Molecular Squares, Boxes, and Cubes

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INTRODUCTION

Molecular squares, boxes, and cubes featuring transition-metal corners are the focus of tremendous activity in contemporary synthetic coordination chemistry. Their design and study comprise a promising subfield of inorganic and organometallic supramolecular chemistry. The interest in these objects is partly aesthetic: they are beautiful high-symmetry assemblies. The interest is also functional: the assemblies contain cavities that are capable, in principle, of encapsulating, and then sensing, processing, or transporting useful molecules or atomic ions—in other words, all the functions associated with organic host–guest chemistry.

Why coordination chemistry? And why discrete molecules? Actually, metal-free squares and boxes exist, albeit without the ubiquity of the metal-containing systems. Notable examples include the various viologen-derived cyclophanes or boxes of Stoddart and coworkers,^[1]—clear antecedents of many molecular squares. What metal ions offer are a readily accessible range of angles for ligand-metal-ligand subunits (including right angles, which is difficult to achieve with carbon chemistry), structural predictability based on well-known metal-ion coordination motifs (linear, octahedral, square planar, etc.), a range of charges, a range of ligand-binding capacities, and, perhaps most importantly, a propensity to engage in highly efficient directed assembly. Metals, of course, can also usefully expand the range of redox, photophysical, and catalytic properties displayed by supramolecular assemblies. In principle, squares and other structures can be assembled not only as discrete molecules, but also as porous two- and three-dimensional arrays or coordination polymers. While the array strategy clearly works^[2] a common complication is the formation of interpenetrating grids that eliminate most of the void volume associated with isolated cavities. Preassembly of discrete squares and related structures avoids the problem; indeed, to date there are no examples of extended catenation, the molecular equivalent of grid interpenetration.

An important idea suggested by the chemistry of coordination polymers is higher-order assembly of squares and other structures into large void-volume, high-porosity

molecular materials. This can be done surprisingly easily using van der Waals interactions (which, of course, are large for large molecules), although more elaborate and controllable strategies are emerging. In any case, the notion of porous molecular materials and the stacking of cavities to make uniformly sized channels is one that is receiving increasing attention as supramolecular coordination chemistry evolves from a mainly synthetic effort toward one that also strongly focuses on function.

Finally, the connection to nanotechnology cannot be overlooked. The cavity sizes of existing molecular squares, boxes, and cubes extend from about 0.4–5 nm, as measured along the cavity edges. These, of course, are the right dimensions to couple to other nanoscale objects or simply to function as building blocks for periodically nanostructured thin films or other materials. In these contexts, descriptions of functional supramolecular assemblies as nanoreactors, nanofactories, nanogates, nanotemplates, and so on, are appropriate.

MOLECULAR SQUARES

Some Early Examples

The first metal-containing molecular squares appeared in 1983.^[3] They featured $M(\text{CO})_4$ ($M = \text{Cr}, \text{W}, \text{or Mo}$) corners and $\text{P}(\text{OCH}_2)_3\text{P}$ ligand edges, **1** (Fig. 1). While these compounds are potentially capable of behaving as hosts for small molecular guests, interest in squares as receptors or hosts really did not take hold until 1990 when an ethylenediamine Pd(II) square featuring 4,4'-bipyridyl edges, **2**, was shown to function as a hydrophobic host for organic guests in water as solvent.^[4,5] Aqueous solubility was engendered by the square's 8+ charge and by the use of nitrate as a counterion. Nuclear magnetic resonance (NMR) titrations revealed association constants on the order of 10^2 for planar, electron-rich aromatic species, while aliphatic compounds showed little propensity to associate. The difference was attributed to the ability of the electron-rich, aromatic guests to form charge-transfer complexes with the bridging bipyridine ligands of the molecular square. Extension of the chemistry to Pt(II) was

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Fig. 1 Two of the earliest examples of tetrametallic molecular squares.

90 followed by the observation that for longer edges, closely
 91 related square and triangle structures can coexist in
 92 dynamic equilibrium. The equilibrium is concentration-
 93 dependent, with entropy favoring triangles, because they
 94 assemble from fewer components.^[6] A related transfor-
 95 mation, observed with a Pd(II) square and a pair of
 96 dimeric Pd(II) loops in D₂O as solvent, is formation of two
 97 copies of a nonsquare catenated assembly.^[7] The driving
 98 force for catenation is primarily the enhancement of
 99 dispersion interactions accompanying van der Waals
 100 contact of pairs of ligands.^[8] Formation of the catenated
 101 species should occur most readily in solvents that offer
 102 comparatively little stabilization via dispersion interactions.
 103 Another early approach, since generalized to more than
 104 70 different squares, triangles, prisms, rectangles, and
 105 dodecahedra, also relies upon Pd(II) and Pt(II) as corners
 106 but with chelating diphosphine ligands in place of
 107 ethylenediamine to provide solubility and enforce subse-
 108 quent *cis* coordination.^[9] The combination of corner units
 109 with difunctional imine edges leads to octa-cationic
 110 squares. The variety of ligand edges used ranges from
 111 porphyrins, luminescent perylene diimides,^[10] and redox-
 112 active ferrocene derivatives,^[9] to chiral linkers, such as
 113 phosphine-functionalized binaphthols.^[9] With chiral
 114 squares, one could easily envision applications such as
 115 enantioselective catalysis, separation, or sensing. Indeed,
 116 several examples of moderately enantioselective sensing
 117 with a chiral-ligand-containing square were reported.^[11]
 118 Elaboration of squares via functionalization of the phos-
 119 phine ligands is also possible. In one instance, squares
 120 featuring pendent crown ethers were prepared.^[9]
 121 What about neutral squares? By using acetylides or
 122 phenylides as edges, and forming metal(II)-carbon lin-
 123 kages, squares lacking net charges can be formed.^[12]
 124 Other routes to neutral squares are described below.

Assembly Principles

Why has the square motif proven so popular in supramolecular coordination chemistry? First, with the right set of ancillary ligands, octahedral and square planar coordination geometries provide pairs of ligation sites oriented at 90° with respect to each other. Second, square formation is typically accomplished with high efficiency, usually in a one-pot reaction. The one-pot formation process is often termed “self assembly,” although a more accurate term might be “directed assembly,” which is the combination of *cis* coordination sites and edge-ligand rigidity, providing the necessary initial directions or instructions.

There is more to the process, however. In nearly every case, the square represents a thermodynamic rather than kinetic product. The reasons are several. The open ligation sites that characterize dimeric, trimeric, and noncyclic oligomeric species are temporarily filled by weakly coordinated solvent molecules; this, in turn, tends to keep these intermediates in solution. In addition, coordinate-covalent bonds tend to be labile, at least at elevated temperatures. Mistakes in the assembly process can be corrected, and assembly can continue until formation of the desired square molecule is complete (Fig. 2).^[13] If the completed tetrametallic cycles are less soluble than open oligomers (often the case), precipitation of the cycles can pull the reaction toward completion. Also favoring reaction completion (i.e., high yields) is the enthalpy released upon replacement of a weak metal-solvent bond with a somewhat stronger metal-ligand (edge) bond. For several reasons, therefore, the choice of solvent is important in square synthesis.

Ignoring occasional complications due to triangle formation, the directed assembly approach works well with rigid difunctional ligands. What about flexible

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Squares can also be obtained by linearly coordinating bent (right-angle-containing) difunctional ligands. A metal ion obviously suggests different applications and different ways of assembling multisquare structures.

Fig. 3 Two examples of porphyrinic molecular squares. In **3**, the *cis* orientation of pyridyl groups, combined with the *trans* binding of the Pt metal units, leads to a coplanar orientation for the four porphyrins. The *trans* configuration of dipyrityl porphyrins in **4** leads to a nominally cofacial arrangement of opposing pairs of porphyrins. For the particular example shown, however, steric demands force the porphyrins to fold in to yield an almost flat structure.

Another alternative square motif is based on carboxylate coordination of triply and quadruply bonded dimeric corner units.^[15] The coordination geometry requires the metal–metal bond axis to be oriented normal to the plane of the square or, in some cases, triangle. An interesting consequence is that monodentate ligand coordination sites at the ends of the dimetallic units can often be accessed, permitting squares to be linked “vertically” in extended structures. Examples of squares based on Mo_2^{4+} , Ir_2^{4+} , and Rh_2^{4+} were reported. In solution, several show multistep metal redox reactivity that is reversible on an electrochemical time scale. Unfortunately, on a longer time scale, the ease of oxidation together with further chemical reactions renders some of the squares structurally unstable in air or in oxygen-containing solutions.

A third alternative simply uses ferrocenes as walls in cyclophane-like structures.^[16] The ferrocenyl units typically are linked via flexible hydrocarbon chains appended to cyclopentadiene ligands. In other words, covalent carbon–carbon bonds rather than coordinate–covalent metal–nitrogen, –carbon, –oxygen, or –phosphorous bonds are used.

202 Porous Molecular Solids

Remarkably, almost all molecular squares crystallize as one-dimensional channel-containing materials, with square cavities defining the channel width. For smaller squares, microcrystallinity typically persists when the squares are cast as thin films. For larger squares, such as porphyrin squares, thin films are more typically amorphous. Films of both kinds, however, can display good microporosity. Obviously, facilitating porosity for neutral squares is the absence of potentially channel-blocking counterions. Many charged squares, however, also feature open channels with counterions positioned above and below metal corners rather than within cavities. (An interesting idea yet to be examined is that the cavity fields generated by the spatially separated charges may engender catalytic activity in a fashion reminiscent of many reactions in zeolites.)

An important characteristic of molecular materials based on squares is their ability to withstand solvent removal without cavity collapse or loss of porosity. The stability reflects the strength of coordinate–covalent bonds. These bonds are often four to 10 times stronger than typical hydrogen bonds.

Explored in most detail with respect to porosity were molecular materials based on neutral tetrarhenium squares $\{[\text{Re}(\text{CO})_3\text{Cl}(\mu\text{-diimine})]_4\}$ species as described further below. One step beyond strictly molecular materials are ones composed of covalently or coordinatively linked square units. Interesting examples here are the dimetallic-

cornered squares mentioned above, although their behavior as porous materials has yet to be explored. Another approach involves liquid–liquid interface polymerization. Acid-chloride functionalized linkers (short alkane chains) in one phase react with hydroxyl-functionalized porphyrin squares in another phase to generate high-porosity thin-film polymers.^[17] Film growth is self-limiting (a few microns), and the density of pinhole defects that fully penetrate the films is low. A third approach uses phosphonate-functionalized porphyrin squares and makes use of the enormous affinity of Zr(IV) for phosphonates. Layer-by-layer porous film assembly can be done on glass, conductive glass, or ceramic platforms. The approach provides exceptional control over film thickness and yields films with channels strongly preferentially oriented in the direction normal to the platform.^[18]

Functional Squares

Thin films of tetrarhenium squares $\{[\text{Re}(\text{CO})_3\text{Cl}(\mu\text{-diimine})]_4\}$ species can function as molecular sieves, in the form of coatings on macroporous membrane supports or as overlayers on electrode surfaces. Sieving can be followed by spectrally observing the passage of dye molecules, via the coated membrane, from a reservoir solution to a receiving solution or by monitoring the electrochemical current produced by passage of a redox-active probe molecule through a porous square coating.^[19] Sharp size cutoffs for probe molecules are observed, with the cutoffs corresponding to the sizes of cavities for isolated squares. Quantitative studies with films as thin as 20 nm show that molecular flux scales inversely with film thickness, demonstrating that rates of transport in these cases are limited by film-based diffusion rather than solution-to-film partitioning. For small- and medium-sized squares, known to form microcrystalline films, the observed molecular transport rates exceed by 20- to 50-fold rates of transport through related amorphous metallopolymer featuring similar size cutoffs. These observations point to the importance of the one-dimensional channels created by alignment of squares and their cavities. Films of larger squares featuring metalloporphyrin walls are amenable to cavity functionalization via axial ligation of porphyrin-embedded metal ions. Extensions of this kind readily permit size cutoffs for film sieving to be rationally altered. In principle, chemical selectivity could also be engendered in this way.

Facilitated transport of sodium tosylate across a chloroform solution separating two aqueous phases was demonstrated. The carrier was a Pt(II)-bipyridine square featuring calixarene receptors as corner appendages.^[9]

Advantage was taken of the luminescence of small- and medium-sized rhenium squares to accomplish chemical sensing: anions in solution^[20] and volatile aromatic

Fig. 4 Two examples of molecular squares designed for enhanced host–guest binding interactions. Structure **5** is able to bind Ag^+ ions between adjacent alkyne ligands via a π -tweezer effect. The corner receptor groups in **6** allow for enhanced binding of various amides through hydrogen-bonding contacts.

compounds in the vapor phase.^[21] Quartz crystal microgravimetry and modulated visible-light diffraction schemes were also used to report on selective uptake of analytes by porous molecular square films.^[22] By expanding the number of potential host sites available, porous thin films of squares offer sensitivity advantages over simple monolayers of host compounds. Nevertheless, squares are usually of limited effectiveness in sensing schemes. Few, if any, candidate guest molecules (analytes) are square shaped, ruling out efficient sensing based on complementarity, and simple squares lack the functionalities to bind analytes in a highly chemically selective fashion. (The examples described above depend on comparatively weak and nonspecific electrostatic, donor/acceptor, and dispersion interactions.)

Interesting exceptions are Pt-acetylide-based squares such as **5**, that bind Ag^+ strongly based on specific interactions with pairs of ethynyl groups (Fig. 4).^[9,23] Another involves a square featuring OsO_4 units as two diagonal corners and pyridine-2,6-dicarboxamides as the other corners (**6**). This assembly selectively binds appropriately sized amides via multiple hydrogen-bonding interactions.^[24]

A potentially more general solution is to decorate the interiors of large molecular squares with receptor ligands, for example, by anchoring them to metal ions embedded in porphyrins (Fig. 5). More than 100 cavity-modified squares were described. Nevertheless, only a handful were exploited for selective chemical sensing (e.g., iodine sensing with tethered thiols, alkali metal ion sensing with cavity-confined crown ethers, and zinc ion sensing with a cavity-confined polyamine ligand).^[25]

Encapsulation of metalloporphyrin-based epoxidation catalysts by a porphyrin square was described.^[26] By

largely preventing the catalysts from destructively encountering other catalyst molecules, the square substantially extends catalyst lifetimes. At the same time, it creates a spatially restricted reaction environment that translates into substrate size selectivity in the epoxidation reaction. In one case, a dipyridylporphyrin catalyst was encapsulated within a Zn(II) -containing square, leaving two of the four porphyrinic zinc sites available for further ligation. By binding sterically demanding ligands to these sites, the substrate size selectivity was shown to be tunable. The degree of selectivity engendered in this way, however, is limited, because the putative cavity-modifying ligands are apparently sometimes bound to the square exterior.

MOLECULAR BOXES AND CUBES

In contrast to the vast assortment of molecular squares now in existence, relatively few examples of molecular boxes or cubes were synthesized, unless one views squares having tall edges (for example, porphyrinic squares) as open-ended flexible boxes. As defined here, molecular boxes are right-angle-containing complexes, where the metal coordination units are arranged in three dimensions, instead of two.

A ruthenium-based molecular cube was described.^[27] Comprising its corners are $\{([9]\text{aneS}_3)\text{Ru}\}^{2+}$ ($[9]\text{aneS}_3 = 1,4,7\text{-trithionane}$) units, linked by 4,4'-bipyridine edges. The assembly was obtained by reaction of stoichiometric amounts of $\{([9]\text{aneS}_3)\text{Ru}\}^{2+}$ and 4,4'-bpy (8:12) in a noncoordinating solvent for 4 weeks. Key to the cube synthesis is the sulfurcontaining macrocycle. By occupying three coordination sites in a facial fashion, it leaves

Fig. 5 Porphyrin square functionalization for selective guest binding. (Go to www.dekker.com to view this figure in color.)

open three additional sites (also facially arranged) for
ligation of the cube's rigid edges. A crystal structure of a
cube fragment, $\{([9]\text{aneS}_3)(4,4'\text{-bpy})_3\text{Ru}\}^{2+}$, clearly illus-
trates the anticipated mutually perpendicular arrangement
of the three *bpy* ligands. Although an x-ray crystal
structure of the cube was not reported, $^1\text{H-NMR}$ of the
sample reveals two sets of 4,4'-*bpy* resonances, consistent
with the formation of the highly symmetrical product.
Two types of molecular boxes featuring (ethylenedia-
mine) Pd(II) corners and polypyridyl linkers were de-
scribed.^[28,29] One uses roughly rectangular tetrapyrro-
l ligands as walls for an open-ended cube. (7) Multiple
isomers were obtained, and one is shown in Fig. 6. By
carrying out the synthesis in the presence of an appropri-
ate guest molecule, the isomer distribution can be
controlled, as can an equilibrium between competing
prism and cube assemblies. The second type comprises a
family of elongated boxes. The walls here consist of 3,5-
linked terpyridine, tetrapyrroline, and pentapyridine
ligands with 6, 8, or 10 (en) Pd(II) units serving as
connectors along the box seams. Remarkably, box
formation is efficiently templated by rod-like guest
molecules. In the absence of templates, either no
supramolecular complex formation is seen, or a range of
complexes (trimers, tetramers, and pentamers) are present,
presumably in dynamic equilibrium. These observations

clearly point toward the idea of employing dynamic
combinatorial libraries to generate optimal supramolecu-
lar inorganic hosts for specific molecular guests. In
addition to x-ray crystallography and solution-phase NMR
spectroscopy, cold-spray ionization mass spectroscopy
was shown to be useful for identifying reaction products,
including thermodynamically unstable products in these
initial synthesis studies.

A series of mixed-metal molecular cubes, based on the
coordination chemistry of Prussian blue and other poly-
meric cyanometalates, was described. The cubes feature
Rh and either Co or Mo on alternating corners, with edges
consisting of bridging CN groups.^[30] The cubes are
formed by the binary combination of molecular squares,
subsequent to removal of axially bound chloride ligands.
The intermediate molecular squares species are formed by
the reaction of $[\text{Cp}^*\text{M}(\text{CN})_3]^-$ (Cp^* = pentamethyl cyclo-
pentadienyl, $\text{M} = \text{Rh}, \text{Co}$) with either $\{[(\text{R})\text{MCl}_2]_2\}$ ($\text{R} =$
 Cp^* , $\text{C}_{10}\text{H}_{14}$; $\text{M} = \text{Rh}, \text{Ru}$) or $(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Mo}(\text{CO})_3$.
The Cp^* ligands serve to block three of the six octahedral
sites, thereby precluding polymer formation. Recently,
however, the controlled formation of a double cube (one
shared corner) was described.^[31]

An interesting property of cyanide-bridged molecular
cubes is their ability to bind alkali metals (especially K^+
and Cs^+) selectively within the cube interior.^[30]

Fig. 6 One of three isomeric boxes that can be obtained from the combination of 3,3',5,5'-tetrakis(3-pyridyl)biphenyl and (en)Pd(NO₂)₂.

Crystallographic analysis of a Rh–Mo molecular cube indicates bond formation between the cationic guest and the cube's CN edges. When K⁺ is encapsulated, the ion is distributed over two equivalent positions, both slightly displaced from the cube center. Encapsulated cesium ions, on the other hand, occupy a central position. The locational differences reflect differences in ionic radii: 2.02 and 1.78 Å for Cs⁺ and K⁺, respectively, with coordination numbers of 12 for each. The structural differences translate into a nearly 4000-fold preference for uptake of Cs⁺ versus K⁺ from salt solutions, where the difference was evaluated competitively via ¹³³Cs-NMR measurements.

CONCLUSION

Inorganic supramolecular chemistry yielded an enormous number of discrete assemblies having square or box-like structures and ranging in size from several angstroms to several nanometers. Many of these compounds feature accessible, well-defined voids, rendering them useful, or at least viable, for several applications, including ones involving host–guest chemistry, mesoporous materials, or catalysis. Substantial possibilities for expansion upon applications in selective chemical catalysis, in particular, appear to exist. Applications yet to be fully realized include transport functions in which assemblies serve as artificial pores for natural or biomimetic membranes, as electron or energy transfer for solar energy conversion, and service as components of molecular electronic devices. Also yet to be exploited is the use of channels for templated growth of polymeric or other materials. If the square or cube templates were retained after polymer growth, new classes of nanocomposites, potentially having exceptional or even unique materials properties, might be obtained. Obviously,

further advances in molecular and higher-order assembly chemistry will facilitate these developments and likely stimulate others.

CROSS-REFERENCES

Classification and Nomenclature of Supramolecular Compounds; Mesoporous Materials; Nanotechnology; Self-Assembly: Definition and Kinetic and Thermodynamic Considerations; Supramolecular Catalysis; Supramolecular Chemistry, Definition; Supramolecular Chemistry, Historical Basis; Supramolecular Chirality; Supramolecular Electrochemistry; Supramolecular Photochemistry; Supramolecular Synthons.

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