Coordination Assemblies from a Pd(II)-Cornered Square Complex

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ABSTRACT

The $[enPd(II)]^{2+}$ (en = ethylenediamine) unit has emerged as a versatile building block in molecular self-assembly. In particular, the 90° coordination angle of the metal has been judiciously used in the design of new discrete two- and three-dimensional structures. Our last 15 years of work with the Pd(II)-cornered unit is summarized in this Account, from the spontaneous formation of a Pd_4 square metal complex to a family of architectures such as cages, bowls, boxes, tubes, catenanes, and spheres.

Introduction

Over the last 15 years, major efforts in our laboratory have been dedicated to metal-directed self-assembly of discrete two- and three-dimensional structures. These metal-containing assemblies possess cavities that can accommodate various guest molecules and often draw them to reveal new properties. This continuous chemistry was kicked off in 1990 by demonstration of the spontaneous formation of a square metal complex with four palladium centers, one at each corner of the square (**1**).[1] Since then, square and related metal-cornered structures, as well as

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the use of end-capped metal components, have been testified by ourselves and many other research groups. In this Account, therefore, we will first present how the square molecule was designed and prepared in our laboratory. The extension of the square into polyhedra and other three-dimensional architectures will be discussed subsequently.[27]
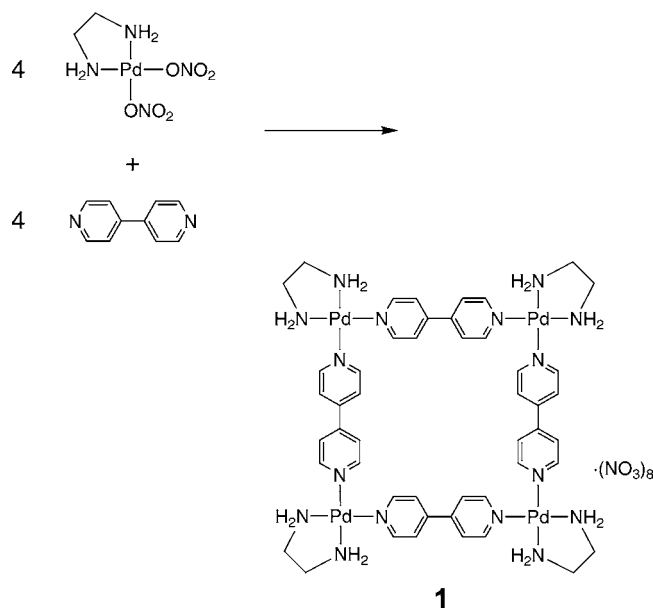
Square Complex

The first consideration that motivated us to design the square molecule was, in fact, ascribed to a quite simple question: How can we incorporate 90° angles into organic frameworks? Since this angle cannot be provided by the hybridization of s and p orbitals of organic elements, even a simple square organic molecule cannot be prepared without framework distortion.[2] Therefore, we thought that if this angle is incorporated into the organic frameworks at will, an infinite number of new structures could be generated. Such a simple idea prompted us to handle transition metals such as organic elements and exploit the 90° coordination angle of the transition metal in the design of new structures.

Square, which is the simplest 90°-incorporating structure, was first targeted. To obtain this structure, we looked for a stable cis-capped square planar transition metal unit. Surprisingly, $[enPdX_2]$ (en = ethylenediamine, X = Cl, NO$_3$, etc.), which are rather classical cis-chelated metal complexes, were sparingly used as components in polynuclear complexes. Accordingly, we designed a square complex (**1**) in which four linear ligands (4,4′-bipyridine) are held together with four $[enPd(II)]^{2+}$ units that occupy the corners of the square.

The discovery of **1** was not straightforward. We examined numerous combinations of metal (Ni, Co, Fe, Mn, etc.), end-cap groups (diamines, diphosphines, dithiols, etc.), and linear bridging ligands (4,4′-bipyridine, dicyanides, diacetylenes, etc.). While in most cases uncharacterizable mixtures or insoluble polymeric materials were formed, very interestingly the best solution was obtained when two classical compounds, $[enPd(NO_3)_2]$ and 4,4′-bipyridine (4,4′-bpy), were combined in an aqueous-alcohol solution (Scheme 1). The quantitative formation of **1** was confirmed by an impressively simple NMR spectrum (only one pyridine ring signal in the aromatic region) and, later, from MS and X-ray studies.[3]

The quantitative formation of the square was beyond our expectation. In general, macrocyclization in conventional organic synthesis is a low yield process and accompanied by a considerable amount of oligomeric byproducts. In fact, we encountered oligomers and insoluble materials when other metals and ligands were employed. Among all experiments, only the complexation of $[enPd(NO_3)_2]$ and 4,4′-bipyridine was successful. Having the desired square complex in hand, we realized that the quantitative formation of the square was explained in terms of self-assembly, which was demonstrated only three years earlier by J.-M. Lehn et al. (1987) by the

Scheme 1. Self-Assembly of Square Complex 1

1

spontaneous formation of Cu(I) double helical complex.[4] Even if the principle remains the same, our results show new features: (1) the first demonstration of a self-assembled square (or a macrocycle) by use of transition metal and (2) the use of an end-capped (nonnaked) transition metal in molecular self-assembly.

In particular, the [enPd(II)]$^{2+}$ unit enjoys its unique coordination with the ligands around the square planar geometry. While aromatic nonchelating ligands (pyridine rings) are substitution-active (kinetically labile) on Pd(II), the ethylenediamine ligand is rather kinetically inert due to its stable five-membered cis-chelating coordination.[5] Thus, by mixing in solution [enPd(II)]$^{2+}$ and 4,4′-bpy, only the bipyridine unit undergoes rapid ligand substitution, giving rise to the most thermodynamically stable square structure without destroying the 90° [enPd(II)]$^{2+}$ block. Accordingly, we achieved the quantitative self-assembly of complex **1**.

The combination of 90° unit blocks and linear ligands leading to the formation of square frameworks has been examined by many research groups.[6] The versatility of this approach was intensively developed by Stang and co-workers, who prepared organic soluble squares,[7a] chiral squares,[7b] crown-,[7c] ferrocene-,[7d] and porphyrin-conjugated squares,[7e] hypervalent element-hybrid squares,[7f] and so on.[7g] Due to their extensive studies, the squares have become a novel class of compounds named "molecular squares". Photoresponsive luminescent squares, a mixed valent Creutz−Taube square, and fully organic squares, as well as their applications to catalysis and porous sensing and filtrating materials have been reported in recent years.[8]

In compound **1**, the use of palladium(II) as a metal center is crucial. When the metal center is replaced by platinum(II), the square did not immediately assemble at room temperature. The kinetically inert nature of Pt(II)−pyridine coordination inhibits the rapid formation of a square complex. Thus, upon treatment of [enPt(NO$_3$)$_2$]

with 4,4′-bpy, we first observed a kinetically distributed oligomer mixture. However, after the solution was heated at 100 °C for several weeks to make the Pt(II)−pyridine bond kinetically labile, the oligomeric mixture converged into a square complex as reveal by NMR spectroscopy.[9] Interestingly, the reaction of [(dppp)Pt(OTf)$_2$] (dppp = 1,3-bis(diphenylphosphino)propane) and 4,4′-bpy smoothly provided the corresponding square probably because the electron donation from the phosphine makes the Pt(II)−pyridine bond kinetically labile even at room temperature.[7a]

It was unexpected and, hence, a big bonus for us that square **1** showed in aqueous media high molecular recognition ability for organic molecules. While 8$^+$ total charges of the metal centers make the compound highly water-soluble, the hydrophobic pocket provided by the four 4,4′-bpy ligands is capable of efficient hydrophobic binding of organic guests. For example, electron-rich 1,3,5-trimethoxybenzene and β-acetamidonaphthalene were successfully incorporated within the square.[10]

It is noteworthy that the general assumption that "90° + linear ligand = a square" is not always true. The self-assembly of a square lies on a delicate thermodynamic balance between enthalpy and entropy effects and often is accompanied by the formation of a triangle, which is favored in terms of entropy because it is formed from fewer components than a square. Therefore the square/triangle ratio depends on the length and rigidity of the ligand, the steric demand of the end-capping ligand on the metal center, the size and shape of the guest included in the cavity, and so on, adding difficulties for the characterization and quantitative synthesis of square complexes. In fact, complex **1** was the only case in which we did not observe the formation of triangles as by-products.
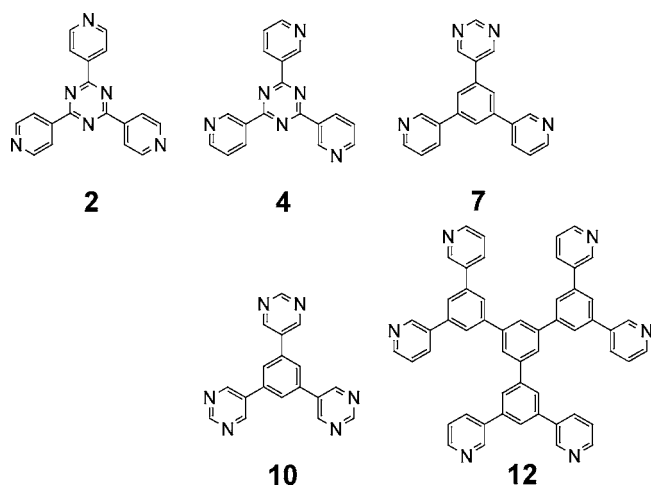
Octahedron Complex

Five years after our first report on the square complex **1**, we extended the two-dimensional structure into a three-dimensional octahedron.[11] While the same [enPd(II)]$^{2+}$ unit was employed, the 4,4′-bpy linear ligand was replaced by an exo-tridentate triangular ligand, 2,4,6-tris(4-pyridyl)-1,3,5-triazine (**2**). We found this ligand to assemble into a discrete three-dimensional structure (**3**) with a M$_6$L$_4$ stoichiometry (Scheme 2). Compound **3** has T_d symmetry (not O-symmetry); however, the structure can be easily understood by considering a hypothetical octahedron. Namely, [enPd(II)]$^{2+}$ centers occupy every corner of an octahedron whereas the triangular ligands alternatively occupy the eight faces of the octahedron. Geometrically related M$_4$L$_6$ cage complexes were first reported by Saalfrank et al. in 1988.[12] Recently, 3D cages with the same M$_6$L$_4$ geometry to ours have been reported by several groups.[13]

Despite its simple and highly symmetrical structure, the cage compound **3** possesses several unique characteristics that are summarized as follows: (1) The diagonal Pd−Pd distances determined by X-ray analysis are quite
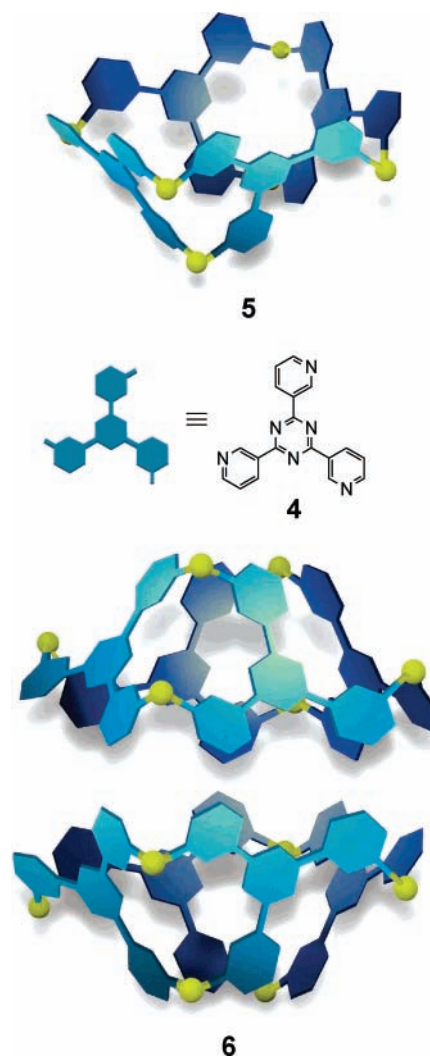
Scheme 2. Schematic Representation of M₆L₄ Cage 3

3

3 (top view)

2
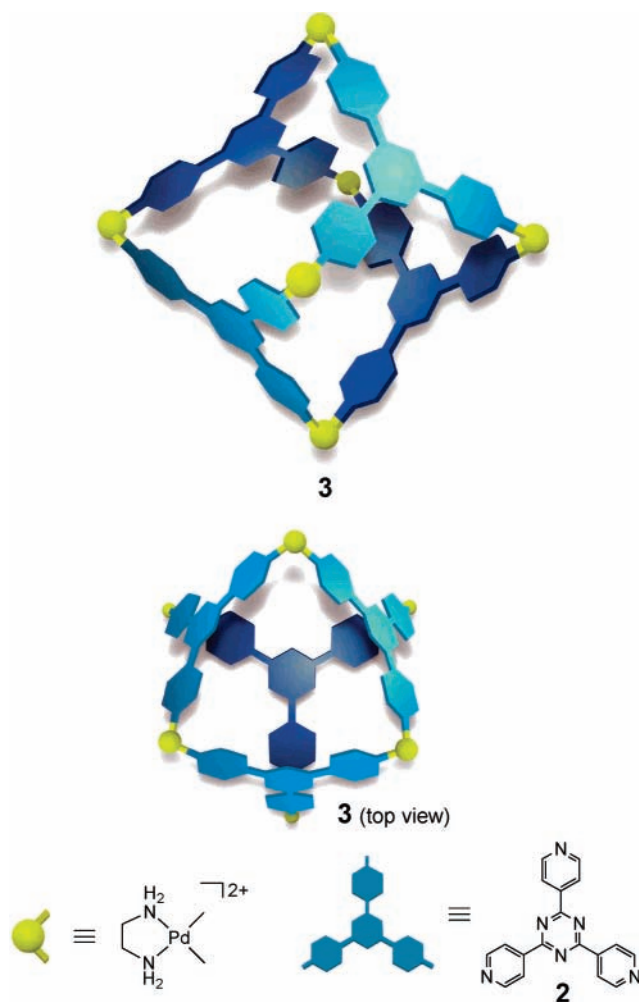
Scheme 3. Triangular Ligands 2, 4, 7, 10, and 12

2   **4**   **7**

10   **12**

Scheme 4. Schematic Representation of Structures of 5 and 6

5

4

6

compound **3** is now commercially available from Wako Co. Ltd. (3) The cage is amphiphilic; the outside is hydrophilic due to the presence of six cationic Pd(II) centers making the cage highly water-soluble, whereas the inside is hydrophobic and capable of binding, for example, as many as four adamantane or *o*-carborane molecules through hydrophobic interactions.[14] (4) The molecular recognition within the cage can be easily monitored by NMR. The guest signals are highly upfield shifted due to the shielding effect of the aromatic ligands and in most cases totally separated from the host signals. When the guest motion is restricted by the cage, the inherent T_d symmetry of the cage is lowered to the symmetry of the guest or its aggregate. Thus, the inclusion geometry can be elucidated by splitting pattern analysis of the host signals from which symmetry elements are suggested. (5) The ligand is extremely electron-deficient due to tridentate coordination at the three extremities on Pd(II) metals. Therefore the cavity binds preferentially electron-rich aromatic guests, which cause colorization of the host–guest complex by charge-transfer interactions. (6) Chemical reactions inside the cavity are often strictly controlled. For example, Diels–Alder reactions are dramatically accelerated by a factor of >100,[15] and [2 + 2] photodimer-
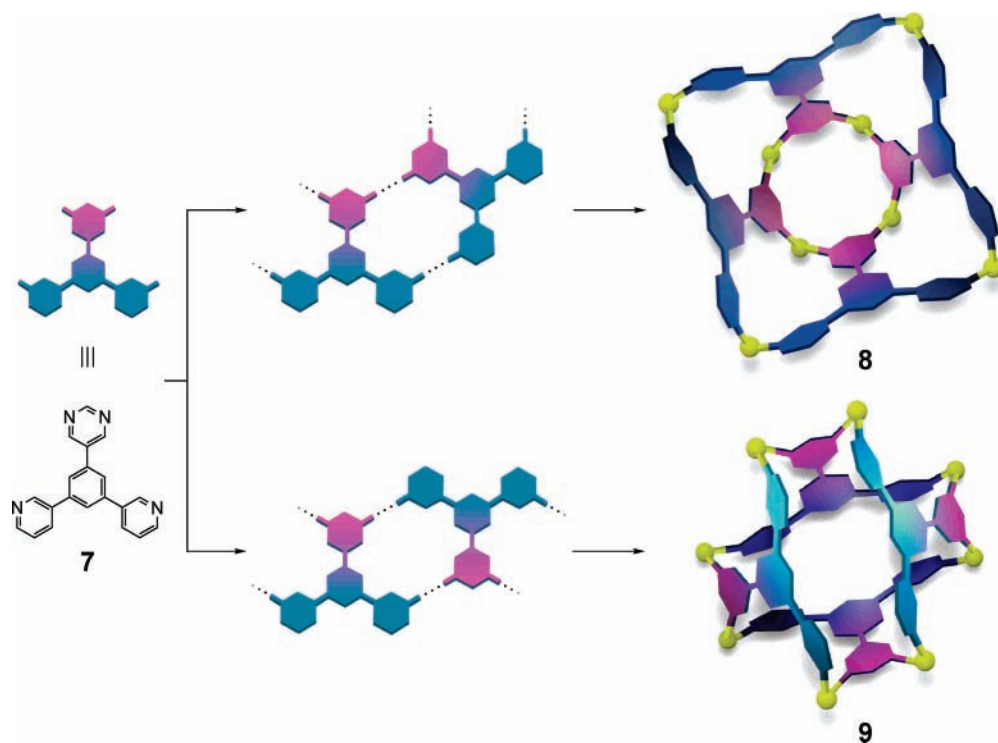
large (22 Å), providing the largest cavity among structurally defined three-dimensional host molecules reported so far. (2) A procedure for large scale production, up to 100 g, has been established thanks to the impressively simple preparation of **3**; that is, mixing in water the ligand and [enPd(NO₃)₂] in a 3:2 ratio followed by the evaporation of the bulk of water precipitates the cage in >90% yield with purity of an elemental analysis grade. Moreover

Scheme 5. Schematic Representation for the Molecular Paneling of 7 into 8 and 9

ization of olefins shows remarkable rate acceleration, high regio- and stereoselectivity, and pairwise-selectivity that leads to selective cross-dimerization of two different olefins.[16]

Polyhedron Complexes

The most important factor in quantitative self-assembly of **1** and **3** is the 90°-unit, [enPd(II)]$^{2+}$, which convergently coordinates exo-bridging ligands (4,4′-bpy or triazine) and prevents the formation of infinite structures. Therefore, we designed a new family of triangular ligands (Scheme 3) in which only the number and position of N-donor sites are different from **2** and studied their complexation with [enPd(II)]$^{2+}$ blocks.

The triangular tridentate molecular panel **4**, though having a similar structure to **2**, was assembled into a bowl-like M$_6$L$_4$ square-pyramidal cone (**5**) upon treatment with [enPd(NO$_3$)$_2$].[17] In aqueous media, the square-pyramidal cone **5** was further assembled into a dimeric capsule (**6**) that accommodates as many as six neutral organic molecules. The molecular structures of **5** and **6** were confirmed by single-crystal X-ray analysis (Scheme 4).

While molecular panels **2** and **4** contain D_{3h}-symmetry, molecular panel **7** (3,5-bis(3-pyridyl)-1-(3,5-pyrimidyl)-benzene) has D_{2h}-symmetry and four donor sites and, therefore, is expected to link in two different ways (parallel or antiparallel) upon treatment with [enPd(NO$_3$)$_2$].[18] Interestingly, these two options are perfectly controlled by the guest molecule. Large guest molecules such as dibenzoyl induce the formation of an open square-pyramidal cone (**8**) via parallel linkage, whereas small tetrahedral guests such as CBr$_4$ induce the templation of a closed tetrahedron structure (**9**) via antiparallel linkage (Scheme

5). Both assemblies have the same M$_8$L$_4$ composition and, therefore, constitute a dynamic library from which conformation of the cage is controlled only by the guest molecule.

Following the exo-tridentate ligands **2**, **4** and **7**, an exo-hexadentate triangular ligand, 1,3,5-tris(3,5-pyrimidyl)-benzene (**10**), was synthesized.[19] Ligand **10** is an almost coplanar triangle and is expected to give an edge-sharing polyhedron when it is coordinated with [enPd(II)]$^{2+}$. In fact, we obtained a M$_{18}$L$_6$ trigonal-bipyramidal (hexahedral) structure (**11**) upon treating **10** with [enPd(NO$_3$)$_2$]. This structure was confirmed by X-ray crystallography and revealed an almost fully closed-shell structure (Scheme 6). When assembled, cage **11** does not allow entry or escape of organic molecules. The free volume inside the capsule, into which guests can be accommodated, is ca. 900 Å^3.

We also designed highly π-conjugated hexadentate ligand (**12**), which is found to assemble into an [enPd(II)]-clipped aromatic sandwich compound (**13**) in the presence of a template (triphenylbenzene) (Scheme 7).[28] Ligand **12** is a roughly 2 nm sized hexagonal planar molecule that possesses six pyridyl donor sites at the periphery. Upon complexation, the ligand adopts concave conformation to maximize the interaction with the triphenylbenzene.

In a different approach, a three-dimensional cavity is obtained from the combination of two different ligands. A pyrazine-pillared 3D receptor that efficiently binds π-conjugated compound is quantitatively assembled from a mixture of ligand **2** and pyrazine.[20] The template effect of a large aromatic compound such as hexamethoxytri-phenylene was essential to the quantitative formation of

Scheme 6. Schematic Representation of the Structure of 11

11

11 (top view)

10

Scheme 7. Schematic Representation of 13 Accommodating Triphenylbenzene
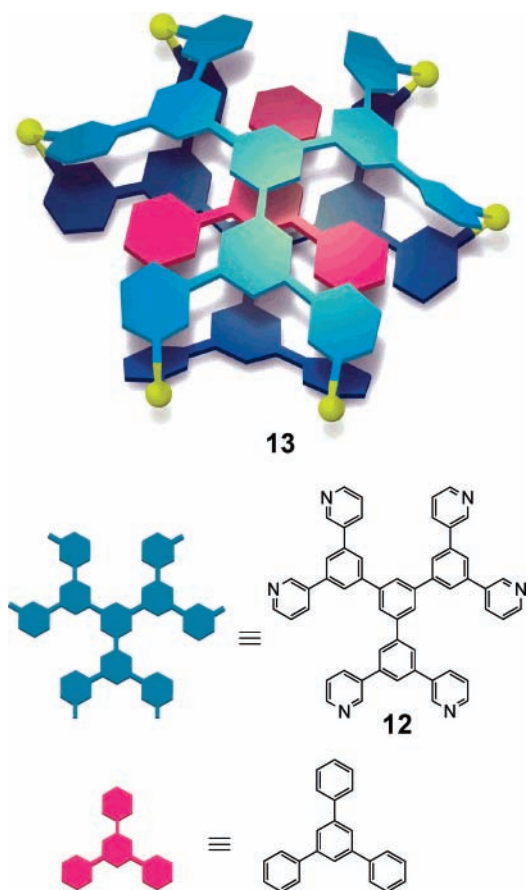

13

12
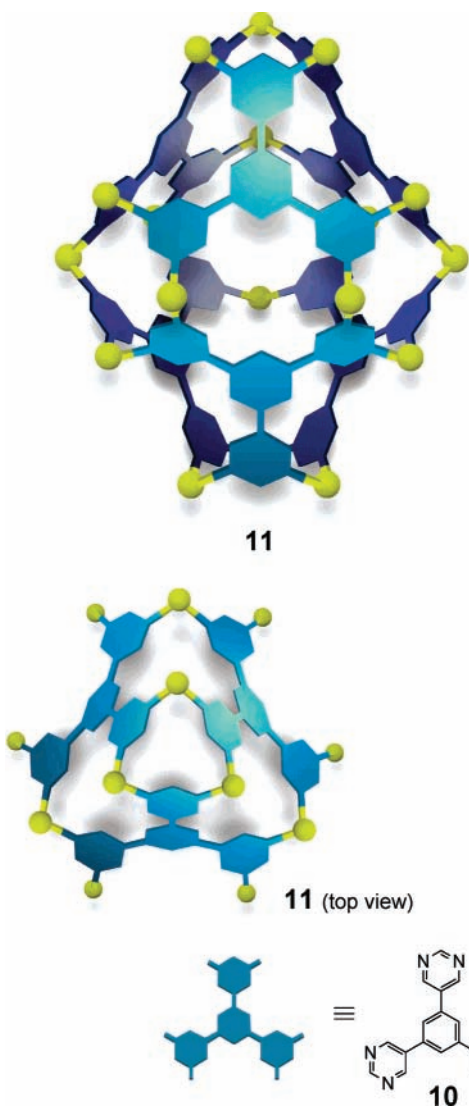
14 (Scheme 8). However, the cage remains stable when the template is removed. The empty cavity can be filled by various organic molecules. In the presence of 1,3-diketone, as confirmed by NMR spectroscopy, the ketone is found to exist only in its enol form, suggesting a stabilization effect of the cage.

In addition to triangles, we also designed squares and rectangles as molecular panels (Scheme 9). This new series of ligands allows us to generate prism, tube, and box structures.

Tetrakis(pyridyl)porphyrins are one of the most common and easily available square panels,[21] yet 3D discrete molecules using porphyrin molecular panels are not reported. We found that zinc tetrakis(3-pyridyl)porphyrin (**15**) assembled into a M_6L_3 triangular prism (**16**) upon complexation with [enPd(NO$_3$)$_2$] (Scheme 10).

The fixed porphyrin ligands surround a large hydrophobic cavity, which can accommodate in aqueous media neutral organic molecules, such as pyrene and perylene. Interestingly, one NO$_3^-$ anion was trapped in the cavity, and all attempts to replace it with a PF$_6^-$ anion were unsuccessful.

Similarly, rectangular panel **17** (3,3′,5,5′-tetrakis(3-pyridyl)biphenyl) provides predominantly a large coordination M_8L_4 box (**18**) (Scheme 11).[22] In addition to box **18**, uncharacterized minor products were also observed. However in coordinating solvent (CH$_3$CN, THF), complex **18** is in a dynamic equilibrium with several other box structures, as demonstrated by MS and NMR spectroscopy. The dynamic property of **18** generates from a single ligand a complete library of new boxes.

In expectation of tubular structures, a rectangular panel, tetrakis(3,5-pyridine) (**19**), was designed.[23] Upon treatment with [enPd(NO$_3$)$_2$] and with the assistance of a template, a coordination nanotube (**20**) was formed. The nanotube **20** consists of four molecules of **19** and 10 molecules of [enPd(II)]$^{2+}$. A rodlike guest such as sodium 4,4′-biphenylenedicarboxylate is essential in the formation of **20**. At room temperature, the rodlike guest stays at a fixed position or only shuttles inside the tube, desymmetrizing the host framework.[24] Above 60 °C, however, the guest is allowed to move out from the tube, making both ends of the host equivalent. The crystal structure of **20** displays the expected tubular structure, efficiently assembled around a template (*p*-terphenyl) via π−π and CH−π interactions (Scheme 12).[25]

Encouraged by the self-assembly of nanotube **20**, a second generation of rectangular panels was drawn. The incorporation of four tripyridine podands on a benzene-tetracarboxylate scaffold generates a dodecadentate ligand

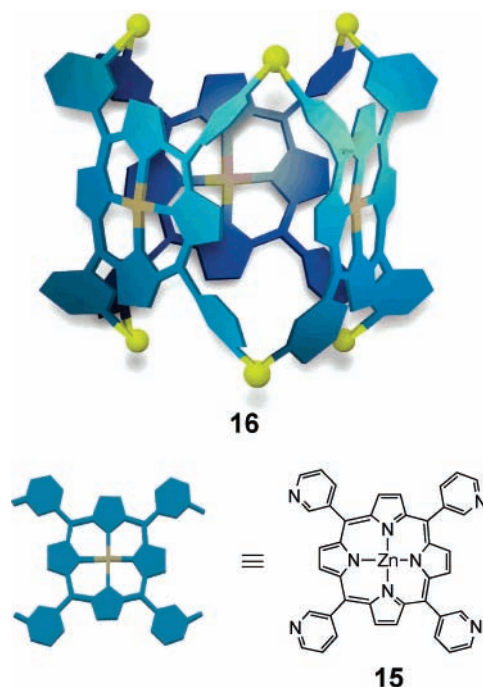**Scheme 8. Schematic Representation of the Structure of 14**

14

2
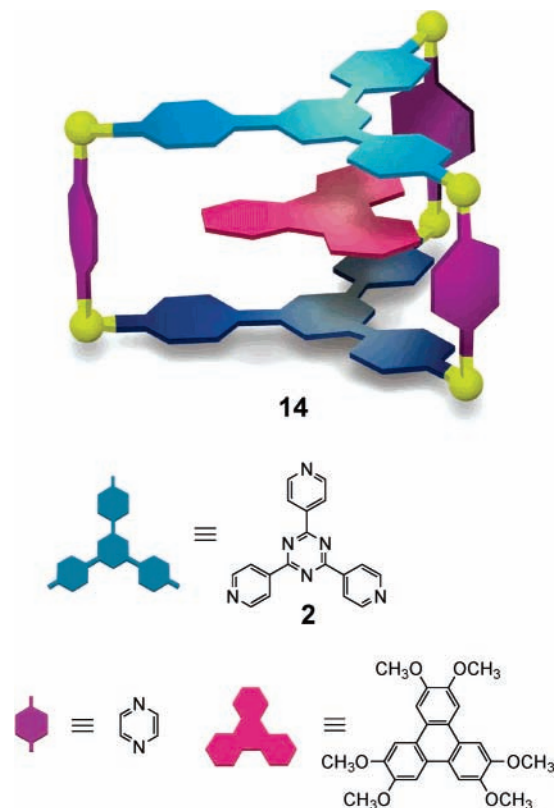
Scheme 9. Square and Rectangle Ligands 15, 17, 19, and 21

15   **17**

19   **21**
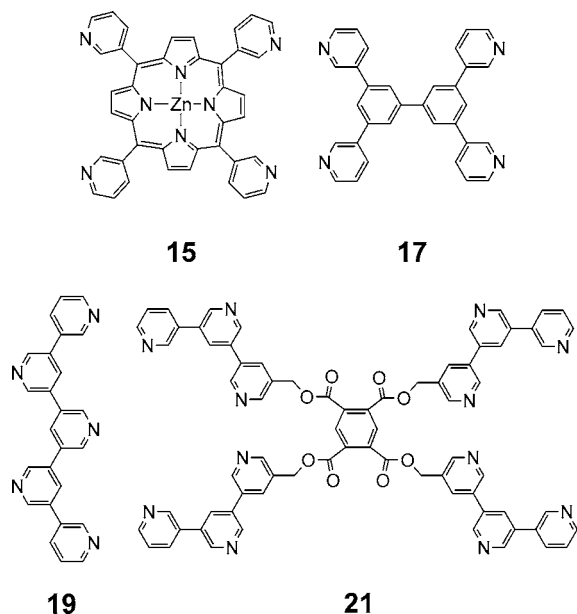
(**21**).[26] In the presence of [enPd(NO$_3$)$_2$] and combined with the template effect of sodium biphenylcarboxylate, the quantitative assembly of **21** into end-capped tube **22** was observed. Nanotube **22**, being formed via intramolecular coordination, is in fact a kinetically favored structure. Subsequent treatment of **22** at higher concentration gives rise to the double opened tube (**23**), in which ligand **21** adopts an extended conformation (Scheme 13). An important feature is that the 16 components (two ligands,

Scheme 10. Schematic Representation of Porphyrin Prism 16

16

15

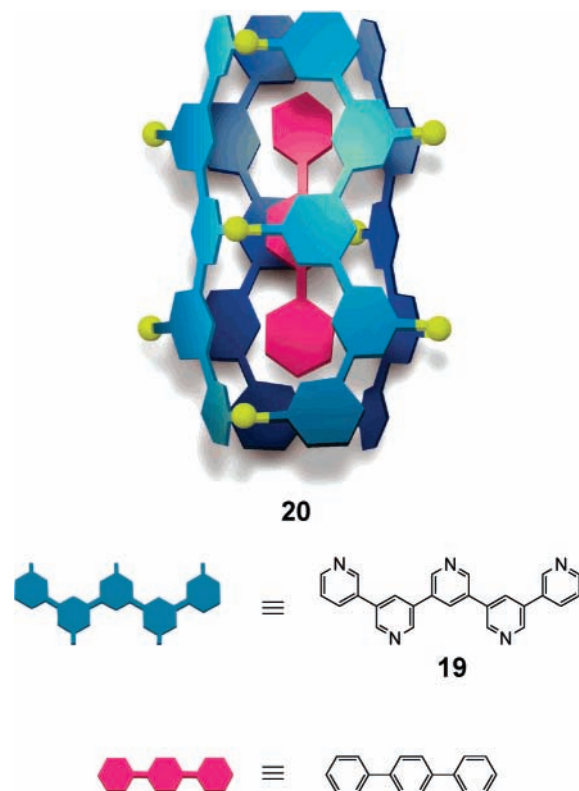**Scheme 11. Schematic Representation of the Structure of 18**

18

17
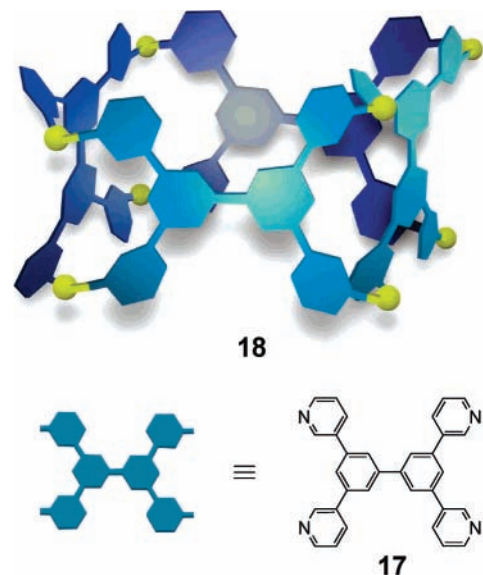
12 metal centers, and two guests) self-assemble into a 3.0 nm molecular tube.

Structural Determination

We have made a persistent endeavor to unambiguously confirm the structures of the self-assembled complexes by X-ray analysis because other spectroscopic methods do not provide definitive evidence for postulated structures. Although we always suffered from difficulties in crystallization, handling little crystal nature and severe disorder of solvents and counterions, our continuous efforts as well as recent developments in the instruments of crystallographic analysis made it possible to provide X-ray structures of key compounds. Figure 1 summarizes the X-ray crystallographic structures of self-assembled

Scheme 12. Schematic Representation of the Structure of 20

Scheme 13. Schematic Representation of Structures of 22 and 23 Assembling from 21 and (en)Pd(NO₃)₂ in which Biphenylcarboxylate Used as a Template Is Accommodated


complexes discussed in this Account. We note that several groups, including ours, have made significant efforts to provide X-ray structures for self-assembled complexes for many years, setting the standard of the structural determination in this field.

Of course, NMR is very supportive for the structural determination. Thanks to the nonparamagnetic nature of Pd(II), the spectra of self-assembled complexes are not disturbed by the metal. In addition, components in a mixture are not averaged, despite rapid equilibrium among them, because ligand exchange on Pd(II) centers is sufficiently slow on the NMR time scale. Thus NMR is a strong tool for analyzing the structure of complexes as well as dynamic behavior of multicomponents. However, self-assembled complexes possess, in general, highly symmetric structures and often give too simple spectra to provide convincing structural evidence.

Mass spectroscopy (FAB, ESI) was previously always disappointing except for simple and stable complexes including only few metal centers. Recently, cold-spray ionization (CSI) MS has been shown to be a powerful tool for analyzing the metal-containing assemblies. By this method, even a self-assembled complex with a molecular weight of over 10 000 can be clearly observed without fragmentation.

In coordination chemistry, solid structure is often different from solution structures. Regarding our complexes discussed in this Account, however, we have confirmed good agreement of solid structure (by X-ray) with solution structure (NMR, CSI-MS, or both). We believe that it is the most convincing way to analyze the solid-state structure by X-ray crystallography and the
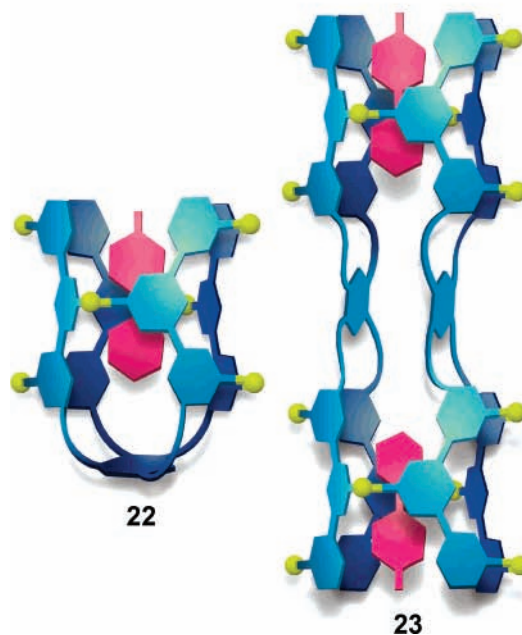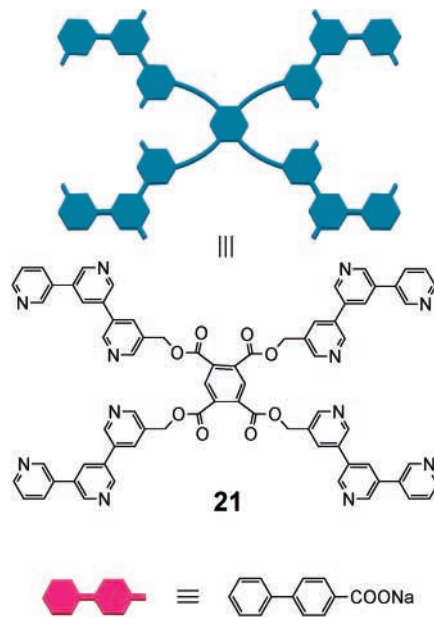
solution structure by NMR and CSI-MS spectra for the structural determination of the self-assembled complexes.

Conclusion

We have shown that the simple combination of the square planer geometry (90° coordination angle) of palladium with pyridine-based bridging ligands gives rise to the quantitative self-assembly of nanosized, discrete organic frameworks, such as macrocycles, linked-ring molecules, cages, and capsules. Our strategy exploiting endcapping transition metals as coordination blocks has been testified by the number of reports on self-assembled cyclic structures incorporating transition metals and di- or multi-
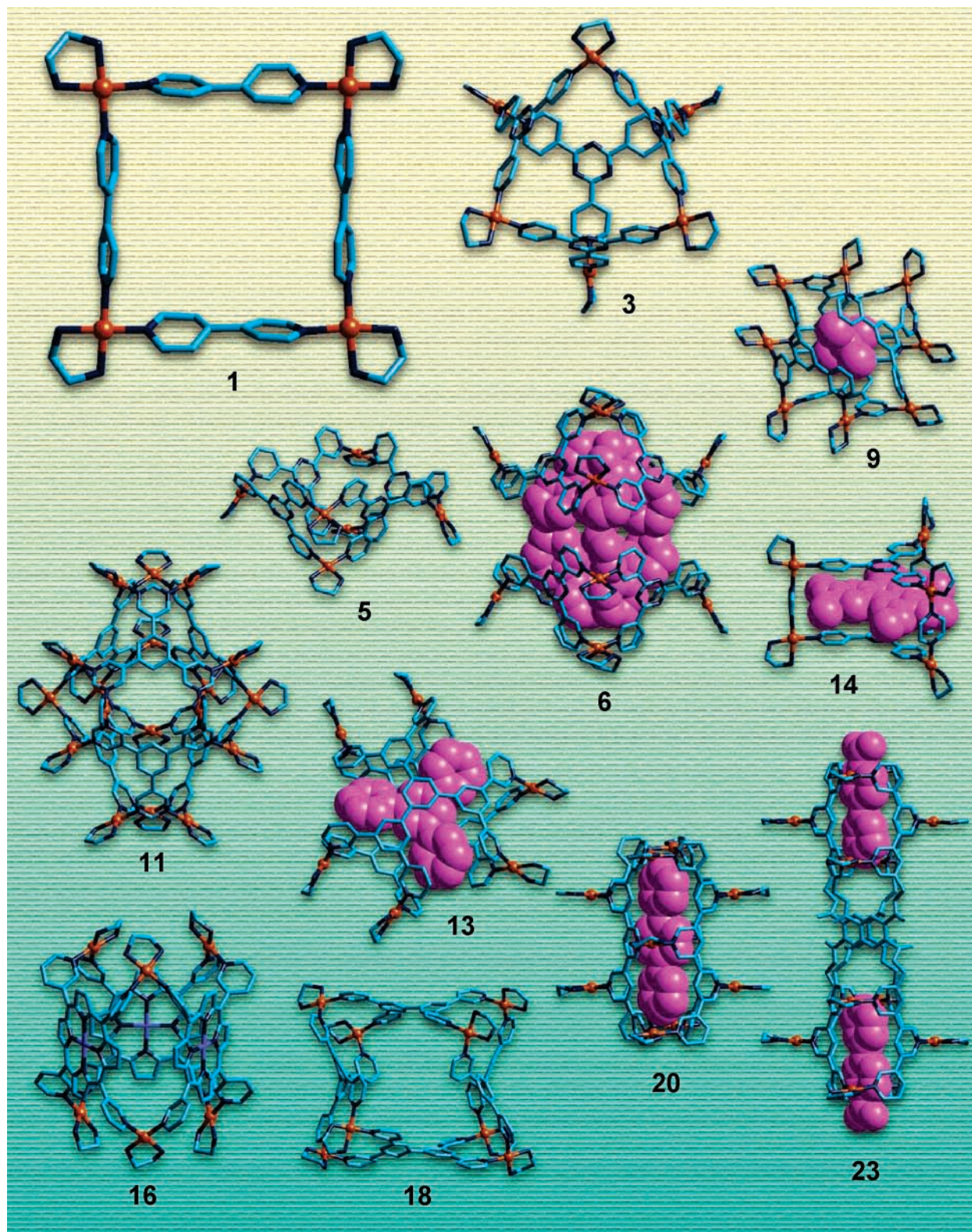
FIGURE 1. X-ray crystallographic structures of self-assembled coordination architectures discussed in this Account.

topic ligands since our first report on the square complex in 1990. Currently, this method is recognized as an efficient approach to variety of coordination architectures.

We also emphasize that our self-assembled cages dominate over previous organic receptors in their molecular recognition ability. The cavities are in general extraordinarily large and are capable of binding neutral

guests: for example, M_6L_4 cage **3** can accommodate as many as four large guest molecules. While most synthetic receptors utilize ionic interaction or hydrogen bonds for host−guest binding, our cages do not require such strong interactions because the compounds provide an efficient hydrophobic cavity in water. Creating new chemical and physical phenomena within the cavities represents one

of the most important features of self-assembled hosts. We are therefore developing such functions with the large cavity of the self-assembled cages. The details will be reviewed elsewhere soon.

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