

Wu's group also reported a self-assembly triple-anion helicate featuring a cavity resembling that of the choline-binding protein ChoX, as revealed by crystal and DFT-optimized structures, which bind choline in a unique dual-site-binding mode (Figure 2.26) [45]. Of particular significance is this host system displays a unique high selectivity toward choline over the closely related acetylcholine

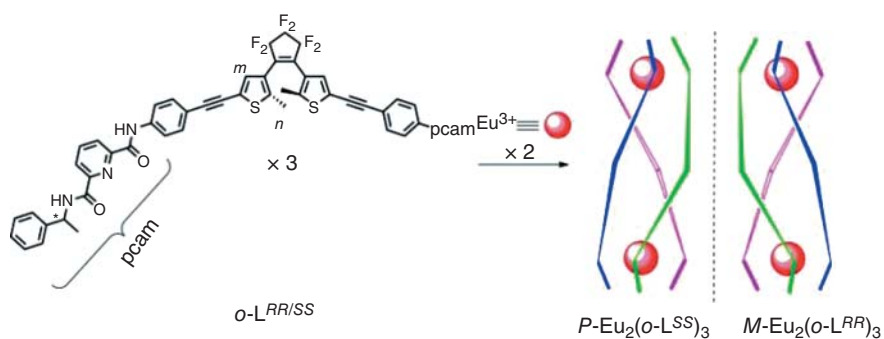


Figure 2.25 Stereocontrolled self-assembly of Eu_2L_3 triple helicates from ligands $o\text{-L}^{RR/SS}$. Source: Cai et al. [43]. © 2018, The Royal Society of Chemistry.

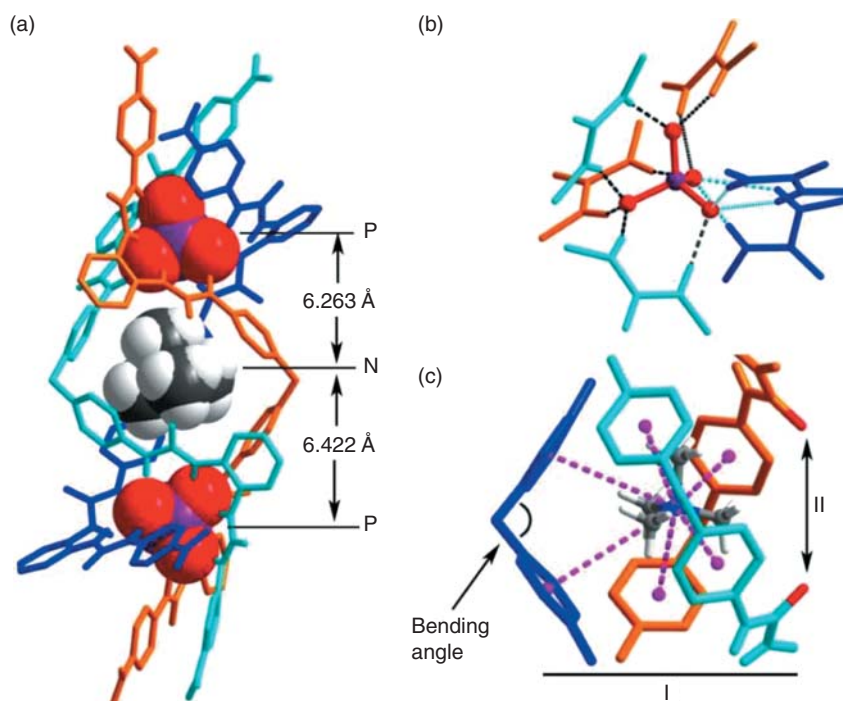


Figure 2.26 (a) Crystal structure of A_2L_3 . (b) Hydrogen bonds formed between a PO_4^{3-} ion and six urea units. (c) The aromatic box (site-I) trapping a TMA^+ through cation- π interactions (purple-dashed lines) and a potential hydrogen-bonding site (II), which together resembles the structure of $\text{Ch}+\text{CChoX}$. Source: Jia et al. [45]. © 2017, Nature Publishing Group.

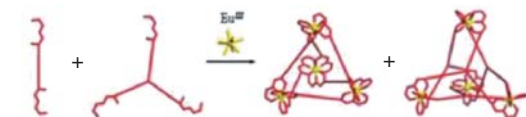
($K_{\text{choline}}/K_{\text{acetylcholine}} > 15$). The triple helicate is able to act as a fluorescence displacement sensor for discriminating choline, acetylcholine, L-carnitine, and glycine betaine effectively.

Based on the molecular helicate constructed by hydrothermal reaction of 3,5-bis(2-pyridyl)pyrazole (HL) with $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (or $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and NaSCN, further solvothermal reaction with CuSCN in the presence of PPh_3 led to the formation of helical coordination polymer complex [46]. The coordination polymer could also be obtained solvothermally in acetonitrile by the one-pot reaction of CuSCN, Ni^{2+} (or Zn^{2+}) salt, HL, and PPh_3 . The intermolecular noncovalent interactions between the helicates and the copper–pseudohalide components respond to the stereochemical induction of the double-helical coordination polymer, resembling the effect of the intramolecular coordination bonds in the assembly of discrete helicates.

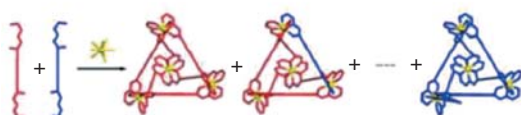
2.3.2 Tetrahedron

In 2015, Sun's group reported the first example of stereoselective self-assembly of chiral luminescent europium coordination tetrahedral cages and their novel self-sorting behavior (Figure 2.27) [47]. Two pairs of R and S ligands are designed on the basis of the pyridine-2,6-dicarboxamide coordination unit, bis(tridentate) L_1 and tris(tridentate) L_2 . Corresponding chiral $\text{Eu}_4(\text{L}_1)_6$ and $\text{Eu}_4(\text{L}_2)_4$ topological tetrahedral cages are independently assembled via edge- and face-capping design strategies, respectively. Narcissistic self-sorting was observed in the self-assembly process when two differently shaped ligands L_1 and L_2 were mixed. More impressively, distinct self-sorting behavior between Eu_4L_6 and Eu_4L_4 coordination cages has been observed for the first time when racemic mixtures of ligands are used. And the results reveal that ligands with different shapes and geometry are easily discriminated.

Case 1: Narcissistic self-sorting



Case 2a: Dynamic mixture



Case 2b: Narcissistic self-sorting

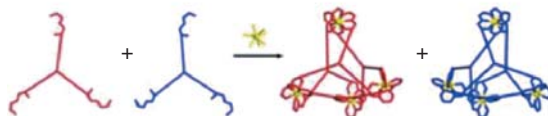


Figure 2.27 Schematic diagram of coordination self-assembly and self-sorting of lanthanide metal chiral cages. Source: Yan et al. [47]. © 2015, American Chemical Society.

Moreover, **L**₂ shows unprecedented self-assembly capacity with metal ions spanning across the periodic table, including alkaline earth (Ca^{II}), transition (Cd^{II}), and all the lanthanide (Ln^{III}) metal ions (M), ascribed to the appropriate rigidity of the C₃ symmetrical scaffolding, high assembly adaptability, and adequate chelating affinity with lanthanide ions of the neutral coordination motif [48]. More importantly, this versatile ligand displays rare and rather high discrimination between metal ions with identical coordination geometries as well as extremely small ionic difference, arising from supramolecular multivalent cooperativity, resulting in absolute or highly efficient metal ion self-recognition during mixed-metal self-assembly process. A supramolecular lanthanide extraction separation method was proposed based on the strong synergistic metal ion self-identification characteristics of M₄L₄ cage, providing a new design principle for the next generation of efficient lanthanide separation.

Concentration-triggered transformation from helicate to tetrahedron cage was obtained using oxazoline-based bis(tridentate) ligand (Figure 2.28) [49]. The improved stability and luminescent property of this new generation of Eu₄L₆ tetrahedral cage facilitated their efficient sensing toward highly explosive nitroaromatic compounds. Moreover, luminescent sensing of nitroaromatic explosives was demonstrated, featuring selective and efficient detection of PA at ppb level.

The bright luminescent self-assembled tetrahedral compound Eu₄L₄ can behave as dual-responsive and highly selective luminescent probe toward both anions and cations, taking advantage of the intraligand charge transfer (ILCT) sensitization mechanism [44]. To improve the luminescent properties of the Ln-based tetrahedral cages, a group of bright luminescent lanthanide organic tetrahedrons with record-high emission quantum yields has been constructed by using two fully conjugated ligands featuring the triazole-pyridine-amido (**L2**) chelating moiety easily accessible from the Click reaction [50]. In addition, using the synergistic energy transfer (ET) between the lanthanide vertices, the ratio luminescent thermometer covering the physiological temperature range in the Eu/Tb mixed tetrahedron is

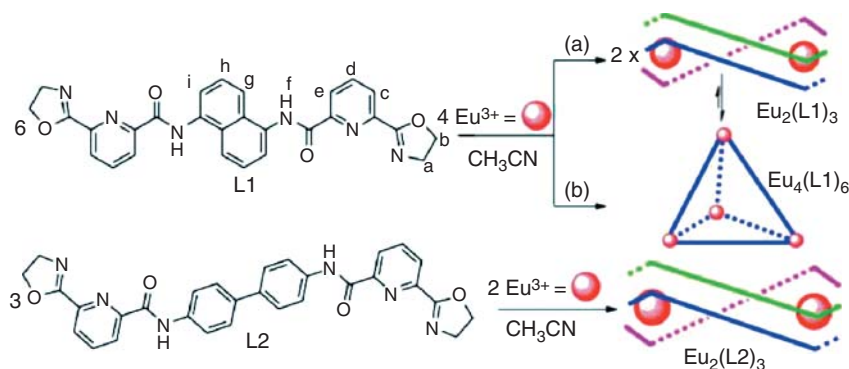


Figure 2.28 Self-assembly of either a Eu₂(**L1**)₃ helicate or a Eu₄(**L1**)₆ tetrahedron from ligand **L1**, and self-assembly of a Eu₂(**L2**)₃ helicate structure from ligand **L2**. Source: Liu et al. [49]. © 2017, The Royal Society of Chemistry.

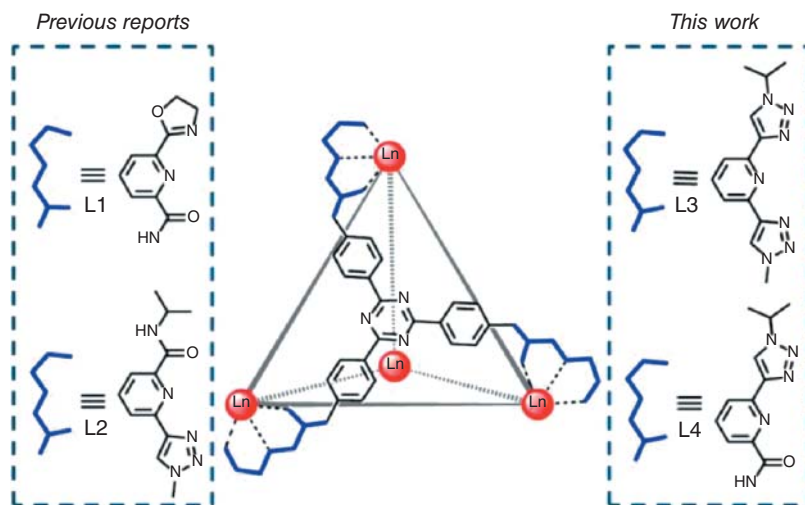


Figure 2.29 Strongly luminescent lanthanide–organic tetrahedral Ln_4L_4 cages based on tris(tridentate) ligands with different chelating groups. Source: Wu et al. [51]. © 2019, American Chemical Society.

proved to be a potential application prospect as a single-molecule cell thermometer. It is well documented that increasing the rigidity of ligands can effectively restrain the consumption of ET process on lanthanide–organic complexes. Thus, they replaced the inner amide bond with triazole on C_3 symmetric ligands to increase both the rigidity and conjugation of ligands. In 2019, they further reported fine-tuned luminescence on a series of Ln_4L_4 -type cages constructed by two new ligands (**L3** and **L4**) with the triphenyltriazine core (Figure 2.29) [51]. They found that the fully conjugated **L3**, with 2,4,6-tris(4-pyridyl)-1,3,5-triazine (TPT) chelating groups, manifests excellent sensitization ability toward all the emitting lanthanide ions ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$) covering both the visible and the NIR regions. A record luminescent quantum yield for $\text{Tb}_4(\text{L3})_4$ is reached ($\Phi = 82\%$). As a control, **L4** with an amido-pyridine-triazole (APT) chelate that differs from the known **L2** only in the relative position of the amido and triazole groups exhibits weaker sensitization ability on the lanthanide-organic polydrons (LOPs). Finally, white-light emission systems have been obtained by combining the desired luminescent compounds. The study could offer important design principles toward strongly NIR-emitting LOPs. Moreover, these strongly luminescent LOPs provide new candidates for photochemical supramolecular devices.

Anion coordination chemistry has developed rapidly in recent years because it plays an important role in biological, environmental, and chemical processes. Some pioneer studies in anion coordination chemistry show that anion displays similar properties with transition metals in coordination chemistry, such as coordination geometry and coordination number. These analogies provide promising ideas for the self-assembly of novel supramolecular systems based on anion coordination. Wu's

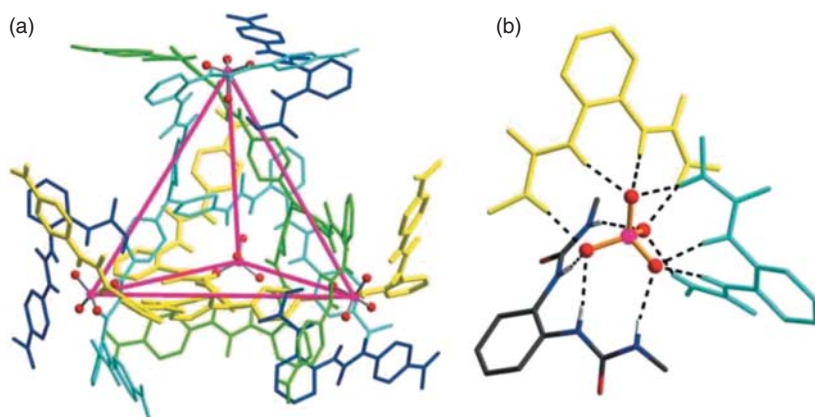


Figure 2.30 (a) The tetrahedral cage $[(\text{PO}_4^{3-})_4\text{L}_4]^{12-}$ in the crystal structure, with the dark-blue facial ligand truncated so that the interior and opposite PO_4^{3-} corner can be seen. (b) Hydrogen bonds around the PO_4^{3-} ion. Source: Wu et al. [52]. © 2013, Wiley-VCH.

group from Northwest University in China has made a series of characteristic works in anion coordination chemistry from 2013.

They developed a series of *ortho*-phenylene-bridged oligoureia ligands, which displayed excellent affinity and complementarity to the tetrahedral phosphate anions. Moreover, the fully deprotonated phosphate anion could form 12 hydrogen bonds with ligand that achieves a theoretical and experimental coordination saturation. In the beginning, they designed the tris(bisurea) ligand by attaching three bisurea moieties to a central C_3 -symmetric triphenylamine platform and reported the first tetrahedral anion cage ($[\text{A}_4\text{L}_4]$ -type (A = anion)) from ligand and PO_4^{3-} ions. The new A_4L_4 crystallizes from diethyl ether/acetonitrile in the centrosymmetric cubic space group $P\bar{4}3n$ (Figure 2.30) [52]. The structure had the ideal T symmetry with one-twelfth of the tetrahedral molecular cage (one-third of a phosphate ion, one third of the ligand, one TMA as the counter-cation) appearing in the asymmetric unit. The phosphate ions occupied the vertices and the ligands lay on the faces. However, the tri(bisurea) group limited the cage's inner space which was estimated to be $121 \text{ \AA}^3$ by DFT and could not encapsulate any guest. To solve the problem of cage's small inner space, Wu's group designed ampliative ligand to build a larger anion coordination cage. They used 1,3,5-triphenylbenzene as linker to replace triphenylamine to amplify its inner space, which was estimated to be about $229 \text{ \AA}^3$ [53]. Then this new anion coordination cage was used to encapsulate some chlorinated hydrocarbons at room temperature to explore anion cage's host–guest chemistry and attempted to broaden its application.

To make further research about A_4L_4 cage's host–guest chemistry, Wu's group chose white phosphorus (P_4) and yellow arsenic (As_4) as guests, which were very unstable and difficult to storage and transport [54]. In this work, they demonstrated a new design strategy for constructing finite cages based on anion coordination chemistry. The phosphate coordination-based tetrahedral cages could readily accommodate the tetrahedral guests P_4 and As_4 , which is facilitated by the shape and size

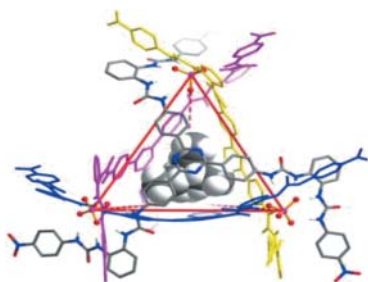


Figure 2.31 Crystal structure of cage $\supset$ TEA⁺.
Source: Zhang et al. [55]. © 2018, American Chemical Society.

complementarity as well as favorable σ – π and lone-pair– π interactions. Moreover, the latter case represented the first example of As₄ inclusion in a well-defined tetrahedral cage.

In 2018, they reported a C_3 symmetric tris(bis(urea)) ligand based on the 2,4,6-triphenyl-1,3,5-triazine spacer, which assembled with phosphate anions to form a new A₄L₄-type tetrahedral cage, with unusually high packing coefficients (up to 99.5% for the best substrate) [55]. This cage was able to adjust its size and shape (from 136 to 216 Å³) by bending of the triphenyltriazine plane (Figure 2.31). This allowed it to accommodate relatively large guests. In the case of DABCO, inclusion within the cage allowed the degree of methylation to be controlled and the monomethylated product to be isolated cleanly under conditions where mixtures of the mono- and dimethylated adduct were obtained in the absence of cage.

Except for the common tetrahedra based on anion coordination chemistry, Wu's group also designed other characteristic anion complexes with different shapes. In 2014, they designed a tetrakis(bisurea)-decorated tetraphenylethene ligand and constructed a special cage with fluorescence “turn-on” over a wide concentration range, from dilute to concentrated solution and to the solid state [56]. This “anion-coordination-induced emission” (ACIE) is another approach for fluorescence turn-on in addition to AIE.

As the simplest platonic polyhedron, tetrahedral cages have emerged a wealth of research prospect in supramolecular chemistry; thus, exploring new novel strategy for the synthesis of tetrahedral assembly is also meaningful. Yuan's group first chose trinuclear zirconocene cluster as vertex to construct two types of tetrahedra in a one step [57]. The trinuclear cluster demonstrated a C_3 symmetry with three C_2 axes along the carboxylate ligands forming an angle of about 60°, which provided a possibility to act as vertex in constructing coordination polyhedra. Subsequently, according to edge- and face-directed strategies, both V₄E₆ (V = vertex and E = edge) and V₄F₄ (F = face) tetrahedra could be synthesized in situ method. As shown in Figure 2.32, the V₄E₆ tetrahedral geometry, four Cp₃Zr₃O(OH)₃ second building units (SBUs) sit on the vertices and four benzene-1,4-dicarboxylic acid ligands are disposed along the edges, while four benzene-1,3,5-tricarboxylic acid ligands span the faces in V₄F₄ tetrahedron. As an expansion of structure based on reticular chemistry, extended version of tetrahedra can be easily obtained using the same method. Further gas adsorption study demonstrates that these tetrahedral cages could maintain their architectural rigidity and permanent porosity after activation.

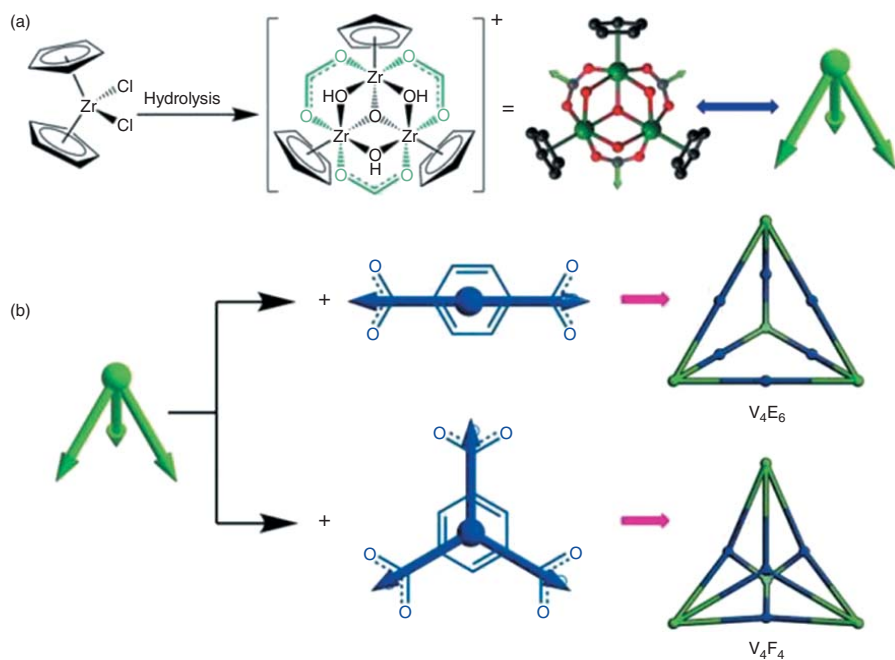


Figure 2.32 (a) Schematic representations of the formation of trinuclear zirconocene nodes. (b) Configurations of [4+6] V_4E_6 and [4+4] V_4F_4 tetrahedra. Source: Liu et al. [57]. © 2013, American Chemical Society.

Rational manipulation of catalytically active ligands in constructing polyhedral cages not only can regulate the catalytic performance but also promote the design of more sophisticated and smart assemblies for enantioselective reaction. In 2018, Cui's group reported the design and synthesis of five chiral single- and mixed-ligand tetrahedral supramolecular cages constructed by metallosalen ligands (a privileged chiral catalyst) as edges and four C_3 symmetry Cp_3Zr_3 clusters as vertices (Figure 2.33) [58]. These tetrahedral cages demonstrate inherent nanoscale hydrophobic cavities and various catalytically active sites, which endow them with prominent catalytic activity and enantioselectivity over sequential asymmetric alkene epoxidation/epoxide ring-opening reactions with up to 99.9% ee.

In 2011, Duan's group reported a novel cerium-based neutral molecular tetrahedron by incorporating amide-containing tridentate chelating sites into the three arms of a triphenylamine fragment which acts as a bright blue emitter (Figure 2.34) [59]. Single-crystal X-ray structural analysis verified the formation of $Ce_4(H_2TTS)_4$ tetrahedron in a crystallographic C_3 symmetry. The tetrahedron involves four vertical metal centers and four deprotonated H_2TTS ligands. Each cerium ion is chelated by three tridentate chelating groups from three different ligands which individually position on the four faces of the tetrahedron. Interestingly, the tetrahedron encapsulates molecules of nitric oxide (NO) and nitronyl nitroxide (PTIO) within the cavity and can be developed as a luminescent detector of PTIO, a specific spin-labeling NO trapper for biological imaging in living cells. The tetrahedron can also be applied in quantificational detection of free tryptophan in serum since the synergistic effects of hydrogen bonding, aromatic stacking, and size/shape matching [60].

The metal–organic tetrahedron can act as a redox vehicle to encapsulate organic dyes for photocatalytic proton reduction [61]. The assembled neutral Co-TFT tetrahedron consists of four ligands and four cobalt ions, in which each cobalt ion is coordinated in a *fac*-configuration by three bidentate thiosemicarbazone NS chelators from three different ligands. The three anionic sulfur donors are positioned on one side with great potential for attaching a proton via hydrogen-bonding interactions. Once organic dyes are encapsulated in the pocket as photosensitizer, these essential components are forced closer together and facilitate the photoinduced electron transfer from the excited state of the photosensitizer to the cobalt-based catalytic sites via a powerful pseudo-intramolecular pathway, resulting in excellent TON for the generation of hydrogen from water. When the ligand is coordinated with redox Ni, redox active Ni-TFT octahedron pocket is formed [62]. The encapsulation of organic dye within the pocket of the redox active vessel modifies photocatalytic proton reduction in the inner space of the pocket and gives molecular hydrogen and oxidized dye. The oxidized dye leaves the pocket and causes sulfide oxidation outside the cavity to give element sulfur, which combines the photocatalytic hydrogen evolution and sulfide oxidation.

In 2017, Zhang's group fabricated a water-soluble and ultra-stable Ti_4L_6 tetrahedron based on the titanium-oxo clusters assembling with embonic acid ligands. This tetrahedron has excellent selective activities for dye photodecomposition through N–H...O hydrogen bonding and also shows stepwise assembly function with other metal ions (such as Co^{2+} , Ln^{3+}) to form novel $Ti_4L_6-Co_3$ cage and Ti_4L_6-Ln cage (Figure 2.35) [63].

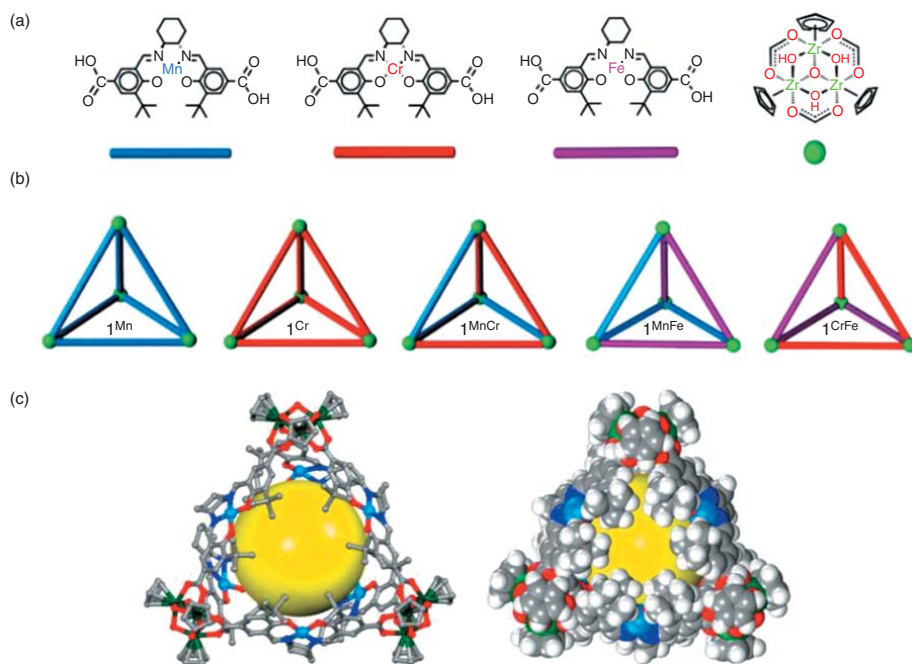


Figure 2.33 (a) Structures of the ligands and trimetallic cluster. (b) Schematic representations of cages 1^{Mn} , 1^{Cr} , 1^{MnCr} , 1^{MnFe} , and 1^{CrFe} . (c) Single-crystal X-ray structure of 1^{Mn} and its space-filling model (light blue, Mn; green, Zr; blue, N; red, O; gray, C; the cavities are highlighted by yellow spheres). *Source:* Jiao et al. [58]. © 2018, American Chemical Society.

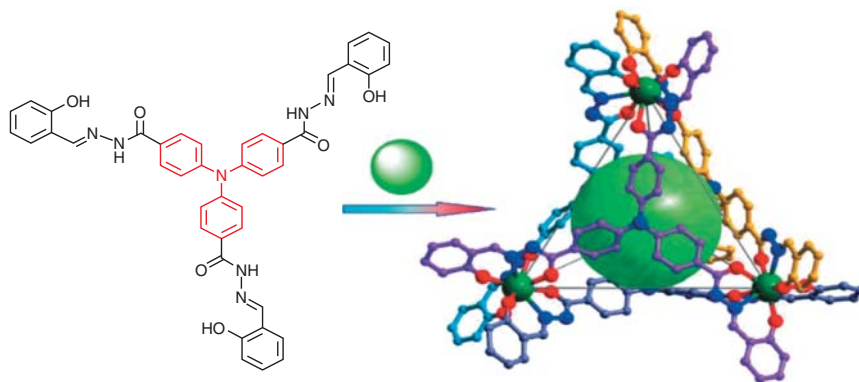


Figure 2.34 Structure of H₆TTS, constructional fragments of the Ce₄(H₂TTS)₄ tetrahedron. Source: Wang et al. [59]. © 2011, American Chemical Society.

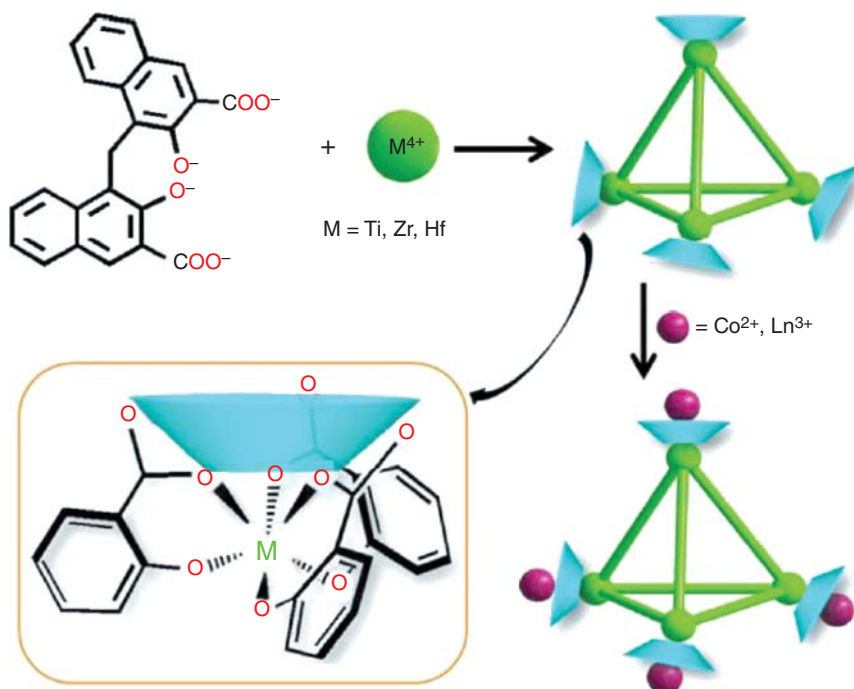


Figure 2.35 Self-assembly of water-soluble and ultra-stable Ti₄L₆ tetrahedron for potential metal ion trapping. Source: He et al. [63]. © 2017, American Chemical Society.

2.3.3 Truncated Tetrahedron

In 2016, Wang's group reported the first example of alkoxopolyoxovanadate-based SBU and its application in assembly to build metal–organic tetrahedrons [64]. They developed a new family of V₄E₆- and V₄F₄-type (V = vertex, E = edge, and F = face) metal–organic tetrahedrons using unprecedented Anderson-like

alkoxo-polyoxovanadate $[\text{V}_6\text{O}_6(\text{OCH}_3)_9-(\mu_6\text{-SO}_4)(\text{COO})_3]^{2-}$ polyanions as 3-connected SBUs.

A rational synthetic strategy was further developed to construct two supramolecular isomers based on polyoxovanadate (POV) organic polyhedra with tetrahedral symmetries (Figure 2.36) [65]. VMOP- α , a product of low temperature, has an extremely large cell volume ($470\,842\,\text{\AA}^3$), which is one of the top three for well-defined metal-organic polyhedra (MOPs). The “corner-to-corner” packing of tetrahedra leads to a pretty low density of $0.174\,\text{g/cm}^3$ with 1D channels about 5.4 nm. While for the high-temperature outcome VMOP- β , the cell volume is only $15\,513\,\text{\AA}^3$. The packing mode of tetrahedra is “corner-to-face,” giving rise to a high-density architecture ($1.324\,\text{g/cm}^3$ and the channel is 0.8 nm). Most strikingly, supramolecular structural transformation between VMOP- α and VMOP- β could be reversibly achieved by temperature-induced solvent-mediated transformation.

2.3.4 Triangular Prism

Metal-organic hosts provide an ideal platform to mimic the highly evolved and finely tuned natural photosynthetic systems [66]. When a quinhydrone (QHQ) cofactor was encapsulated in the inner pocket of cobalt triangular prisms, extensive electron delocalization and decrease of the over potential of the metal sites for proton reduction were induced by host-guest interactions and allowed the tandem reductions being combined to efficiently reduce nitrobenzene using active H-sources from the light activation of water (Figure 2.37).

Thiacalix[4]arenes, representing a versatile class of macrocyclic containers in supramolecular and molecular recognition chemistry, are structural analogs of calixarenes by replacing the methylene groups with sulfur linkages [67]. The thiacalixarene scaffold is a unique host with vast possibilities for functionalization not only at the upper and lower rim but also at the bridging sulfide groups. The corresponding sulfinyl and sulfonyl derivatives are accessible by direct oxidation of thiacalix[4]arene using the hydrogen peroxide or sodium perborate as the oxidant under mild condition. Thiacalix[4]arenes and their oxidized derivatives are excellent multidentate ligands for constructing polynuclear coordination complexes with various metal ions through their O- and S-donor atoms. For example, the shuttlecock-like tetranuclear clusters $[\text{M}_4(\text{calix})(\mu_4\text{-Y})]$ ($\text{Y} = \text{Cl}, \text{OH}, \text{H}_2\text{O}$, or CH_3OH) (Figure 2.38a), consisting of four metal ions, four acetates, a calixarene ligand, and a $\mu_4\text{-Y}$ ($\text{Y} = \text{Cl}, \text{OH}, \text{H}_2\text{O}$, or CH_3OH) were well stabilized with each metal center octahedrally coordinated by two phenolic O atoms, one sulfur atom or sulfonyl oxygen atom, two carboxylate O atoms, and one $\mu_4\text{-Y}$. This type of tetranuclear cluster subunit is a useful building block, serving as a unique vertex, to construct coordination cages through substitution of acetate with suitable bridging ligands.

In 2016, Liao's group obtained a trigonal prismatic coordination cage from solvothermal reaction of $\text{H}_4\text{L5}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and 2,5-thiophenedicarboxylic acid (H_2TDC) under a basic condition to confine them (Figure 2.38b) [68]. In the structure of $\text{Ni}_{24}(\text{L5})_6(\text{TDC})_{12}(\text{H}_2\text{O})_6$, three tetranuclear units are bridged by three

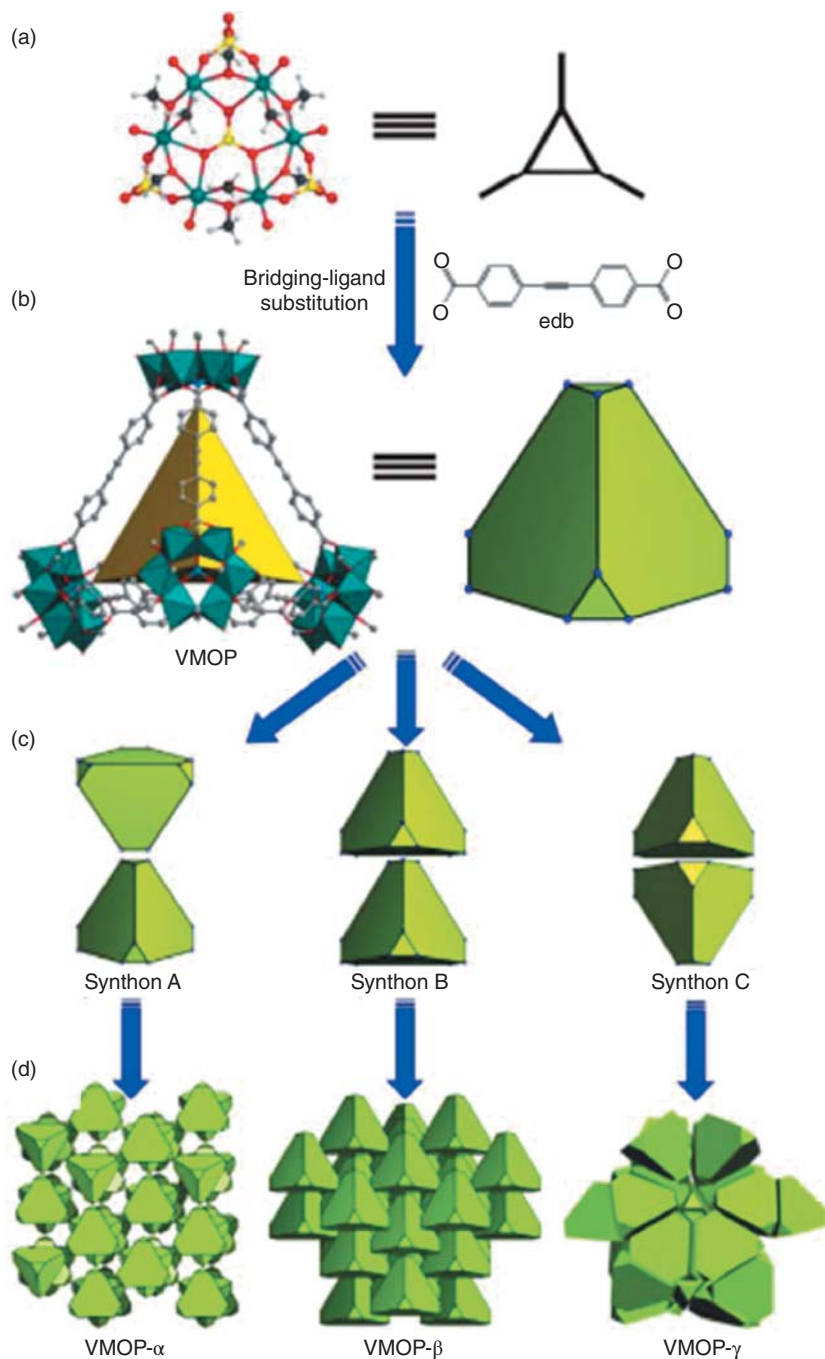


Figure 2.36 (a) Ball-and-stick view of the hexavanadate cluster that corresponds to a trigonal vertex. (b) A VMOP built from four $[V_6(SO_4)]$ clusters and six edb ligands with the dimension of 26.34 Å, which can be simplified as a truncated tetrahedron. (c) Three types of supramolecular synthon. (d) The diverse superstructures formed by the packing of truncated tetrahedra. Source: Gong et al. [65]. © 2019, Wiley-VCH.

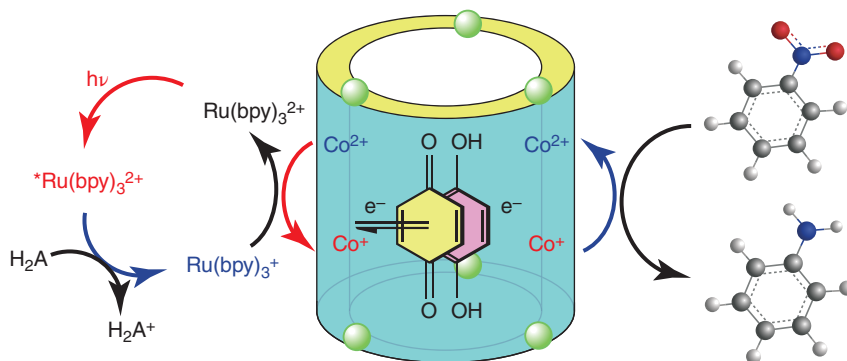


Figure 2.37 The construction of the host–guest charge-transfer systems for the combined light-driven proton reduction and biomimetic hydrogenation of nitrobenzene. Source: Zhao et al. [66]. © 2017, Wiley-VCH.

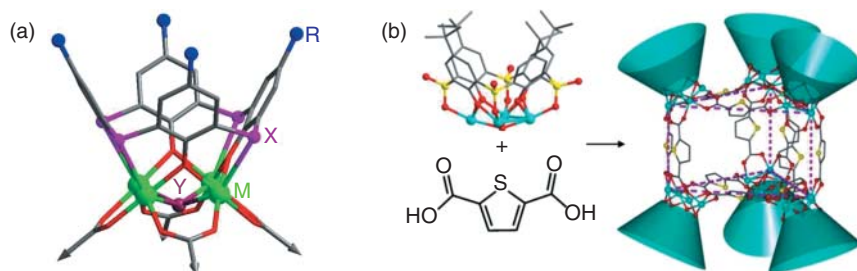


Figure 2.38 (a) Calixarene-based tetranuclear cluster building block possessing four points of extension, (b) assembly of trigonal prismatic coordination cage from 2,5-thiophenedicarboxylic acid. Source: Kumagai et al. [67, 68]. © 1997, Elsevier, © 2016, American Chemical Society.

TDC ligands into a coordination triangular framework and two such triangles are pillared by three pairs of TDC ligands to form a trigonal prism. The nanocage has an inner cavity of about $12.1 \times 12.1 \times 9.6 \text{ \AA}^3$ measured between opposite μ_4 -oxygen atoms of the coordinated water molecules, featuring five apertures on the side facets and two bases.

3D polyimidazolium cages may act as receptors for advanced applications, and it has been suggested that they can be considered a new generation of cryptands for the encapsulation of anions. However, the method of preparing large 3D polyimidazolium derived from conventional strategy, based on the cyclization reaction of imidazole precursors with di(bromomethyl)benzene derivatives or related halogenated alkanes, is found to be unsuitable. In 2018, Han's group employed a template-controlled strategy to accomplish large 3D polyimidazolium cages [69]. Given the simplicity and high efficiency of the described procedure, this strategy could be used in the future particularly for large-scale preparation of biomedical and functional materials.

They also reported the narcissistic and social self-sorting during the formation of homo- and heteroligand poly-NHC metal assemblies [70]. The formation of donor–acceptor $\pi \cdots \pi$ stacking interactions between the electron-rich and electron-poor ligand backbone groups was assumed to be responsible for the formation of the heteroligand assembly. Upon formation of the heteroligand assembly $[\text{Ag}_3(\mathbf{A1})(\mathbf{D1})](\text{BF}_4)_3$, a donor–acceptor interaction between the two central building blocks could be formed via aromatic stacking. This led to an additional stabilization for $[\text{Ag}_3(\mathbf{A1})(\mathbf{D1})](\text{BF}_4)_3$. An equimolar mixture of the imidazolium salts $\text{H3-A1}(\text{BF}_4)_3$, $\text{H3-B1}(\text{BF}_4)_3$, $\text{H3-C1}(\text{BF}_4)_3$, and $\text{H3-D1}(\text{BF}_4)_3$ reacted with a slight excess of Ag_2O in acetonitrile at 70 °C for two days in the dark. The reaction mixture containing three trinuclear silver(I) assemblies was obtained (Figure 2.39).

2.3.5 Cubes

Coordination-driven self-assembly acts as a powerful chemical approach for the construction of a series of 3D structures with precise geometries and sizes to mimic nature's activities. Up to date, many previous studies of tpy-M(II)-tpy only concentrated on linear and 2D structures. But few 3D supramolecular cages and prisms were reported using tpy -based building blocks. Giant 3D highly symmetric cubes $[\text{M}_{12}\text{L}_8]$ were self-assembled using three-armed tpy -based ligands constructed on adamantane, with the ligands acting as directing unit in the vertices and metal ions as edge gluing elements (Figure 2.40) [71].

In 2018, Cui's group selected two TPE-derived tetraamines as ligands for sub-component self-assembly of octanuclear Zn_8L_6 cages with tunable cavity sizes (Figure 2.41) [72]. The high π -electron density of assembled walls on the coordination cages endow them with prominent catalytic activity to promote a cascade condensation and cyclization to produce nonplanar 2,3-dihydroquinazolinones. Notably, the reaction is highly efficient with high rate enhancements (up to $k_{\text{cat}}/k_{\text{uncat}} = 38\,000$) and multiple turnovers compared to the bulk reaction mixture.

Sun's group reported a sensitive structural switching phenomenon during the stereocontrolled self-assembly of a group of $\text{Ln}_{2n}\text{L}_{3n}$ (Ln for lanthanides, L for organic ligands, and $n = 1, 2, 4$) compounds (Figure 2.42) [73]. This is the first time the boundary between the helical complex and the tetrahedral switches clearly revealed by using the eutectic structure. Three pairs of enantiopure ligands were synthesized by stepwise amide formation reactions according to an established method starting from dimethylpyridine-2,6-dicarboxylate, where the peripheral chiral amide groups were introduced first, followed by coupling of the central diamine spacers. Furthermore, M_8L_{12} -type supramolecular cubes were obtained for the first time by taking advantage of a concentration-dependent self-assembly process.

Researchers have also focused on how to assemble a desired cage with a certain geometry and size and to explore its inner cavities (e.g. host–guest chemistry). However, approaches for organizing cages into more complex or architecturally controlled frameworks through supramolecular interactions to achieve new

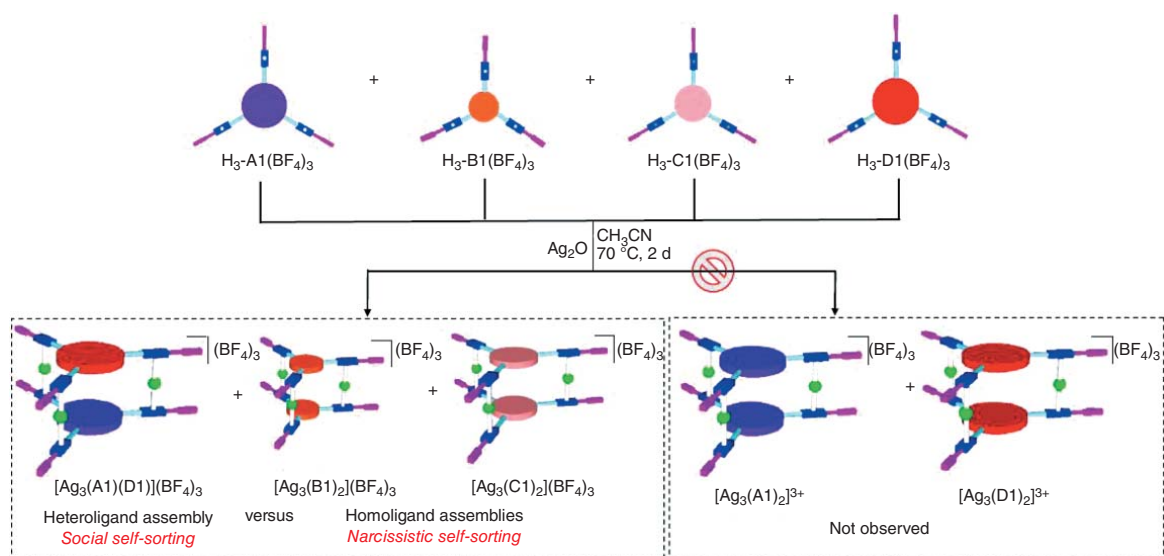


Figure 2.39 Self-sorting of organometallic assemblies from tris-NHC ligands with different backbones. *Source:* Wang et al. [70]. © 2018, Wiley-VCH.

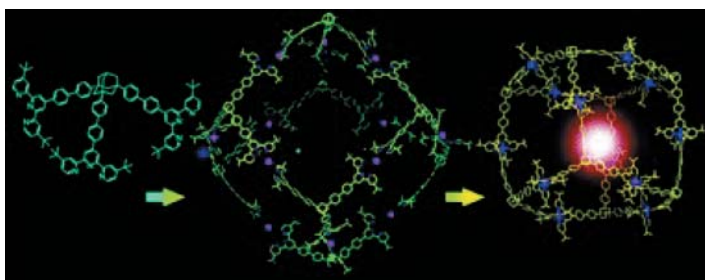


Figure 2.40 Self-assembly process of $[M_{12}L_8]$. Source: Wang et al. [71]. © 2014, The Royal Society of Chemistry.

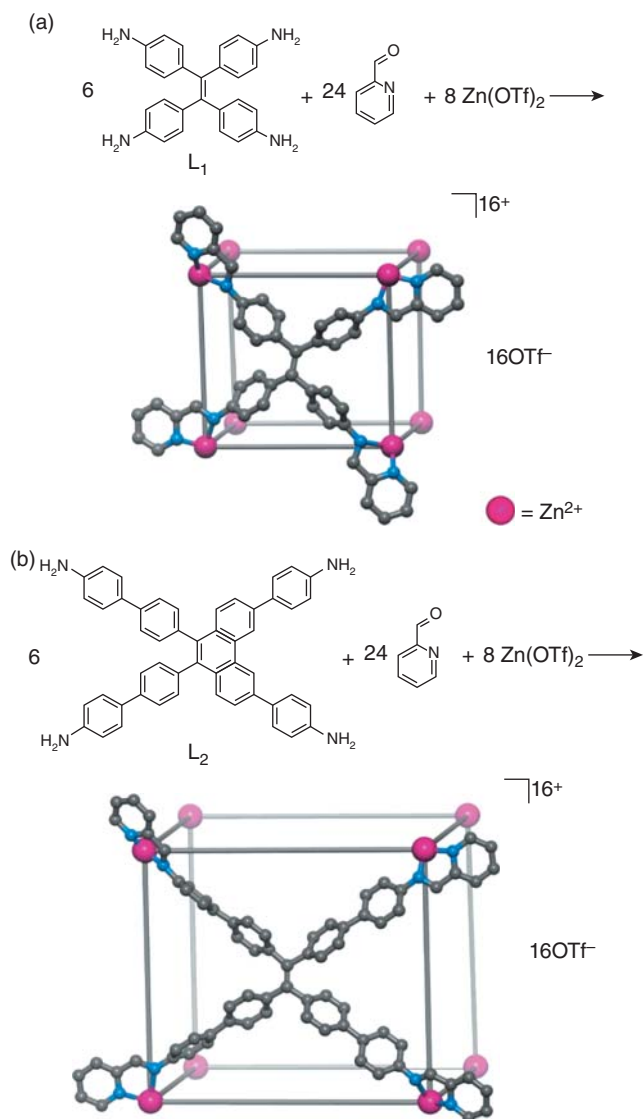


Figure 2.41 Subcomponent self-assembly. (a) TPE-1 and (b) TPE-2. Source: Jiao et al. [72]. © 2018, Nature Publishing Group.

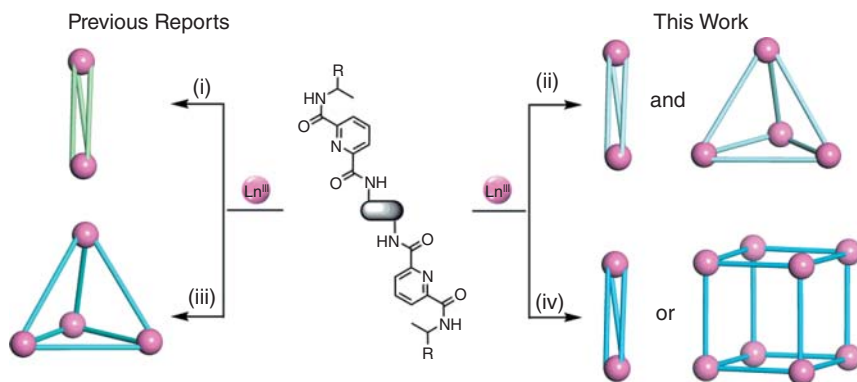


Figure 2.42 Self-assembly of L with $\text{Ln}(\text{OTf})_3$. Source: Li et al. [73]. © 2017, American Chemical Society.

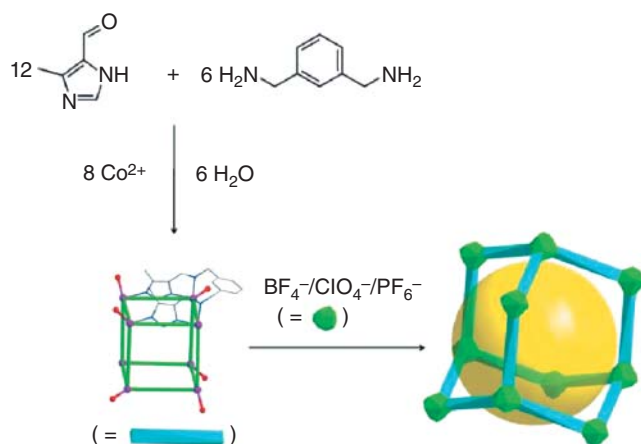


Figure 2.43 Illustration of the hierarchical self-assembly of the supramolecular framework. Source: Luo et al. [74]. © 2015, Wiley-VCH.

advanced functions are still unusual. Li's group have developed the solvothermal subcomponent self-assembly of metal-imidazolate coordination cubes, which further assembled hierarchically with anions to yield supramolecular frameworks (Figure 2.43) [74]. Each hierarchical architecture was assembled from small components (metal ions, amines, aldehydes, anions, etc.) through multiple interactions including covalent bonds, dative bonds, and weak $\text{C-H}\cdots\text{X}$ ($\text{X} = \text{O}, \text{F}, \text{and P}$) hydrogen bonds. The supramolecular frameworks with giant cavities of mesoporous size are capable of taking up large molecules (an organic dye, metal coordination cages, or the biomolecule vitamin B12), and thus, a procedure has been developed in which aggregations give rise to a desired function. A mesoporous supramolecule constructed from large aggregates of ordered structures will open up a general avenue for using such similar strategies and provide a potential platform for obtaining advanced crystalline materials.

As a continuing study of metal–imidazolate cages and gyroidal metal–organic frameworks (MOFs) constructed using the subcomponent self-assembly technology under solvothermal reaction conditions, Li's group successfully obtained a series of mesoporous supramolecular frameworks by the self-assembly of Co–imidazolate cages and inorganic anions (BF_4^- , ClO_4^- , and PF_6^-) through unconventional $\text{C-H}\cdots\text{X}$ ($\text{X} = \text{O}, \text{F},$ and π) hydrogen bonds. The combination of nickel(II) salts, 5-methyl-4-formylimidazole, *m*-xylylenediamine, and judiciously chosen inorganic anions resulted in a series of cages or cage-based products featuring diverse structures ranging from discrete cages to 2D sheets [75]. They anticipated that plenty of coordination polymers or MOFs with interesting structures and advanced functions can be constructed by this technology and approach.

In 2018, Zhang's group reported a Ti_8L_{12} cube, which could be further applied to encapsulate an octahedral $[\text{Ti}(\text{H}_2\text{O})_6]$ species based on host–guest interaction. The obtained $[\text{Ti}(\text{H}_2\text{O})_6]@\text{Ti}_8\text{L}_{12}$ complex was demonstrated to be stable both in solid and in solution states by X-ray diffraction and ESI-MS analysis (Figure 2.44) [76]. Compared with Ti_8L_{12} cube, $[\text{Ti}(\text{H}_2\text{O})_6]@\text{Ti}_8\text{L}_{12}$ complex exhibits slightly longer lived excited state due to the influence of $\text{Ti}(\text{H}_2\text{O})_6$ species. This work provides an interesting supramolecular model for the host–guest photophysical study.

2.3.6 Octahedron

MOPs constructed through the coordination of metal ions and organic linkers often display unique molecular recognition properties and glamorous enzyme-like reactivity due to their high symmetry, stability, confined microenvironment, and rich chemical/physical properties and have attracted considerable attentions. In 2008, Duan's group developed a new strategy for the preparation of octahedral nanocages (Figure 2.45) [77]. Metal-variable isostructural octahedral nanocages with considerable stabilities were constructed using a C_3 symmetric facial ligand with three tridentate coordinating sites and various metal ions. The disk-shaped ligand is composed of three quinoline groups by meta-substitution of a central benzene ring. The ligands were alternatively arranged onto four of the eight triangle faces of the S_4 symmetric octahedron defined by the six metal ions which were coordinated with two planar tridentate N_2O chelators in a mer configuration. Each quinoline group acted as both chromophore and fluorophore, thus serving as an N_2O tridentate coordinating site for the amide groups, which were introduced as trigger sites to achieve efficient guest interactions and a consequently good signal response. Once guest was encapsulated and formed donor-type hydrogen bonds with the amide groups, the electronic distribution on the conjugated backbone of the ligand was perturbed. As a result, host–guest interactions affected the charge transfer associated with the quinoline units and led to significant changes in the optical properties. Appropriately modulating the quinoline groups to pyridine groups, the several lanthanide ions based octahedral nanocages were gained. Each metal was coordinated by two N_2O tridentate chelating units and two bidentate coordinating nitrate anions.

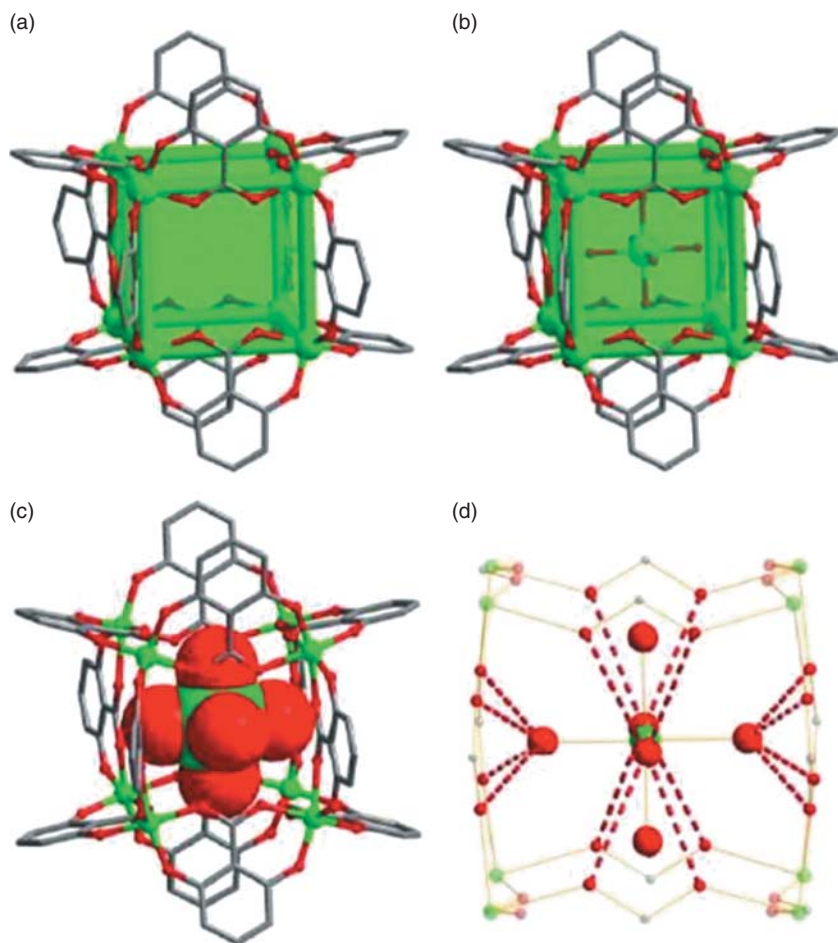


Figure 2.44 Structure of the free (a) Ti_8L_{12} cube and (b,c) $[\text{Ti}(\text{H}_2\text{O})_6]@ \text{Ti}_8\text{L}_{12}$. (d) Selected strong host-guest hydrogen bonds inside the cube of $[\text{Ti}(\text{H}_2\text{O})_6]@ \text{Ti}_8\text{L}_{12}$. Source: Zhu et al. [76]. © 2018, Wiley-VCH.

In particular, when using paramagnetic Gd^{3+} as metal node, each Gd^{3+} ion was coordinated to two tridentate chelators from two different ligands and one disordered nitrate anion and one disordered water molecule, which possibly led to the increase in the proton relaxivity [78]. The addition of glucosamine caused a significant decrease in the longitudinal relaxivity due to the decreased number of bound water molecules replaced by the coordination of glucosamine. Thus, such a robust gadolinium-based metal-organic octahedron achieved high selective and sensitive MRI responses toward glucosamine.

Except for the above octahedrons with a single metal as center or single ligands as edges, there are other octahedrons with special structures, such as POV-based octahedrons, heterometallic coordination octahedrons, and so on. V-based MOPs exhibit beautiful structures. Since 2016, Wang's group has reported a series of

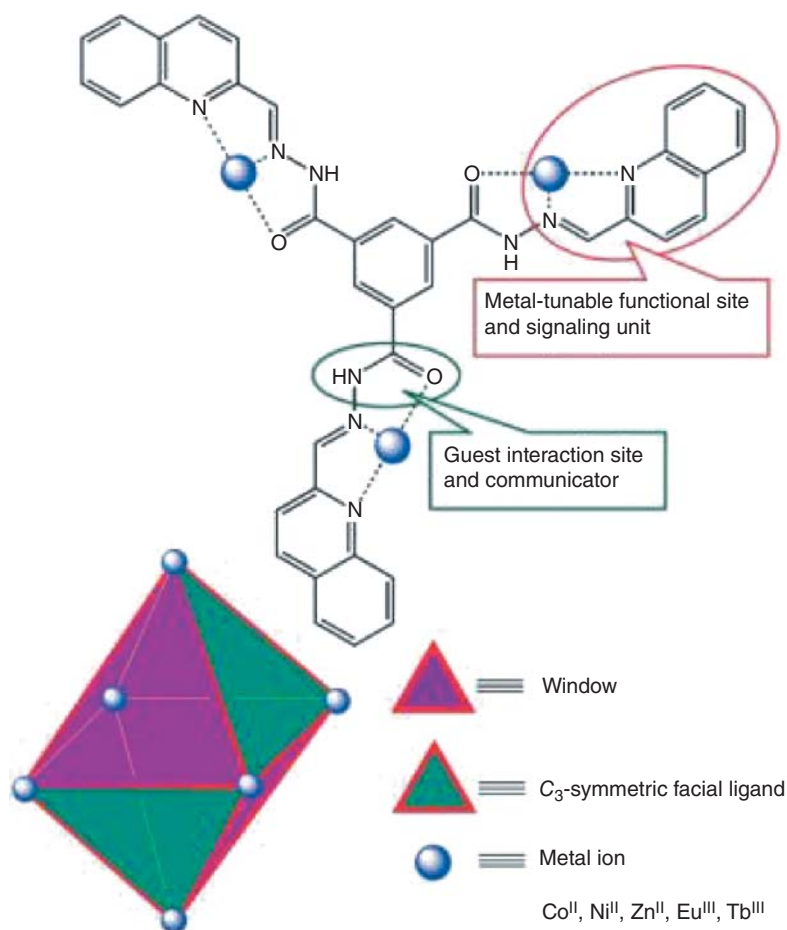


Figure 2.45 Structure of the ligand H_3L^1 and constitutive/constructural fragments of the functional octahedral cages. *Source:* He et al. [77]. © 2008, Wiley-VCH.

excellent structures built by POVs. They successfully synthesized three isostructural POV-based MOP under solvothermal conditions [79]. These compounds were characterized by single-crystal X-ray diffraction (SCXRD), PXRD, IR, TGA, and N_2 adsorption. By the same logic, **VMOP-4**, **VMOP-5**, and **VMOP-6** have been synthesized by employing different carboxylate ligands to assemble with vanadium–oxygen clusters (Figure 2.46) [80]. Though all of the three hybrids feature the same $[\text{V}^{\text{V}}\text{V}^{\text{IV}}_4]$ units, their structures exhibit differences changing from truncated triangular prism to truncated quadrangular prism to the octahedron, mainly depending on the nature of carboxylate ligands.

By introducing a tritopic tricarboxylate ligand of 1,3,5-benzenetricarboxylic acid (BTC) or 4,4',4''-benzene-1,3,5-triyl-tribenzoic acid (BTB), discrete calixarene-based coordination cages (Figure 2.47) were successfully synthesized through the self-assembly of metal ions, thiacalixarenes or sulfonylcalixarenes, and tricarboxylate

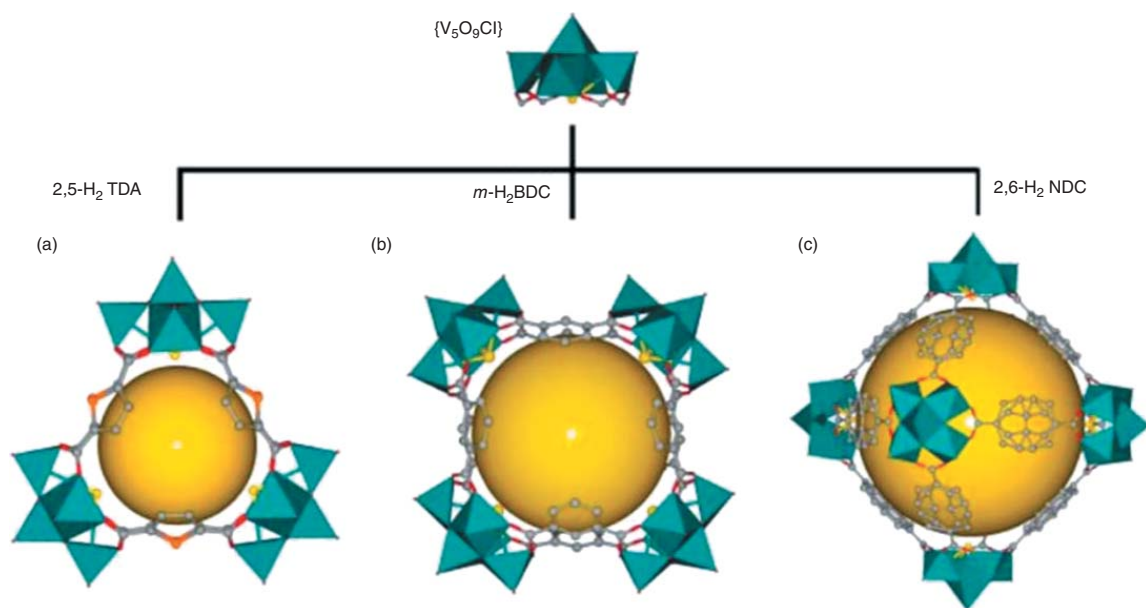


Figure 2.46 Schematic representation of the preparation of **VMOP-4** (a), **VMOP-5** (b), and **VMOP-6** (c), highlighting the ligand-directed structure diversities. *Source:* Zhang et al. [80]. © 2016, American Chemical Society.

ligands [81]. They adopted a octahedral geometry where six $[M_4(\text{calix})(\mu_4\text{-Y})]$ tetranuclear units were located on the vertices and eight tricarboxylate ligands resided on the triangular facets. Each $[M_4(\text{calix})(\mu_4\text{-Y})]$ unit was bonded by four tricarboxylate ligands through four quadrangle metal borders, while each tricarboxylate ligand was bonded to three $[M_4(\text{calix})(\mu_4\text{-Y})]$ units with its three carboxyl groups. The internal cavities of cages could be significantly increased from 0.55 to 2.75 nm³ when the tricarboxylate ligand was changed from BTC to BTB elongating with a phenyl ring, while the peripheral diameters of the cages were tunable from 3.3 nm for the BTC-bridged cages to 4.7 nm in BTB-bridged cages (Figure 2.47).

In addition to the abovementioned face-directed octahedral cages formed by the [6+8] condensation of $[M_4(\text{calix})(\mu_4\text{-Y})]$ units and tricarboxylate ligands, cages mimicking the shape of an edge-directed octahedron were also feasible when linear dicarboxylate bridging ligands were employed. Hong and coworkers [82] and Wang and coworkers [83] introduced 1,4-benzenedicarboxylic acid (1,4-BDC) ligands into this system and obtained a new edge-directed octahedral coordination cage from the self-assembly of cationic tetranuclear-metal building blocks and linear anionic ligands (1,4-BDC) through a [6+12] condensation process. Six $[M_4(\text{calix})(\mu_4\text{-Y})]$ units as the vertices were connected by 12 1,4-BDC ligands locating on the octahedron edges. The outer diameter of this type of cages was comparable to that observed in the BTC-bridged face-directed octahedral cages. However, they featured a larger internal cavity volume that is twice as big as that of corresponding BTC-bridged cages, possessing even wider apertures than those in BTC-bridged cages.

Recently, Cui's group further utilized a cage extension strategy to construct chiral permanent porous hydrogen-bonded frameworks (HOFs) (Figure 2.48) [84]. Multiple noncovalent interactions including hydrogen bonds and hydrophobic interactions between *tert*-butyl groups direct the hierarchical assembly of the cages into a permanent porous material. Moreover, the HOFs possess channels decorated with chiral phosphoric acid groups which make them as potential catalysts to promote [3+2] coupling of indoles with quinone monoimine and F–C alkylations of indole and aryl aldimines with high enantioselectivities.

Porous coordination cages (PCCs) are nanoscopic structures assembled by metal clusters and organic linkers, which bear intrinsic porosity in both solid and solution states. In 2018, Zhou's group reported a series of PCCs synthesized by the solvothermal method [85]. PCC-1 and PCC-2 hold similar carboxylic acid ligand and transition metal cluster. The difference between them comes from the charge. For PCC-2, anionic sulfate groups (SO_3^-) replaced *tert*-butyl groups (*t*Bu) of PCC-1, making the whole structure negatively charged. And PCC-3 cage was synthesized from pyridine ligand and noble metal knot (Figure 2.49). This cage shows distinct positive net charge and hydrophilic surface. These PCCs show different subcellular distributions as a result of their varied charge and affinity features. In addition, the PCC-2 cage was applied to study catalytic activity [86].

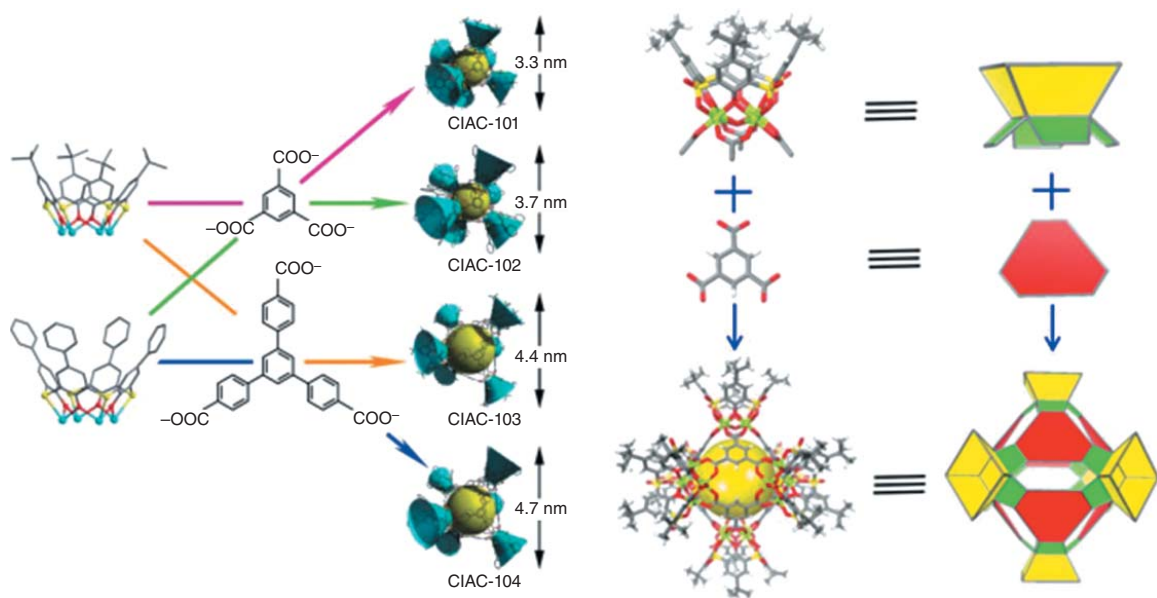


Figure 2.47 Assembly of octahedral calixarene-based coordination cages from $[M_4(\text{calix})(\mu_4-\text{Y})]$ and tricarboxylate ligands. *Source:* Dai et al. [81]. © 2012, American Chemical Society.

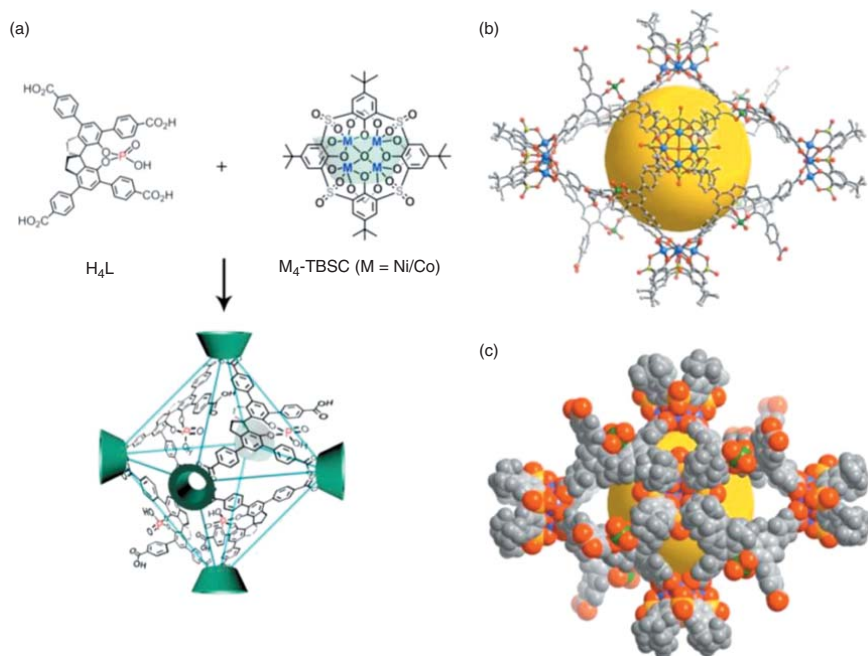


Figure 2.48 (a) Self-assembly of cages **1-Ni** and **1-Co** (only half of the HL^{3-} ligand is shown in the cage for clarity). (b) The single-crystal structure of the octahedral cage in **1-Ni**. (c) The space-filling model with an elliptical shape viewed along the short axis (sky-blue, Ni; green, P; yellow, S; gray, C; red, O). The cavities are highlighted by colored spheres. *Source:* Gong et al. [84]. © 2019, Nature Publishing Group.

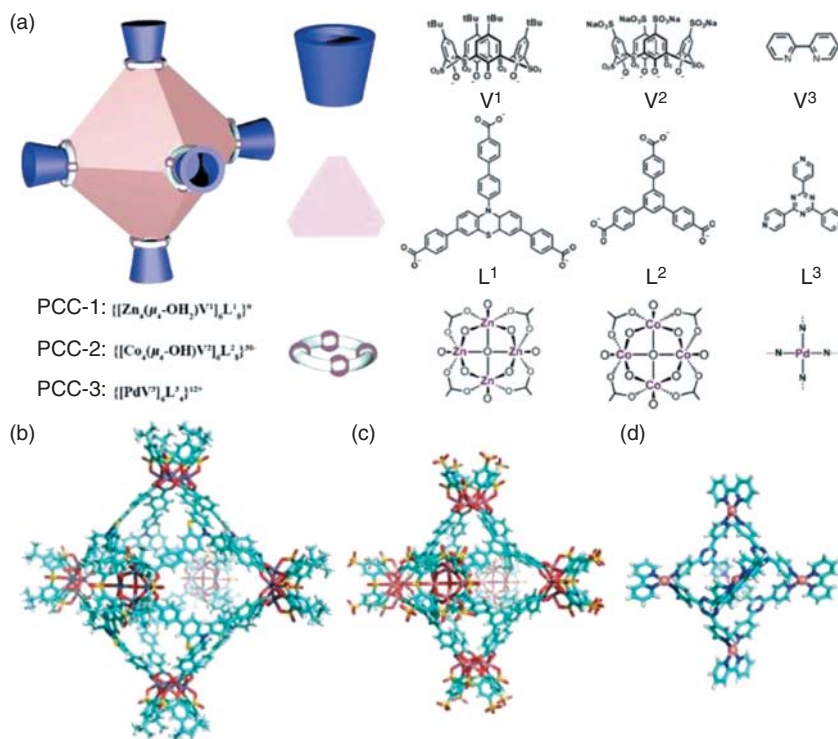


Figure 2.49 Schematic structure and X-ray structure of PCCs. (a) Cartoon of octahedron cage PCC and the cage components. Single-crystal X-ray crystal structure of (b) PCC-1, (c) PCC-2, and (d) PCC-3. Source: Fang et al. [85]. © 2018, Wiley-VCH.

2.3.7 Dodecahedron

Natural systems are capable of fabricating supramolecular ensembles with complexity and diversity via a spontaneous self-assembly protocol. The polyhedral coordination cage **1** with *O* symmetry and formulated as $[\text{Ni}_{14}\text{L}_{24}] \cdot 4\text{NO}_3 \cdot x\text{guest}$ [HL = *N*-methyl-1-(4-imidazolyl)methanimine] was obtained by the solvothermal reaction of 24 L and 14 Ni^{2+} or the one-pot assembly of 62 subcomponents, including 24 methylamine, 24 4-formylimidazole, and 14 Ni^{2+} (Figure 2.50) [87]. The 62-component assembly involved synchronized formation of both dynamic covalent bonds and coordination bonds, demonstrating the vigorousness of the sub-component self-assembly technique in complicated supramolecular self-assembly involving a large number of units. There are two types of Ni^{2+} centers in the nonsymmetric unit (Figure 2.50b): Ni1 adopts an octahedral geometry chelated by three L (located on the threefold axis), and Ni2 adopts a square geometry bound by four L (located on the fourfold axis). It is notable that the square Ni2 is unsaturated and probably acts as an active site for further attack by other molecules, providing the possibility of postmodification of the polyhedron. Li's group also described the control of assembly for a series of neutral cubic nickel(II)–imidazolate cages formulated as $\text{Ni}_8\text{L}_{12}\text{X}_4$ (**1**) by the variation of substituents and anions [88].

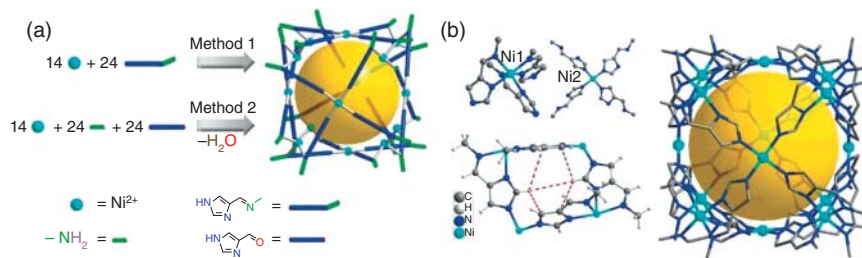


Figure 2.50 (a) Self-assembly of **1** by two methods. (b) Single-crystal structure of **1**. Source: Zhou et al. [87]. © 2012, American Chemical Society.

The structures of this multicomponent system are sensitive to both substituents and anions. A change of a substituent of imidazole ligand or anion switches the final structure observed across the ensemble of building blocks between cubic $\text{Ni}_8\text{L}_{12}\text{X}_4$ and dodecahedral $\text{Ni}_{14}\text{L}_{24}$ (**4**) cages. Cubic cage **1** can transform to a rhombic dodecahedral cage **4** in the presence of methylamine molecules. The transformation is irreversible and accompanies an obvious color change. The cage-to-cage transformation involving the stereoelectronic preference of metal ions and color is discovered, which might provide a unique example to understand the supramolecular dynamic transformation process.

Heterometallic coordination cages incorporating multiple metal centers have attracted increased attention on account of their novel properties and advanced function. In 2014, Su's group constructed nanosized heterometallic metal–organic cages $[\text{Pd}_6(\text{RuL}_3)_8]^{28+}$ (**MOC-16**) from photoredox-active and stereogenic Ru(II)-metalloligand and naked Pd(II) ion using a stepwise assembly approach (Figure 2.51) [89]. The metalloligand RuL_3 possesses spatially triangular C_3 symmetry, which was prepared by treating RuCl_3 with 2-(pyridin-3-yl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline (**L**) in a microwave method, while the naked Pd(II) has coplanar-squared D_4 symmetry. Crystal structures of the cages indicate that the cages show the shape of a rhombic dodecahedron defined by Pd_6Ru_8 centers and have 12 rhombic boxlike windows, with 6 Pd occupying the vertices of a truncated octahedron and RuL_3 lying on each face. The overall cage size was estimated to be $3.1 \times 3.4 \times 3.4 \text{ nm}^3$, possessing six Pd vertices with separations of 27.9, 29.5, and $29.5 \text{ \AA}$ and a large cavity of $5350 \text{ \AA}^3$. In this work, formation of racemic Δ/Λ - $\text{Pd}_6(\text{RuL}_3)_8$ (*rac*- Δ/Λ -**MOCs-16**) cages from mixed precursors has been accomplished. Large hydrophobic cavity and relatively narrow windows of the **MOC-16** cage were capable of a maximum of 18 phen guests inclusion, as well as 12 pyrene or anthracene molecules encapsulation.

Later in 2016, they developed a general approach to assemble enantiopure Δ - and Λ - $\text{Pd}_6(\text{RuL}_3)_8$ cages (Δ/Λ -**MOCs-16**) from pre-resolved Δ -**3** and Λ -**3** metalloligands [90]. This is the first example of constructing enantiopure MOCs from predetermined chiral metalloligands. X-ray crystallographic analysis verified the formation of absolute $\Delta\Delta\Delta\Delta\Delta\Delta$ and $\Lambda\Lambda\Lambda\Lambda\Lambda\Lambda$ homoconfigurations in Δ -**MOC-16** and Λ -**MOC-16**, respectively. Stereoselective separation of two types of racemic organic guests has been examined by ^1H NMR enantiodifferentiation

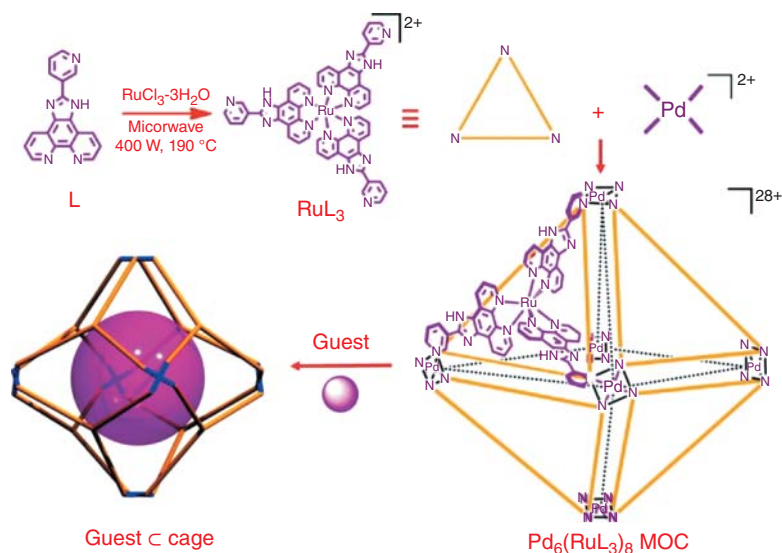


Figure 2.51 Stepwise assembly of $\text{Pd}_6(\text{RuL}_3)_8$ metal-organic cages via metalloligand strategy. Source: Li et al. [89]. © 2014, American Chemical Society.

experiments of host-guest diastereomers, which demonstrated better stereoselectivity toward chiral compound with C_2 symmetric chirality than that containing C^* stereocenters. In the same year, photocatalytic H_2 production has been explored using this metal-organic cage **MOCs-16**, containing eight Ru^{2+} photo-centers and six catalytically active Pd^{2+} -centers [91]. The efficient hydrogen production might derive from the directional electron transfers through multiple channels owing to proper organization of the photo- and catalytic multi-units within the octahedral cage.

Since enantiopure Δ/Λ -**MOCs-16** cages can provide achiral coordination space for chiral guest recognition and separation, such active MOCs could serve as dual-functional photoredox- and stereochemically active nanoreactors for stereoselective photoreactions. In 2017, they reported an unprecedented photoinduced regio- and enantioselective coupling of naphthols and derivatives using this Ru^{II} metalloligand-based cage (Figure 2.52) [92]. Naphthol guests encapsulated in the confined chiral coordination space undergo a regiospecific 1,4-coupling, rather than the normal 1,1-coupling, to form 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinones. This unusual dimerization constitutes a very rare example of asymmetric induction in biaryl coupling by making use of coordination cages with dual functionality-photoredox reactivity and stereoselectivity.

Recently, Su's group expanded this stepwise strategy to the stereolabile D_3 symmetry tris-chelate-Fe-type metalloligand, demonstrating the successful assembly of configurationally stable $[\text{Pd}_6(\text{FeL}_3)_8]^{28+}$ (Δ/Λ -**MOCs-42**) homochiral octahedral cages via strong face-directed stereochemical coupling and facile chiral-induced resolution processes based on stereodifferentiating host-guest dynamics [93]. Excellent enantiopurity of Δ/Λ -MOCs-42 is achieved via an in situ assembly process for

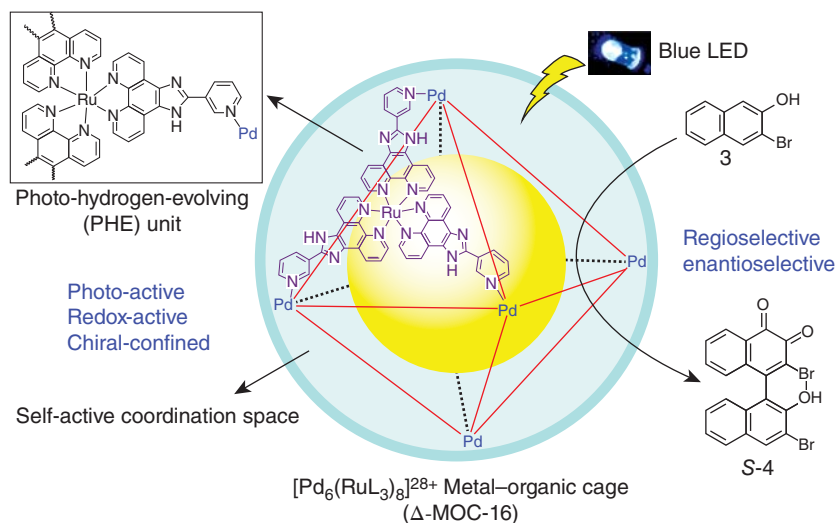


Figure 2.52 The photoinduced biaryl coupling of 3-bromo-2-naphthol to give its 3-bromo derivative proceeds with unique selectivity using homochiral **MOCs-16**. Source: Guo et al. [92]. © 2017, Wiley-VCH.

enantioresolution of *rac*-MOCs-42, of which the chiral-induced precipitation leads to kinetic resolution, while cocrystallization leads to thermodynamic resolution, both are superior to the normal post-assembly process. Recyclable enantioseparation of racemic atropisomers has been successfully accomplished, giving good ee value.

Cui's group utilized privileged ligand (Mn(salen)-derived dicarboxylic acids) as linear linkers and six Zn_4 -*p*-*tert*-butylsulfonylcalix[4]arene clusters as tetravalent four-connected vertices to synthesize a chiral octahedral cage **1**, which contained a large hydrophobic cavity of about $3944 \text{ \AA}^3$ decorated by catalytically active metallosalen moieties (Figure 2.53) [94]. In the single crystal, six shuttle-like $[Zn_4(\mu_4-O)(TBSC)]$ sit on the vertexes of the octahedron, and each Mn(salen) ligand acts as the edge bridging two vertices. Notably, this cage could efficiently catalyze the oxidative kinetic resolution (OKR) of racemic secondary alcohols with ee value up to 99.3%. The strategy of incorporating metallosalen into rigid polyhedral cage not only provides a hydrophobic cavity for concentrating reactants but also avoids the deactivation of catalytically active Mn(salen), resulting in obviously enhanced catalytic activities and enantioselectivities.

Similarly, a series of asymmetric metallosalen catalysts were incorporated into a highly stable Zr-based UiO-68 MOF via ligand exchange strategy. They demonstrated that MOFs with potentially acid-labile chiral catalysts could be synthesized via postsynthetic exchange [95]. This could not be synthesized through direct solvothermal synthesis. The single-M(salen)-linked MOFs display active and efficient catalytic activity for asymmetric cyanosilylation of aldehydes, ring opening of epoxides, OKR of secondary alcohols and aminolysis of stilbene oxide, and the mixed-M(salen) linker variants are active for sequential asymmetric alkene

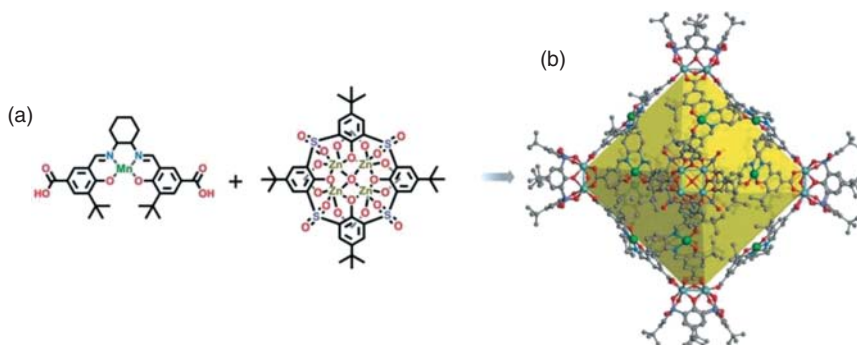


Figure 2.53 (a) Structures of the Mn(H₂L) linker and calix[4]arene-based metal node. (b) Single-crystal X-ray structure of the octahedral cage in **1** (brown, Zn; green, Mn; blue, N; red, O; purple, S; gray, C). For clarity, the coexisting Zn₄ clusters and the coordinated DMF and H₂O molecules in **1** are not shown. The cavity was highlighted by a yellow polyhedron. Source: Tan et al. [94]. © 2018, Wiley-VCH.

epoxidation/epoxide ring-opening reactions. Furthermore, the chiral MOF catalysts are highly enantioselective and completely heterogeneous and recyclable, which make them attractive catalysts for eco-friendly synthesis of fine chemicals.

2.3.8 Cuboctahedrons

In 2010, Zhou's group reported a porous coordination cuboctahedron nanocage constructed from the Cu paddlewheel clusters and bridged by the isophthalate moieties of 5-((triisopropylsilyl)ethynyl) isophthalic acid (TEI) (Figure 2.54) [97]. The CuTEI cage has eight triangular and six square windows. The bulky triisopropylsilyl (TIPS) groups left outside are highly likely to function as gates by undergoing thermal vibration within CuTEI, giving this material the thermosensitive gate opening property. The discrete CuTEI molecule tends to move around due to the lack of a strong holding force. Such movement leads to an amorphous structure. As a result, channels and openings toward the inner void in the perfect crystal model are partially reduced and blocked by the close packing of adjacent nanocages and extruded TIPS groups in the activated sample, yielding abundant "kinetically closed pores." By grafting with azide-terminated polyethylene glycol (PEG) through "click chemistry" or adhering to each other, they made the surface of the CuTEI cage functional [96].

2.3.9 Hexadecahedrons

Comparing to tricarboxylate ligands, 5-(pyridin-4-yl)isophthalate (PIP) ligand is also a tritopic ligand that is still able to connect metal ions in three directions but has a lower symmetry (*C*_{2v}). Liao and coworkers reported a novel *J*₁₇ Johnson hexadecahedronal coordination cage, in which 10 calixarene-based clusters are located on vertices and 16 PIP ligands are served as the triangular tiles (Figure 2.55) [98]. It is constructed by pillaring two square pyramids with a square antiprism. The 10 Ni₄(L1)(μ₄-Cl) units adopt three types of coordination modes: (1) two

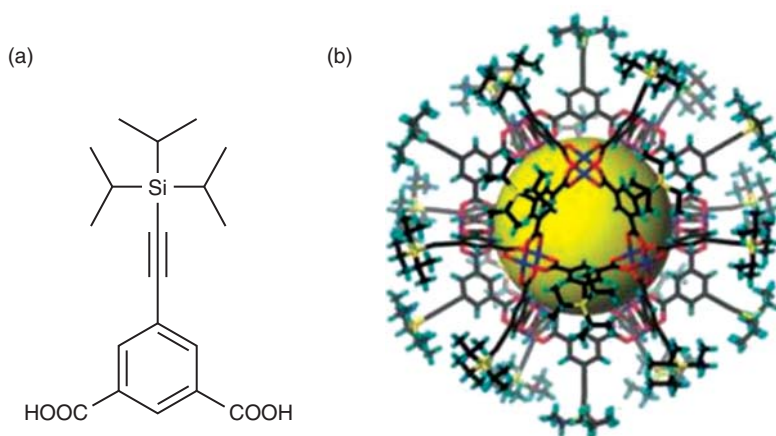


Figure 2.54 (a) Ligand TEI. (b) The porous coordination nanocage CuTEI. *Source:* Liu et al. [96]. © 2011, Wiley-VCH.

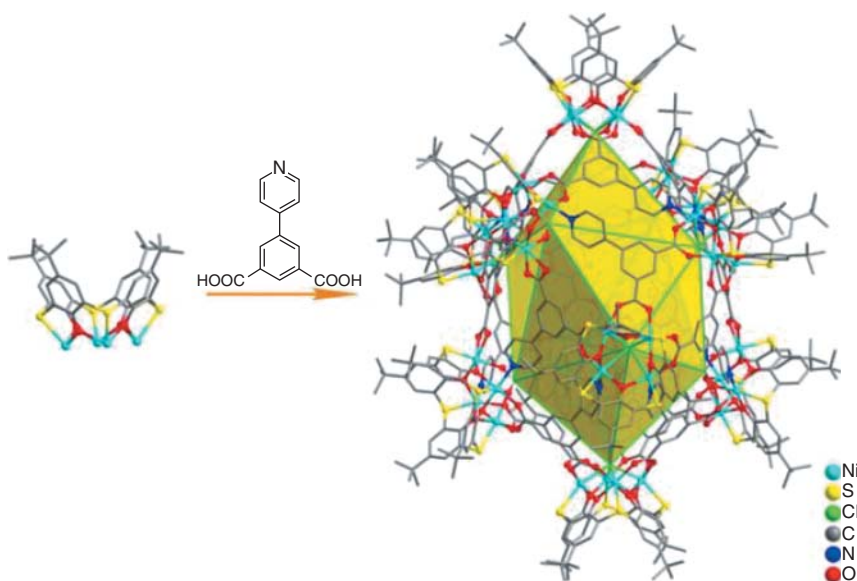


Figure 2.55 Assembly of J_{17} Johnson hexadecahedronal coordination cage from 5-(pyridin-4-yl)isophthalate ligand. *Source:* Hang et al. [98]. © 2016, American Chemical Society.

$\text{Ni}_4(\text{L1})(\mu_4\text{-Cl})$ units have the same coordination modes through chelated coordination to four -OCO- groups from four PIP ligands, forming the similar tetranuclear units established in the octahedral cages. Therefore, each nickel atom is surrounded by two oxygen atoms and one sulfur atom in **L1**, one chlorine ion, and two oxygen atoms from two adjacent PIP ligands. (2) For another four $\text{Ni}_4(\text{L1})(\mu_4\text{-Cl})$ units, each chelated to three -OCO- groups from three PIP ligands with two pyridines in two

PIP ligands coordinating to two nickel atoms, fulfilling the octahedral coordination geometry of each nickel atom. (3) In the remaining four tetranuclear units, there are only five PIP ligands coordinated to four nickel atoms, in which two $-\text{OCO}-$ groups bridge three nickel atoms, two pyridines coordinate to two nickel atoms separately, and one carboxylate group of the PIP ligand chelates a nickel atom.

2.3.10 Barrel-Shaped Cages

2.3.10.1 Calixarene Constructed Barrel-Shaped Cages

A novel calixarene-based wheel-like coordination cage, $[\text{Ni}_{18}\text{Cl}_6(\text{L1})_6(\text{MNA})_6]$ (H_2MNA = 2-mercaptonicotinic acid), was successfully synthesized by Liao and coworkers in 2018 (Figure 2.56) [99]. A unique shuttlecock-like $\text{Ni}_3(\text{L1})(\mu_3\text{-Cl})$ building block (Figure 2.56a) is formed by the coordination of an L1 to three nickel atoms through four phenolic oxygen atoms and three sulfur atoms and the three nickel atoms are further capped by a $\mu_3\text{-Cl}$ anion. The wheel-like entity consists of six $\text{Ni}_3(\text{L1})(\mu_3\text{-Cl})$ units bridging by six MNA ligands, forming a hexagonal prismatic inner cavity. The nickel ions are six coordinated by two phenoxy oxygen

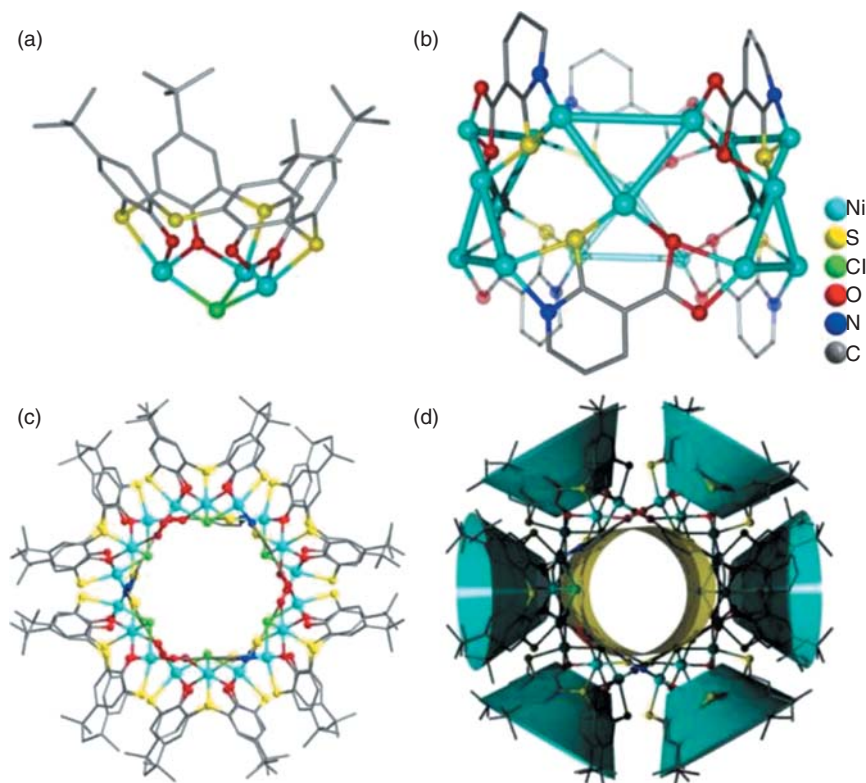


Figure 2.56 A shuttlecock-like $\text{Ni}_3(\text{L1})$ building block capped by a Cl^- anion (a) and crystal structure of calixarene-based coordination wheel (b–d). Source: Wang et al. [99]. © 2018, American Chemical Society.

atoms, one μ_3 -Cl, one sulfur atom from L1, and two oxygen atoms or one sulfur and one nitrogen or one sulfur and one oxygen of a same MNA ligand. The dimensions of the coordination cage are approximately $25.7 \times 27.5 \times 15.1 \text{ \AA}^3$, and the size of the hexagonal prismatic pore is about $9.0 \times 9.0 \times 13.3 \text{ \AA}^3$.

Besides the linear dicarboxylate ligand, the angular dicarboxylate ligand is also applied to construct calixarene-based coordination cages. When the linear 1,4-BDC ligand was replaced by 1,3-benzenedicarboxylic acid (1,3-BDC), barrel-shaped coordination cages were isolated [100]. They can be thought to form by cutting two opposite vertices of the BTC-bridged coordination octahedron, consisting four tetranuclear units that are bridged by eight 1,3-BDC linkers. Therefore, the internal cavity features two wide opposite square windows.

Calix[4]resorcinarene is another important subset of calix[4]arenes, featuring a bowl-shaped aromatic cavity that can be easily modified with various functional groups. Yang and coworkers demonstrated a design strategy for the assembly of metal-coordinated calix[4]resorcinarene cavitands and cages [101]. First, two new calix[4]resorcinarene cavitands with four chelating 2-(4*H*-pyrazol-3-yl)pyridine moieties at the upper rim were designed. The assembly of the calix[4]resorcinarene cavitands (TPC4R) with zinc ions and isophthalic acid analogs (Figure 2.57a) provided a series of intriguing isostructural metal coordinated cavitands $[\text{Zn}_4(\text{TPC4R})(1,3\text{-BDCs})_4]$ with highly deep cavities ranging from 10.7 to 12.5 Å. Each zinc atom is chelated by a 2-(4*H*-pyrazol-3-yl)pyridine group and two carboxylate groups from two 1,3-BDCs liners. By introducing tetracarboxylic acid analogs with appropriate spacers between two isophthalic acids (Figure 2.57a), a family of coordination cages was successfully achieved. The $[\text{Zn}_8(\text{TPC4R})_2(\text{Ln})_4]$ nanocages were constructed by connecting two $[\text{Zn}_4(\text{TPC4R})]$ units with four semiflexible tetracarboxylic acids (Figure 2.57b). The internal cavities of these coordination cages are tunable in shape and size by simple modification of the tetracarboxylic acids. With the increasing length of the tetracarboxylic acids, the internal cavities were changed from the spindle shape to ellipsoid shape with the longitudinal dimensions increasing from approximately 2.3 to 3.0 nm.

2.3.10.2 Dimetallic Clips-Constructed Barrel-Shaped Cages

In 2005, Yu et al. reported a series of nanosized cavity-containing metallomacrocycles by the self-assembly of the bipyrazolate ligands and dimetal (Pd/Pt) centers in aqueous solution [102]. During the assembly, the pyrazole spontaneously deprotonated and coordinated to the dimetal (Pd/Pt) centers and the pH value of the solution sharply decreased. However, these complexes exhibit high kinetic stability in acidic aqueous solution due to the strong bonding between the dimetal centers and the anionic ligand. Next, many fascinating 2D and 3D supramolecular architectures have been built based on these dimetallic clips [103]. In view of these highly stable dimetallic clips, they constructed homo- or hetero-metallomacrocycles and organo-heterometallic cages through a programmable, stepwise self-assembly process [104].

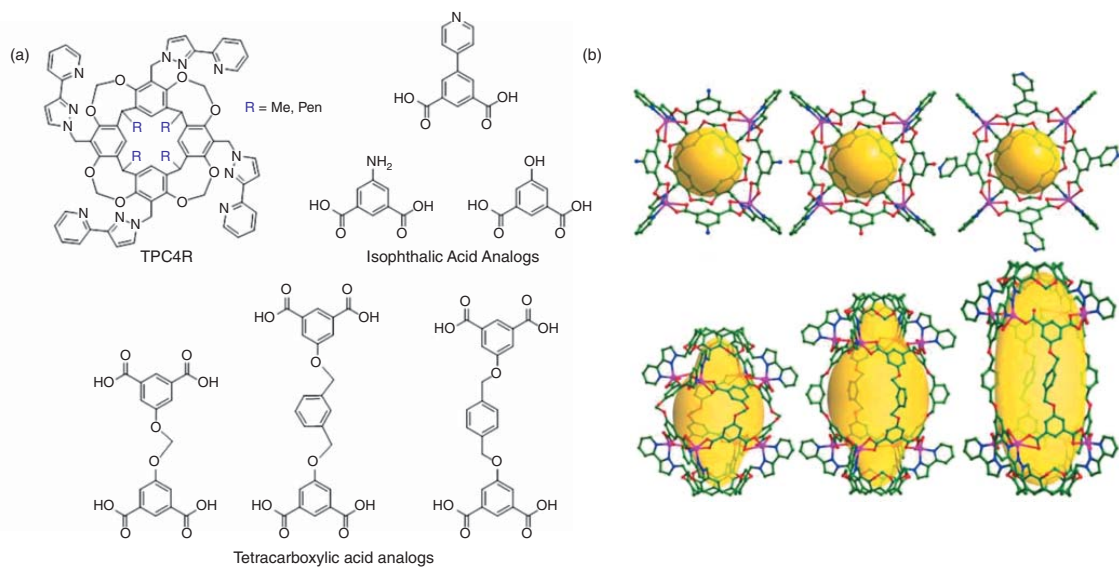


Figure 2.57 (a). Structures of TPC4R, isophthalic acid analogs, and tetracarboxylic acid analogs. (b). Structures of metal-coordinated cavitands $[\text{Zn}_4(\text{TPC4R})(1,3\text{-BDCs})_4]$ (top) and $[\text{Zn}_8(\text{TPC4R})_2(\text{Ln})_4]$ cages (bottom). *Source:* Pei et al. [101]. © 2017, American Chemical Society.

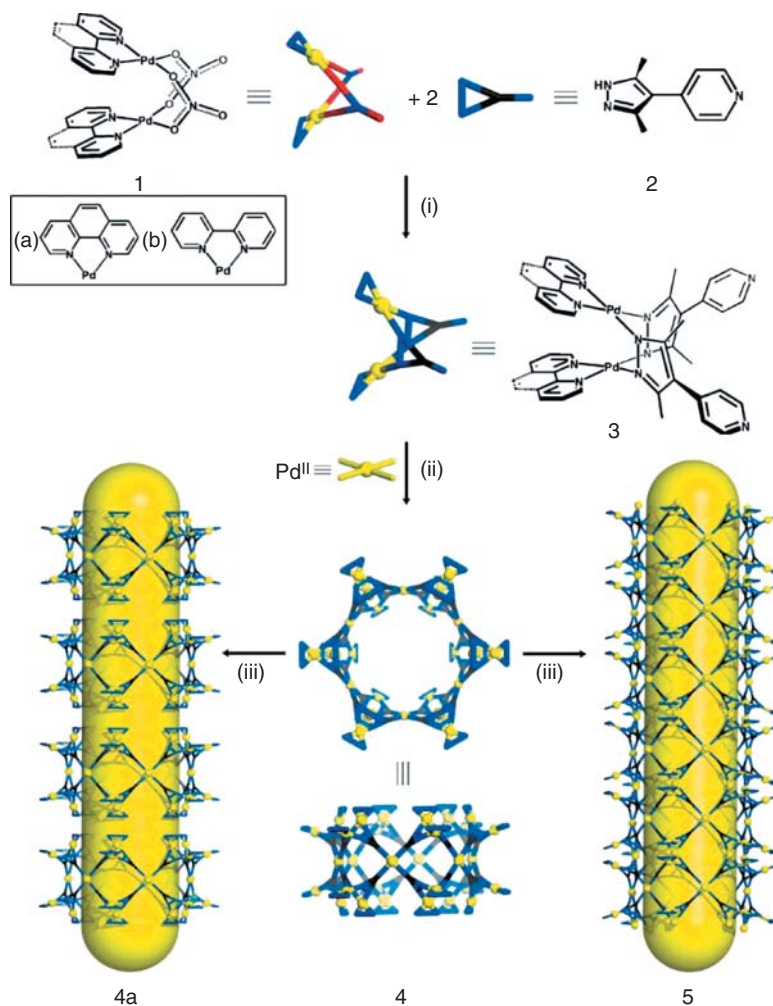


Figure 2.58 Representation for the hierarchical self-assembly of segmental (**4a**) and continuous (**5**) MMONTs starting from dimetallic clips **1** and ligand **2**. Source: Zhang et al. [105]. © 2015, Wiley-VCH.

Based on the similar dimetallic Pd clip, Sun's group reported the rational bottom-up self-assembly of discrete hexagonal nanobarrels **4** formulated as $[\text{Pd}_{30}\text{L}^1_{24}\text{L}^2_{24}]$ which consists of as many as 78 components (Figure 2.58) [105]. They reported the crystallization-driven conversion into segmental or continuous mesoporous MONTs (MMONTs) with a large out-diameter of up to 4.5 nm and a channel size of 2.4 nm. An unprecedented crystallization-driven cross-linking between discrete nanobarrel building units by spontaneous loss of the capping ligands to form infinite nanotubes was observed. Formation of either segmental or continuous MMONTs can be easily controlled by choosing appropriate starting materials.

2.3.11 Multiple Structural Cages

Although coordination patterns or chelating moieties are the same, there may be different structural cages achieved because of ligands with different length, angle, and so on. Some ligands assembling with metal centers can also form multiple structural cages in different conditions. It may be possible to successfully realize their transformations among different structures in replying external conditions. When researchers need to synthesis highly symmetric coordination polyhedra, the dinuclear paddlewheel unit is a popular building block [106]. The combination of a ditopic bridging ligand with 120° bend angle and such a dinuclear paddlewheel unit leads to a coordination cuboctahedron. In the same way, a 90° bend angle bridging ligand gave rise to a coordination octahedron. With the utilization of different bend angle ditopic bridging ligands and dinuclear metal nodes, coordination polyhedra with an odd number of faces and an odd number of vertices can be assembled.

Cage structures constructed by the low-coordination-number Cu^+ ion have been rarely explored, probably due to the redox instability of Cu^+ at ambient atmosphere. In 2009, Su's group reported the self-assembly of copper(I) cuboctahedral coordination cages with distinct counter-anions of varied shapes and sizes, which were constructed from the L ligand possessing a rigid triangular N_3 plane and the trigonal Cu^+ ion providing another kind of CuN_3 triangular face (Figure 2.59) [107]. Cu_4L_4 cage was considered to be a truncated tetrahedron with trigonal Cu^+ centers at the apices and triangular L ligands at the faces. These Cu^+ cages show host-guest-dependent redox activity. Complexes **1–2a** are stable and redox inert because of good adaptability of spherical ClO_4^- and I^- to the cuboctahedral cavity, thereby stabilizing the cage and protecting the four Cu^+ ions against O_2 attack. In contrast, complexes **3–4a** with linear CF_3SO_3^- or planar $\text{MeC}_6\text{H}_4\text{SO}_3^-$ are redox active and Cu^+ could be slowly oxidized to Cu^{2+} complexes with concomitant hydroxylation of the ligand, resulting in the structural conversion to the dinuclear complex **3b** and the tetranuclear complex **4b**.

As we can imagine, limited by geometrical constraints, a series of discrete $\text{M}_{3n}\text{L}_{2n}$ with different sizes of internal cavities may be obtained by changing the length,

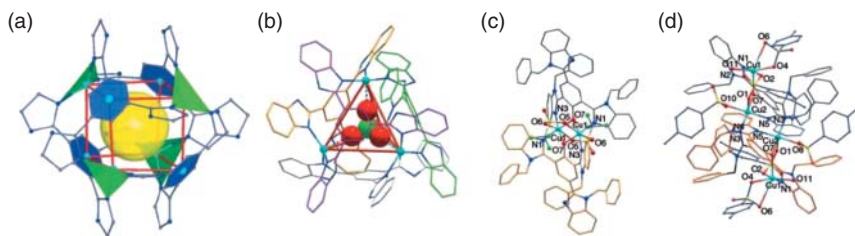


Figure 2.59 (a) Representation of the $[\text{Cu}_4\text{L}_4]^{4+}$ cages in **1–4a** showing a rectified cube. Benzyl groups and hydrogen atoms are omitted for clarity. The internal cavity is indicated by a yellow ball, and rectification is demonstrated by trigonal Cu^+ coordination plane and central benzene plane. (b) Crystal structure of **1a** showing tetrahedral arrangement of Cu^+ ions and ClO_4^- guest anion as a space-filling model. (c) Crystal structure of **3b**. (d) Crystal structure of **4b**. Source: He et al. [107]. © 2009, Wiley-VCH.

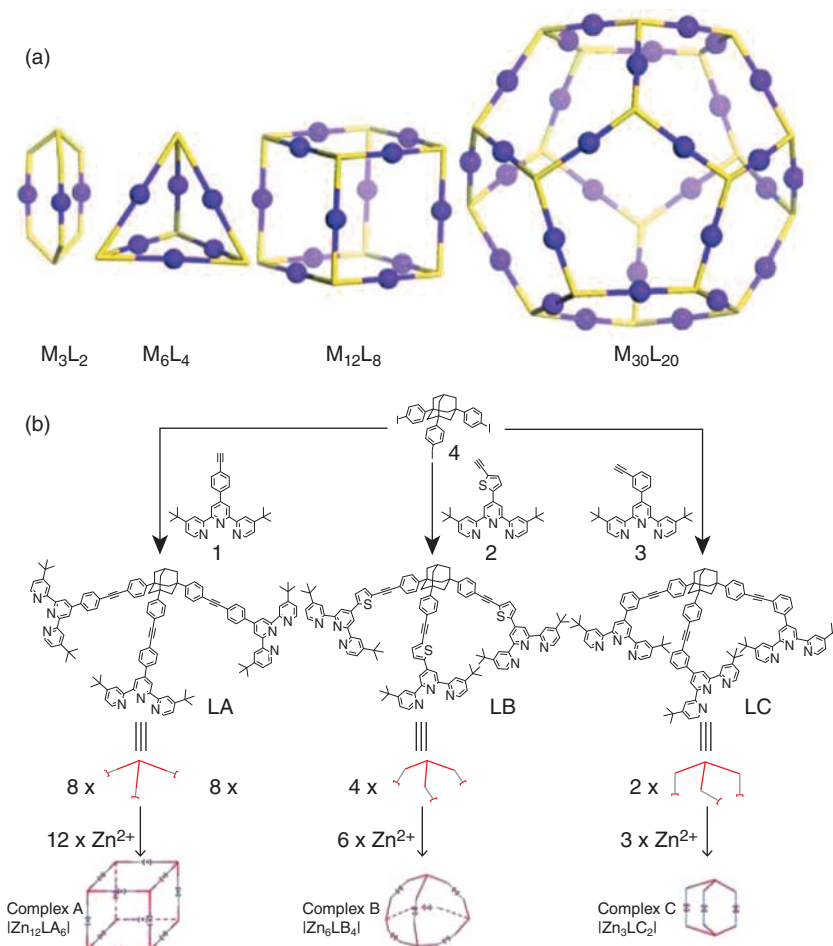


Figure 2.60 (a) Self-assembly of $M_{3n}L_{-2n}$ family with metals (M) as edges and tritopic ligands (L) as vertices, respectively. (b) Synthetic route of ligands and complexes $Zn_{3n}L_{-2n}$. Source: Wang et al. [108]. © 2014, American Chemical Society.

angle, and rigidity of adamantane-based terpyridine ligand (Figure 2.60a). Thus, Li's group successfully achieved the construction of the trigonal bipyramidal-like dimer (M_3L_2), tetrahedron (M_6L_4), and cubes ($M_{12}L_8$) with the ligands as corner directing units and Zn^{2+} metal ions as edges by changing the angles of the linkers between adamantane and tpy (Figure 2.60b). Meanwhile, they also explored the behavior of self-sorting among the binary mixtures of LA and LC or LB and LC [108].

Chiral coordination cages feature both chirality and defined inner space, providing advanced molecular materials. However, such resulting cages tend to form racemic crystals or racemic conglomerates of homochiral crystals in the absence of chiral additive. Thus, Li's group reported the subcomponent self-assembly of a series of emerging polyhedral metal–imidazolate cages (Figure 2.61), resulting from the self-assembly of 72 components featuring an unusual tetartoid (tetragonal

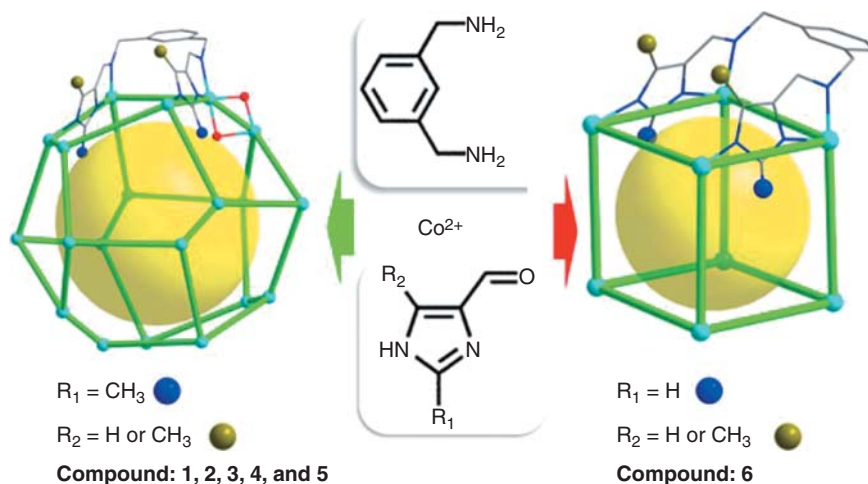


Figure 2.61 Subcomponent self-assembly of metal-imidazolate tetartoids and cubes.
 Source: Luo et al. [109]. © 2018, American Chemical Society.

pentagonal dodecahedron) geometry [109]. Spontaneous resolution of racemic tetartoidal cage into a conglomerate of homochiral crystals is confirmed by both SCXRD analyses and solid-state CD spectra. Additionally, enantiomerically pure $\Delta\Delta\Delta\Delta$ -1 and $\Lambda\Lambda\Lambda\Lambda$ -1 can be obtained by homochiral crystallization through chiral induction of (D)- and (L)-enantiomers of menthol, providing a way to prepare homochiral cages by chiral induction. The 2-methyl group on the imidazolyl plays a structure-direct role for forming the tetartoidal cages, while cubic cages are obtained in the absence of steric effect of the 2-methyl group.

Bridging-ligand-substitution reaction and “polyhedral projection labeling” provide excellent synthetic and theoretical analysis strategies for the preparation and isolation of novel MOPs based on a square four-connected $\text{Cu}_2(\text{O}_2\text{CR})_4$ unit and various carboxylate ligands acting as building blocks [110]. In the nine kinds of MOPs as shown in Figure 2.62, we can divide them into two types. With metal nodes being viewed as vertices and ligands as edges, the cuboctahedron was found in MOPs 1, 2, 3, 5, 6 and 9, and octahedron was associated with 4 and 8 (Figure 2.62). The ligands can be arranged and linked properly to form new polygonal rings, with each corner considered as a ligand.

Various stimuli has been used to control supramolecular structural transformations, including light, electricity, temperature, concentration, ligand and metal substitution, host-guest interaction, and so on. The Yuan's group reported a special example of solvent-responsive structural transformation process between two V_{24} metal-organic nanocapsules (MONCs) (Figure 2.63) [111]. The geometries of these two nanocapsules are completely different, one displays an expanded ball-shaped molecular cage (V_{24} -ball) with the cavity of about $1400 \text{ \AA}^3$, and another one presents an octahedral cage (V_{24} -oct) with the cavity of about $1000 \text{ \AA}^3$. Interestingly, a solvent-controlled interconversion can be reversibly realized following the addition of different solvents. As the structural transformation, the quasi-isomers

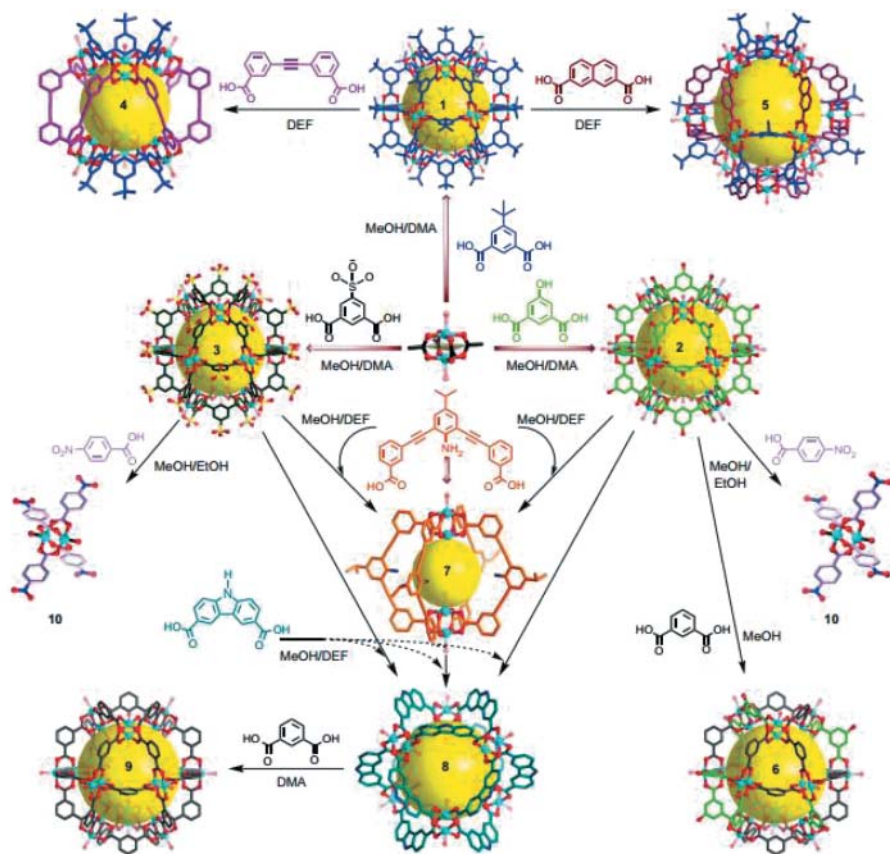


Figure 2.62 Schematic of the syntheses and crystal structures of compounds 1–10.
Source: Li et al. [110]. © 2010, Nature Publishing Group.

demonstrate obviously different magnetic properties. This research work provides a new strategy for the design and synthesis of the new isomers and quasi-isomers and informs the relationship between transformation process and structural property.

In 2018, the first four examples of nanoscale Goldberg MOPs constructed by isolation of a pentagonal $[\text{WV}_5\text{O}_{11}(\text{SO}_4)_6]^{8-}$ cluster reported by Wang's group [112]. The largest Goldberg **MOP-4** exhibits a diameter of 4.3 nm and can trap fullerene C60 molecules in its interstitial cavities.

2.3.12 Other Cages

In 2014, Yu's group reported a new class of gold(I)-containing metallasupramolecular cages $[\text{Au}_8\text{L}_2]$ (L = tetrakis-dithiocarbamato-calix[4]arene) featuring a quadruple-stranded helicate structure (Figure 2.64) [113]. The flexible polydentate bridging dithiocarbamate ligands functionalized on the upper rim of the bowl-shaped calix[4]arene have been employed to coordinate to four sets of dinuclear gold(I) units to form a 3D cage, $[\text{Au}_8\text{L}_2]$. In the metal–organic gold(I)-centered

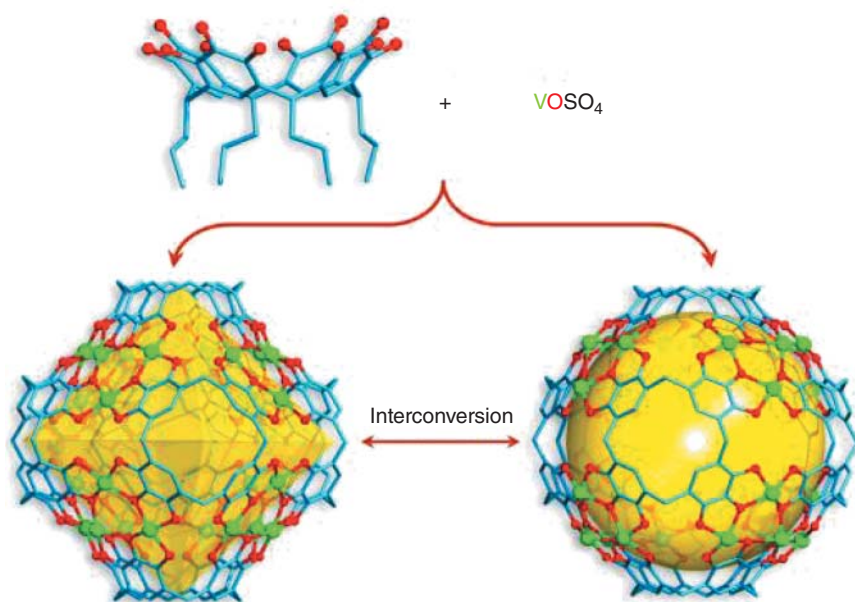


Figure 2.63 Controlled self-assembly and interconversions of V₂₄ capsules. Chemical structure of hexameric pyrogallol[4]arene V₂₄ octahedron and V₂₄ ball from 6 PgC3 ligands and 24 vanadium ions. Vanadium is green, oxygen red, and carbon blue. *Source:* Su et al. [111]. © 2018, Nature Publishing Group.

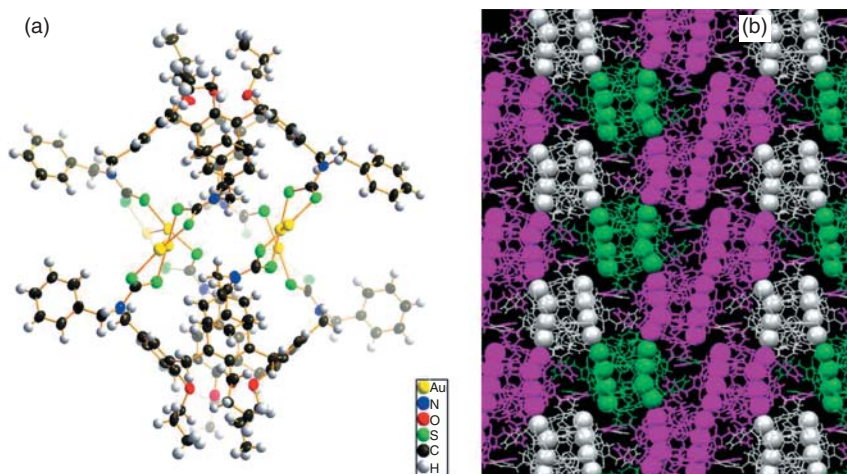


Figure 2.64 Au^I...Au^I bonding interaction driven the self-assembly from [Au^I...Au^I]...coupled cages (a) to the cage-built 2-D [Au^I...Au^I] arrays (b). *Source:* Jiang et al. [113]. © 2014, American Chemical Society.