

Metallosupramolecular squares: from structure to function†

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Metallosupramolecular squares have been successfully evolved over the past years as versatile substitutes of the conventional organic macrocycles owing to the development of reliable synthetic protocols and abundant structural variability (metals and ligands). In this review we have presented the fundamental aspects of metallosupramolecular squares such as the strategies for their construction (self-assembly vs. kinetically controlled macrocyclization) and characterization. The major emphasis of this *tutorial review* lies on the function of metallosupramolecular squares. Thus, the introduction of functionality into these systems has been discussed in detail by highlighting the recent progress toward application in various fields, including molecular recognition, enantioselective sensing, photoluminescence, redox activity and electrochemical sensing, and homogeneous catalysis.

1 Introduction

The extensive studies on macrocyclic compounds such as crown ethers, cyclodextrins, calixarenes, cyclophanes, cavitands, cryptands, spherands, carcerands, cyclopeptides, and other structurally related species have greatly contributed to the development of the challenging field of supramolecular chemistry.¹ The design and preparation of novel macrocycles and the exploitation of their application have attracted considerable attention in the past three

decades. In general, conventional kinetically controlled organic synthesis is not very advantageous for the preparation of macrocycles since the required reaction conditions are often severe and the desired products are usually obtained in low yields. Based on coordination chemistry, successful strategies have been developed over the past years for the construction of complex macrocyclic structures.² Through directional coordinative bonding, two- and three-dimensional self-assemblies are readily available by the spontaneous reaction of metal starting materials with appropriate organic ligands. Recently, this novel strategy of metal-mediated self-assembly has been successfully applied to construct numerous metallosupramolecular squares with interesting functions.

† This work is dedicated to Professor Julius Rebek, Jr. on the occasion of his 60th birthday.

Frank Würthner was born in 1964 in Villingen-Schwenningen (Germany). He studied chemistry at the University of Stuttgart where he received his PhD degree in Organic Chemistry in 1993 working with Franz Effenberger. After a postdoctoral stay (1994/95) as an Alexander von Humboldt Fellow at MIT in Cambridge/MA (USA) in the laboratory of Julius Rebek, Jr. he spent two years at the BASF Central Research Center in Ludwigshafen (Germany). In 1997 he joined the group of Peter Bäuerle at the University of Ulm where he received the *venia legendi* (Habilitation) in 2001. Since October 2002 he is full professor at the University of Würzburg. His research interests include merocyanine, perylene and porphyrin dye chemistry, noncovalent synthesis of nano- and mesoscopic structures, liquid

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Although several excellent review articles on coordination supramolecular chemistry have also included some aspects of molecular squares,² there appears to be no review article that deals exclusively with this class of supramolecular structures, and focuses on their functional properties. Significant progress has been made in the past few years in the area of functional supramolecular assemblies in general, and especially squares. In this review, we highlight the recent advances in functional metallosupramolecular squares and discuss the fundamental aspects of metal-mediated self-assembly of these supramolecular motifs.

2 General aspects

Molecular squares are termed for discrete cyclic assemblies that possess per definition 90° turns in the assembly. Because of the constraints imposed by the coordinative bonding, metallosupramolecular squares usually exhibit considerable conformational rigidity, which leads to remarkable stabilities and unique properties. It is well known that coordination bonds are relatively weak interactions which impart the features of flexibility, directionality and complementarity. The energies of coordination bonds range from 40 to 120 kJ mol⁻¹ per interaction, which lie between the strong organic covalent bonds (*ca.* 400 kJ mol⁻¹) and other weak noncovalent interactions such as hydrogen bonding (< 40 kJ mol⁻¹). Therefore, this kind of interaction is most suitable for sewing ligand components into well-ordered entities with appropriate stability and topology. In principle, coordination bonds can possess kinetically inert or kinetically labile metal–ligand interactions. The former type of metal bonds behave like conventional organic covalent bonds and are kinetically stable with respect to ligand displacement. However, in systems with kinetically labile metal–ligand interactions, ligands may exchange readily. So that associations through such interactions are reversible and allow facile interconversion to the favorable formation of thermodynamically most stable products. Under these conditions the desired macrocyclic product may be obtained in quantitative yield in contrast to kinetically controlled macrocyclization reactions. From the synthetic point of view, it is especially appealing to direct a reaction to the thermodynamic product (the macrocycle) at a higher temperature in a relatively polar solvent (conditions of reversibility) and subsequently employ the macrocycle at a lower temperature in less polar solvents (conditions where the kinetic barrier for disassembly is high) for the desired applications. Herein we focus primarily on molecular squares assembled through relatively labile metal–ligand linkage, especially those involving aromatic aza ligands.

2.1 Concepts for the preparation of molecular squares

For the formation of square macrocycles in high yield, the proper selection of metal corner units and bridging ligands is crucial. Since it is rather difficult to control the coordination number and direction

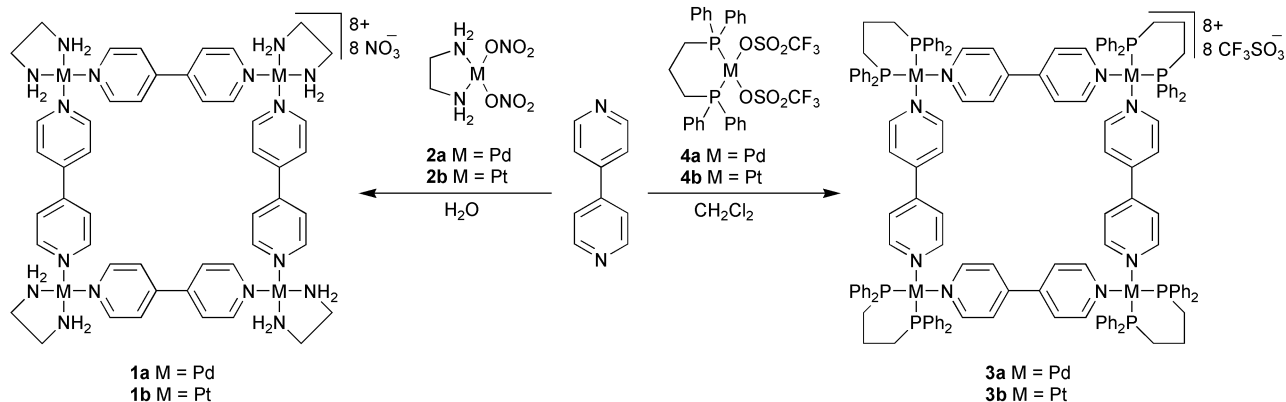
in the self-assembly process of ligands by “naked” metal ions,[‡] the latter are not properly suited for the preparation of molecular squares in high selectivity.³ In most cases, some of the metal ions’ coordination sites are protected with strongly coordinated organic ligands whereas other coordination sites are either free or only occupied by weakly coordinating ligands, allowing a thermodynamically and kinetically feasible exchange by more strongly coordinating ligands such as aromatic aza ligands.

Transition metals with square planar coordination geometries, in which the four coordination sites are separated by about 90° from the adjacent one, are most suitable as metal corner building blocks for the square formation. *Cis*-metal corner units with 90° angle may be easily derived from such metal species by blocking two adjacent coordination sites with strong chelating reagents, but keeping the other two sites accessible for further coordinative interactions. Indeed, the readily available *cis*-protected Pd(II) and Pt(II) corners have proven to be versatile metal building blocks for molecular squares.

Fujita *et al.* have reported the first square self-assembly **1a** that contains *cis*-protected palladium corner.⁴ The structurally pre-defined metal corner [(en)Pd(NO₃)₂] (**2a**) provides two vacant coordination sites of a 90 degree angle, while the rigid 4,4'-bipyridine ligand possesses two lone pairs of 180 degree divergence. These structural features of metal and ligand contribute convergently to the formation of a square framework of assembly **1a** at room temperature in water. Notably, whilst 4,4'-bipyridine precursor is insoluble in water, square **1a** dissolves in water up to high concentration. This novel concept, pioneered by Fujita, has been abundantly applied for the construction of various metallosupramolecular squares.

In contrast to Pd(II) complex **2a** that produced quantitatively the square **1a** on mixing with stoichiometric amounts of the 4,4'-bipyridine ligand under ambient conditions, the treatment of the Pt(II) complex **2b** with 4,4'-bipyridine gave initially the kinetically distributed oligomeric products, which could be converted to the thermodynamically favorable square species **1b** by heating at 100 °C for more than four weeks.⁴ Molecular square **1b** is more stable than **1a** under ordinary conditions due to the relative inertness of platinum–pyridine bond, which is also responsible for the required long reaction time. Accordingly, this represents a convincing example of kinetically stable macrocycles, which could be obtained in high yield under the conditions of thermodynamic control.

Recently it was reported that the formation of square **1b** was brought to completion within 10 min simply by grounding a powdered 1:1 mixture of **2b** and 4,4'-bipyridine under ambient conditions.⁵ Despite dramatic acceleration of the reaction rate in the solid state, the reaction course is identical to that of self-assembly in solution, that is, initial formation of linear oligomeric inter-



[‡] In this context, “naked” metal ion means a metal ion that is ligated only by weakly coordinated ligands, which can be easily exchanged.

mediates followed by conversion to square scaffold. This solid state reaction is facilitated by efficient molecular interactions through physical friction. The self-assembling process under solvent-free conditions offers attractive opportunities for simplified synthesis of coordination assemblies.

An even more effective route to palladium and platinum-containing molecular squares was developed by Stang *et al.* by employing metal corners with chelating bisphosphino ligands that are well-soluble in organic media.⁶ Representatively, molecular squares **3a,b** were made accessible by self-assembly of 4,4'-bipyridine with the phosphine complexes **4a,b** in dichloromethane at room temperature. While Fujita's squares **1** are water soluble, metallosupramolecular squares **3** are highly soluble in various polar organic solvents, including chloroform, acetone, and nitromethane. The phosphorus atoms at the corner units enable convenient monitoring of reaction course and reliable characterization of self-assembly products by ³¹P NMR. X-Ray analysis of square **3b** revealed that the high degree of π -stacking between one of the phenyl groups of the phosphine ligand and the pyridine rings imposes considerable rigidity on the corner unit and fixes the angle between the two adjacent coordination sites. These favorable interactions between the ditopic ligand and chelated bisphosphine, on the one hand, promote square formation and, on the other hand, contribute to the stability of square. The fortunate choice of phosphine complexes as corner units by Stang's group led to distinct advancement in the area of metallosupramolecular squares during the mid-nineties. Thus, self-assembly between numerous linear and right-angle bidentate aromatic aza ligands with phosphine complexes afforded diverse metallosupramolecular squares (Fig. 1).⁶ Likewise the equimolar reaction of dicyanobenzene and

dicyanobiphenyl with the Pd(II) phosphine complex **4a** gave the corresponding macrocyclic molecular squares, while the reaction with the Pt(II) complex **4b** generated only oligomeric products; evidently, no specific macrocyclic product was formed in the latter case. Although cyclic bis(phosphine) was proposed to be essential for maintaining the *cis* geometry in self-assembly,⁶ complexes **4a,b** proved to be the most reliable 90 degree metal corners for coordination squares.

Drain and Lehn have expanded the application of Pd(II) and Pt(II) metal building blocks towards porphyrin square assemblies.⁷ The significance of this work is, that for the first time *trans*-substituted metal ions were used as 180 degree bridging units and porphyrins as 90 degree corners for square assemblies such as **5** (structures of *tetra*-porphyrin squares with 90 degree metal corners reported by these authors are not shown here).

Tetra-porphyrin squares are also accessible from properly substituted zinc porphyrins through self-complementary coordinative interactions. For example, Hunter *et al.* have reported on the construction of the molecular square **6** from a zinc porphyrin bearing a *p*-(*iso*-nicotinamide)phenyl group.⁸ In the monomeric structure, the angle between the Lewis-acidic coordination site of the zinc porphyrin and the Lewis-basic lone pair of the pyridine ligand is approximately 90 degrees. Thus, a tetrameric macrocycle was achieved through the intermolecular axial coordination of the pyridyl moiety to the zinc porphyrin in a head-to-tail fashion.

Based on the same design principle, Osuka *et al.* have constructed the tetrameric square **7** from a conformationally more rigid 5-*p*-pyridyl-15-(3,5-di-*tert*-butylphenyl)porphyrinato zinc(II).⁹ In contrast to tetramer **6** that exists only in chloroform solution of an appropriate concentration (8 to 25 mM), square **7** could also be

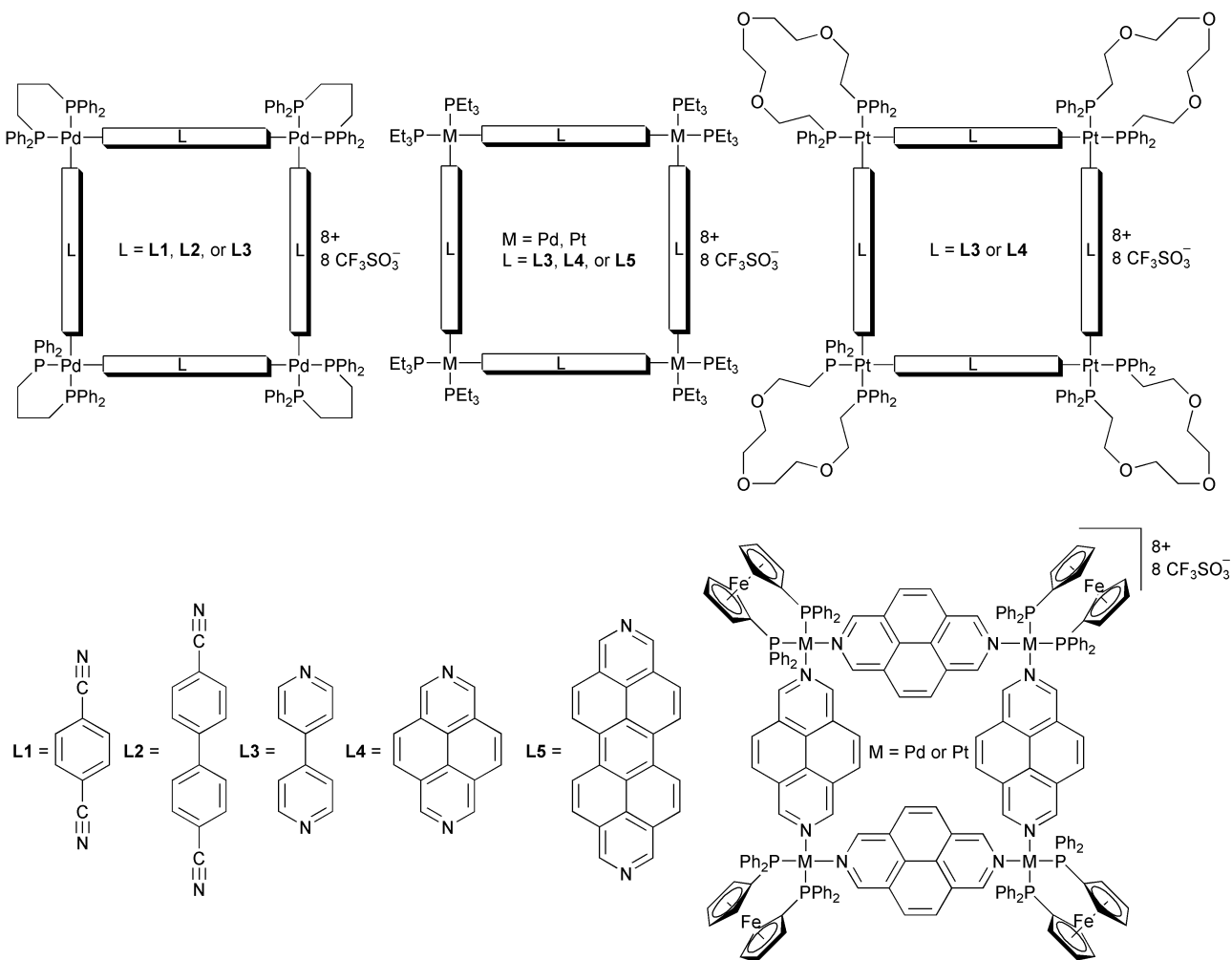
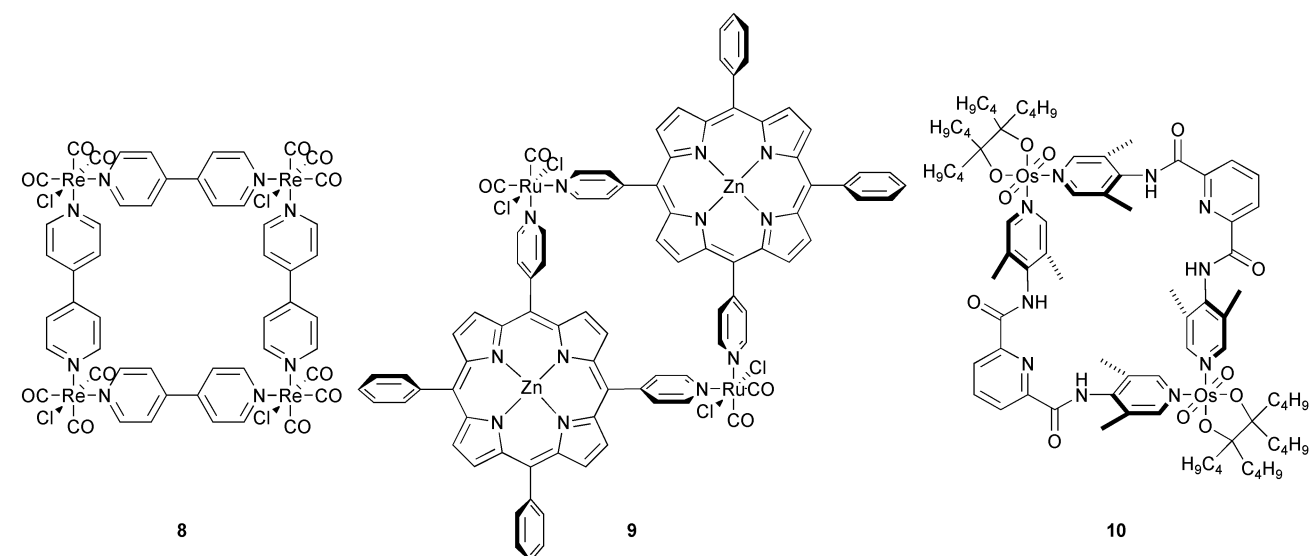
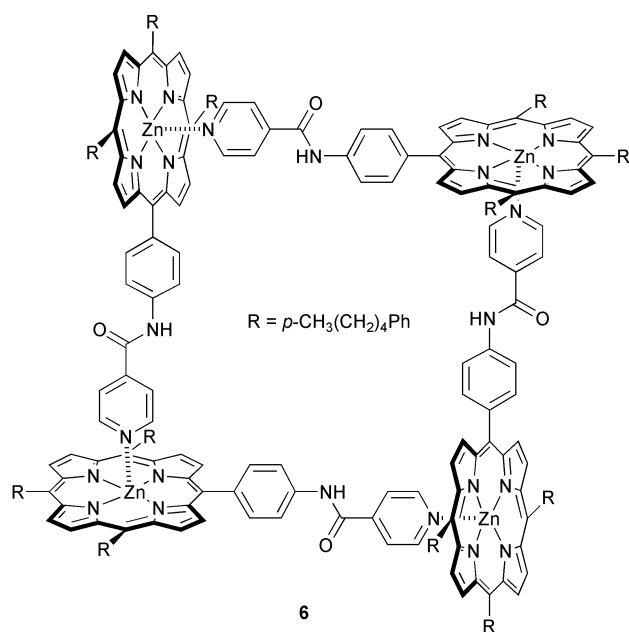
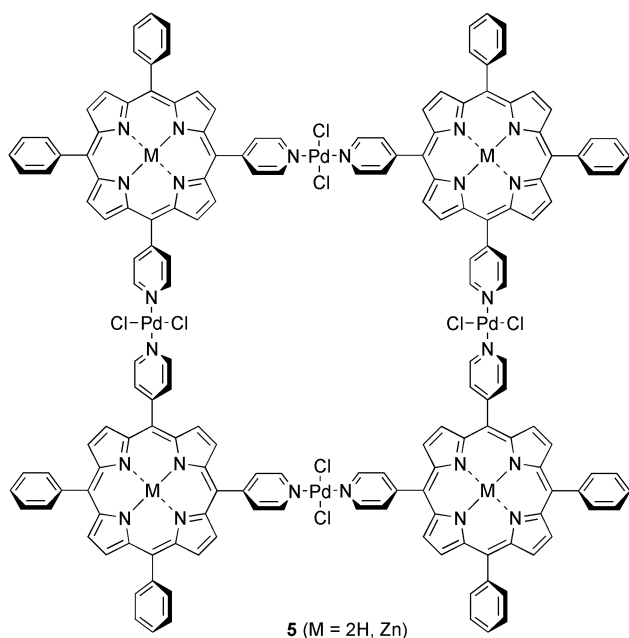
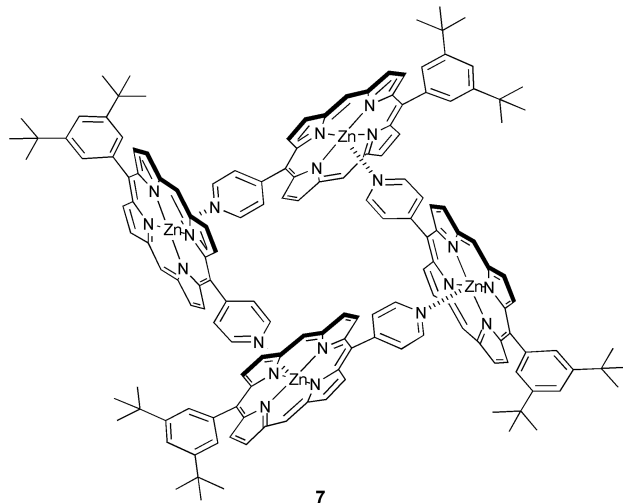


Fig. 1 Examples of phosphino metal corner-containing metallosupramolecular squares constructed by Stang *et al.*⁶

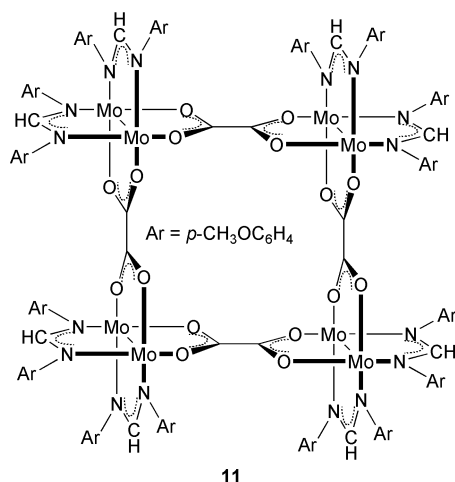


isolated in the solid state and its structure was unequivocally confirmed by X-ray analysis.⁹ In this regard it should be mentioned that Goldberg and coworkers have contributed significantly to understand the high stability of supramolecular metalloporphyrin assemblies formed by axial coordination through aza ligands.¹⁰



Although Pd(II) and Pt(II) are the most widely used metal corners for supramolecular squares, a variety of transition metals have been employed to constitute the 90° metal corners of square assemblies. Hupp and coworkers have constructed the molecular square **8** from octahedral rhenium corner and 4,4'-bipyridine ditopic ligand.¹¹ Although the square **8** possesses the same organic ligand wall as the Pd(II) or Pt(II) containing squares **1** or **3**, they differ distinctly in several features. First, the molecular square **8** is neutral, while assemblies **1** and **3** are positively charged. Thus, the former has an empty cavity whereas the cavities of the latter two systems are usually occupied partially by counterions. Second, under ambient conditions molecular square **8** is persistent against ligand exchange due to the kinetically inert Re–N bond, while equilibria between the square species and their free ligands have to be considered in most solvents for **1** and **3**. Further examples of neutral metallosquares were reported by Alessio and coworkers (square **9**)¹² and Jeong *et al.* (square **10**).¹³ The inertness of Ru–N bond in square **9** allows its purification even by conventional silica-gel chromatography.

Cotton's group has made available numerous molecular squares based on dimetal corner units.¹⁴ Structural characterization of square **11** and other Mo₂⁴⁺ and Rh₂⁴⁺ analogues was accomplished by X-ray crystallography.



2.2 Thermodynamic fundamentals of self-assembled molecular squares

The results obtained so far^{4–6,11} suggest that the formation of metallosupramolecular squares is a thermodynamically favored process. In our most recent studies,¹⁵ we have explored the thermodynamic origin of square formation by employing the coordination of pyridine to complexes **4a,b** as a model system. In these studies the addition of aliquots of pyridine to *cis*-metal corners **4a** and **4b** was followed by isothermal titration calorimetry (ITC) and the data were evaluated within a 2:1 model of two dependent binding sites (Fig. 2). The obtained results suggest that the substitution of both triflates by more strongly coordinated pyridine ligands is a highly exothermic process which is driven by enthalpy and exhibits only a small entropic cost. Because of this strong exothermicity, the binding constants are rather high (in the order of 10^6 M^{-1} in chloroform) which explains that the aza coordination as well as the square formation are observed as quantitative processes in the millimolar concentration regime in CDCl_3 by NMR methods. Remarkably, in this two-step coordination process, which leads to the final 2:1 complex as shown in Fig. 2, the second step is more exothermic than the first one. This leads to a situation where the conversion to the final 2:1 complex takes place even in such case, where the concentration of pyridine is lower compared to that of the metal corner. These observations provide a strong argument for the spontaneous and exclusive formation of the metallosupramolecular squares shown in Fig. 1 from ditopic ligands and (dppp)Pt(II) and (dppp)Pd(II) corner units already at rather low concentrations of *ca.* 10^{-6} M (as independently confirmed by optical methods¹⁶). On the other hand, these squares remain the preferred species up to high concentration owing to their highly preorganized rigid building blocks, which can be related to a large value for the effective molarity (as discussed later).

The reversibility of metal–ligand coordination plays a pivotal role in the formation of metallosupramolecular squares in high yields by avoiding other macrocyclic or polymeric by-products. Based on rapid chemical exchanges among starting materials, intermediates (*e.g.* oligomers and polymers) and final ensembles during the coordinative assembling processes, the composition of

the final products depends primarily on the thermodynamic parameters of the possible products and intermediates. Such exchange provides an efficient mechanism for error correction, which may result in the conversion of thermodynamically unfavorable intermediates into a single final product. This concept was also applicable for the photoisomerization of molecular square **12** to **13**.¹⁷ The isomerization of the 4,4'-*trans*-azopyridine ligand to its *cis*-isomer imposes significant strain on the square structure of **12** and, promotes the rupture of the reversible Pd(II)–N bonds. Subsequently, the Pd(II)–N bonds are recombined to form the dinuclear species **13** with less strain. The square **12** with the *trans*-geometry of bridging ligands may be regenerated by heating species **13** in the dark. When the Pd(II) in molecular square **12** is replaced by Pt(II), the photolysis causes exclusively disassembly of the square structure without formation of a defined dinuclear species. This result is associated again with the less labile Pt(II)–aza ligand bond compared to that of Pd(II) in solution.

However, thermodynamic control only affords the formation of a single product if this product has a sufficient thermodynamic advantage over the other possible species. For many metallosupramolecular systems, two or more species are in equilibrium because no clear thermodynamic preference for one species is given. Even for the perfectly preorganized (dppp)Pd(II) and (dppp)Pt(II) corner units, complex dynamic equilibria between molecular triangles **14a–d** and molecular squares **15a–d** in solution were observed once tetraphenoxy-substituted diazadibenzoperylene bridging ligands were employed.¹⁶ From the viewpoint of thermodynamics, enthalpy favors the formation of squares which have less conformational strain (90° corner) than triangles (60° corner), while entropy favors the formation of triangles which are assembled from fewer components than squares. As a consequence, both the triangular and square species may co-exist in solution. Detailed studies for **14/15** revealed that the equilibria depend on several factors, including the metal ions [*i.e.* Pd(II) and Pt(II)], the solvent, and the steric demand of the phenoxy substituents of the diazadibenzoperylene ligands.¹⁶ Thus, bulky *tert*-butylphenoxy substituents shift the equilibrium significantly towards molecular squares due to the sterical congestion for triangular species.

Taking together all the information available on metal-directed self-assembly, it can be concluded that the formation of metallosupramolecular squares is a more complex process than simple chemical equations of their preparation disclose. For a typical self-assembly process, open polymeric intermediates have to be considered which can be transformed to a specific macrocyclic product only under the conditions of reversibility. The possible equilibria in such a self-assembly process are schematically presented in Fig. 3. As can be seen, the coordinative interactions between metals and ligands lead initially to the formation of open-chain oligomers ($n = 1, 2, 3, \dots, \infty$), which may be transformed to the corresponding cyclic products through a macrocyclization process. In this context, the generation of a specific macrocycle depends on its thermodynamic advantage compared to other cyclic species. In order to achieve this desired situation, the building blocks must be designed properly.

Hunter, Ercolani and others have examined carefully the physical basis of self-assembly macrocyclization and several parameters, including the lower self-assembly concentration (*Isac*),

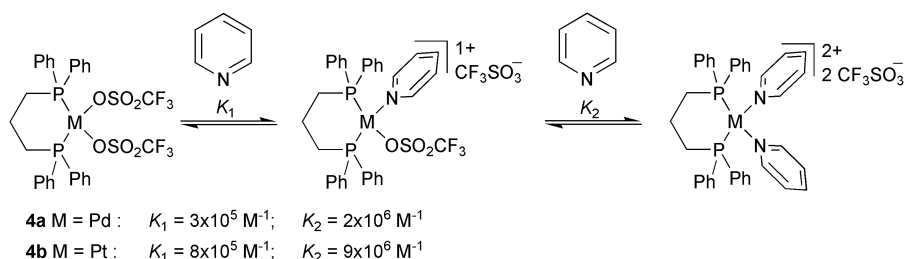
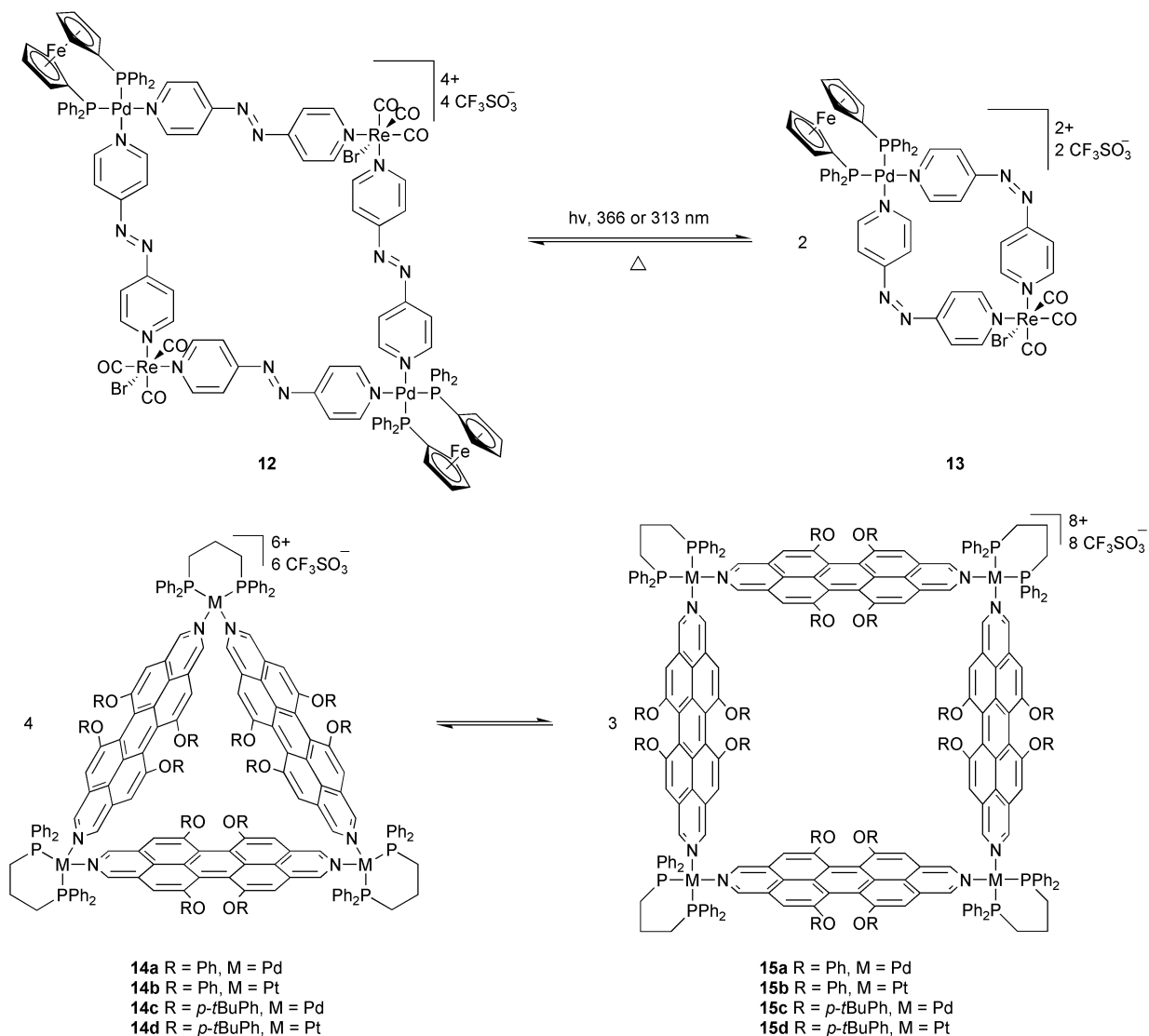


Fig. 2 The schematic representation of the two-step binding process between *cis*-metal corners **4a,b** and pyridine, and the corresponding binding constants at 293 K determined in chloroform by ITC.



the effective molarity (EM) of the self-assembled macrocycle, and the equilibrium constant (K) observed for the 1:1 model system (*i.e.* coordination between monotopic receptors of the same kind), have been suggested to evaluate the formation of macrocyclic assemblies.^{8,18} The parameter EM is a measure for the concentration at which open polymeric structures start to compete with the respective macrocycles (here the squares), while l_{sac} refers to the concentration at which the macrocycle is half-assembled from the

initial building blocks. According to these studies, the formation of macrocyclic species can only be accomplished in a certain concentration range (between l_{sac} and EM) since monomer and linear oligomers prefer to exist in the lower and higher concentration ranges, respectively. In a qualitative manner, this distribution of various self-assembled species as a function of concentration is illustrated in Fig. 4. A similar diagram has been known for a long

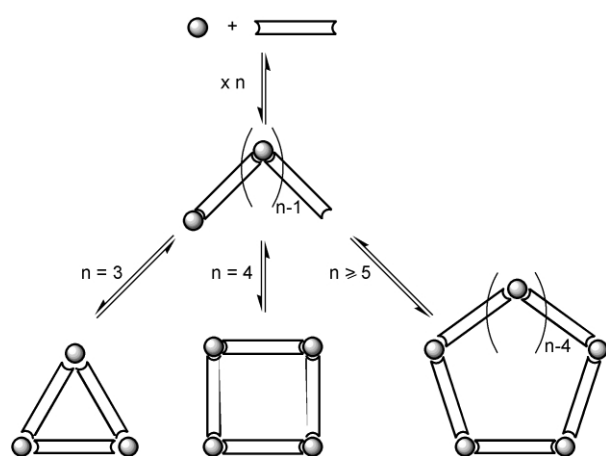


Fig. 3 Possible equilibria between linear and cyclic oligomeric species in the self-assembly process (metal corners shown as grey circles, ditopic ligands shown as connecting the corners).

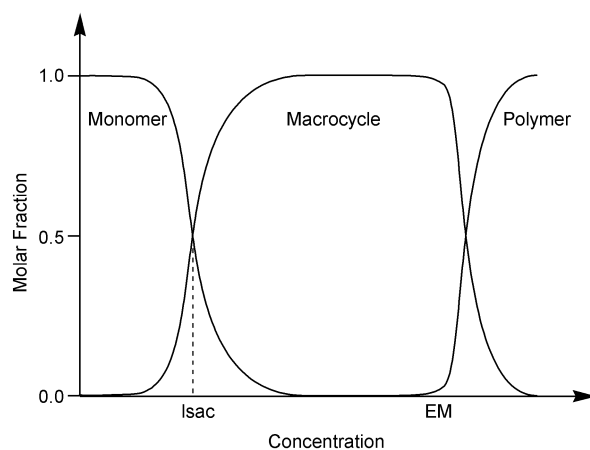


Fig. 4 The distribution of self-assembly species as a function of concentration.

time for biochemical equilibrium processes such as protein oligomerization.

According to this thermodynamic analysis of self-assembly macrocyclization, desired macrocyclic products exist as major species only within a limited range of concentration under given temperature and solvent conditions. In order to accomplish self-assembly already at low concentration, the coordinative bonds should exhibit considerable thermodynamic stability. To achieve this, the binding constant (and the related Gibbs free energy) for the respective monotopic model building blocks should be high. However, an extremely stable (irreversible) coordinative bond has to be avoided for the recovery of square species from a kinetically controlled oligomer distribution, as discussed previously. Second, a large EM is desired for the square macrocycle to avoid transformation into metallosupramolecular polymers even at high concentrations. Finally, other cyclic species should exhibit much smaller EM values than that of the square to provide a clear thermodynamic advantage for square macrocycles. To accomplish these goals rigid building blocks are required whose structural predisposition affords square macrocycles that are free of strain. These conditions seem to comply with most of the systems discussed in this review, even though only the less-favorable example of Hunter has been the subject of a rigorous thermodynamic analysis.^{8,18}

2.3 Characterization of molecular squares

The structure and stability of coordination squares are critically dependent on various factors such as the ligand itself, metal ions, solvent, concentration, temperature and even counterions. Since different assemblies might be preferred in the gas phase (mass spectroscopy) and the solid state (XRD) compared to solutions, proper characterization of metallosupramolecular square compounds is not a trivial task. The unequivocal characterization of these self-assembled species requires different complementary methods such as NMR, IR, UV/Vis spectroscopy, X-ray analysis, size exclusion chromatography, vapor phase osmometry, and mass spectrometry.

As the most common and widely used method, NMR can provide the basic structural information about coordination sites, components, and symmetry of the assembly if no paramagnetic metals are present in the system. Usually, a single set of proton signals in ¹H NMR spectra indicates symmetrical geometry of the species. In addition, for molecular squares that contain phosphorus atoms at the corner units (e.g. Stang's squares **3**), a sharp singlet would display for the equivalent phosphorus atoms in the ³¹P{¹H} NMR spectra.⁶ In the case of Pt(II) as metal centers, concomitant ¹⁹⁵Pt satellites can also be observed. However, these spectral properties alone reveal neither the particular symmetry of the assembly nor the number of building block pairs involved in its formation (e.g. squares or triangles).

Undoubtedly, X-ray crystal structure analysis is one of the most reliable and effective methods for the characterization of assemblies in the solid state, which provides directly structural details, including constitution, molecular shape, bond lengths and bond angles. However, independent verification is required as to whether the solid state truly reflects the solution structure, since it is possible that one species crystallizes out preferentially over the other ones in the case of equilibria.^{8,19} In other words, the solid state structure of a thermodynamically controlled system may not necessarily be identical with the structure that prevails in solution. Additionally, characterization of molecular squares based on X-ray crystallography is often hampered by difficulties in growing high-quality single crystals, especially for those with large cavities.

Mass spectrometry (MS) may provide information on molecular size, stability, and fragmentation pathway.²⁰ The most widely used ionization modes for the analysis of supramolecular structures by MS include fast atom bombardment (FAB), matrix-assisted laser desorption ionization (MALDI) and electrospray ionization (ESI). These relatively soft ionization methods are suited particularly for weakly bound, noncovalent species such as aza metallosupramolecular squares. Nevertheless, it is often not possible to ionize such

self-assemblies to generate sufficient ion abundance without fragmentation. Recently, coldspray ionization (CSI),²¹ a variant of the ESI method, has been developed which allows MS analysis at temperatures below 0 °C. This mild method enables observation of intact ions of metallosupramolecular squares and other complex coordination assemblies in a broad distribution of different charge states. However, the assignment of square structures based on MS signals should be made with caution, since triangles or unspecific aggregates may generate during ionization processes.²⁰ High resolution electrospray Fourier transform ion cyclotron (ESI-FTICR) technique has proven to be the most useful method for unambiguous assignment of macrocyclic products, e.g. the equilibrium between **14** and **15**, because the loss of counterions affords +2, +3, +4, and higher charged molecular ions with distinct *m/z* patterns.^{16,20}

Clearly, one single method does not provide comprehensive and accurate structural information. Therefore, several complementary analysis methods are necessary for the unequivocal characterization of these assemblies.

3 Functional molecular squares

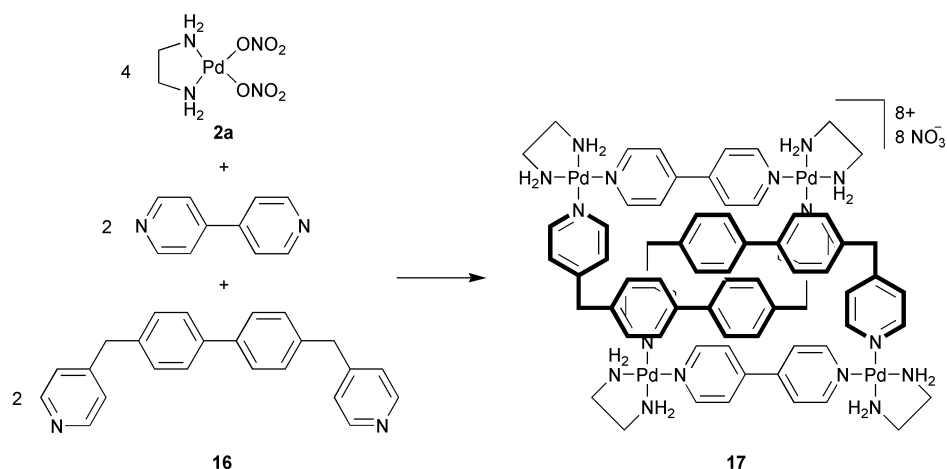
Attractive features of molecular squares are their suitability for various functional applications. On the one hand, functionalities can be readily introduced onto metallosupramolecular squares by employing functional ligands or/and metal corners in the assembly processes. Upon square formation these functions may interact leading to a higher level of functionality. Additionally, cavities are created which may accommodate guest molecules. On the other hand, macrocycles containing transition metals are generally more sensitive and responsive on electro- and photochemical stimuli compared to metal-free organic macrocyclic molecules. Therefore, the employment of metallosupramolecular squares may open up new opportunities to develop novel molecular switches and devices. Molecular squares have been applied in various fields of science and technology. A selection of functional squares and their applications are highlighted below.

3.1 Squares for molecular recognition

Since cavities of variable sizes are easily accessible with molecular squares, selective complexation of a broad series of organic molecules and ions by molecular squares could be achieved. In fact, the initial purpose for the construction of molecular squares was to utilize them as artificial receptors. For example, Fujita's molecular square **1a** (see Section 2.1) encapsulates electron-rich guest 1,3,5-trimethoxybenzene into the cavity in water to form a 1:1 complex with association constant of $7.5 \times 10^2 \text{ M}^{-1}$.⁴ During the binding process, both the hydrophobic and electrostatic interactions contribute to the formation of host-guest complexes. Similarly, positively charged molecular squares **3a,b** recognize 1,5-dihydroxynaphthalene in deuterated methanol to give corresponding inclusion complexes.⁶ Apparently, no hydrophobic but only electrostatic interaction operates in the latter system.

The inclusion ability of molecular squares has been successfully used to construct complex macrocyclic structures such as catenanes. On mixing of metal corner **2a**, 4,4'-bipyridine, and the bispyridyl ligand **16** in water in a 2:1:1 ratio, catenane **17** was produced instantaneously as the single product.²² In principle, some other thermodynamically comparable coordination complexes, including molecular square **1a** and its [2]catenane, could also form during this assembling process. X-Ray structural analysis revealed that catenane **17** is stabilized by efficient stacking of aromatic rings and probably also hydrophobic interactions. The interpenetration of the two ring components of **17** results in an ideal van der Waals interplane separation (ca. 3.5 Å) in its framework. Accordingly, this structural advantage of catenane **17** rules out the formation of regular molecular square **1a** and corresponding [2]catenane.

The rational design of efficient hosts for molecular recognition involves the introduction of specific recognition sites into square



assemblies. Stang *et al.* have designed and synthesized some molecular squares with Lewis base receptor sites, which show a variety of metal-binding capabilities and geometrical predictability.^{6,23} Representatively, molecular square **18** incorporates acetylene moieties on the backbone and, thus, may interact with two equiv. of silver triflate to give host-guest complex **19** with considerable stability in solution.²³ Complex **19** is able to further serve as receptor to bind Lewis basic guests with appropriate size through the π -complexed silver cations. Indeed, the reaction of **19** with an equimolar amount of pyrazine, phenazine, or 4,4'-dipyridyl ketone in acetone at room temperature results in the formation of corresponding ternary complexes, *e.g.* **20**. Complex **20** and its analogues may be isolated as stable microcrystalline solids in excellent yields. The structural features of **20** were investigated by single-crystal X-ray analysis. The results revealed that the distance between the two π -coordinated Ag^+ is well matched to the distance of the phenazine nitrogens. Accordingly, a lock-key relationship is given in this system.

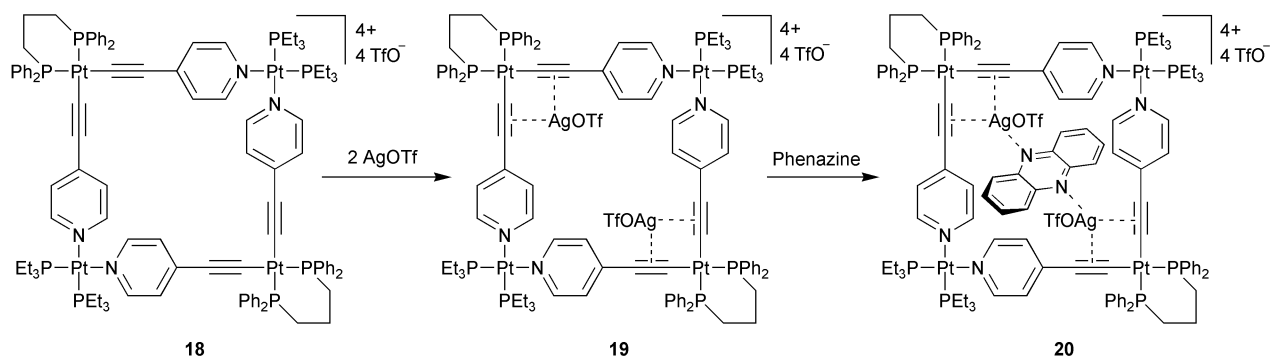
Besides Lewis acid/base sites, hydrogen-bonding sites have also been extensively introduced to molecular squares for the recognition of amide guests. In a recent study, Jeong and coworkers have designed a series of osmium(IV)-bridged molecular squares, including structures **10** and **21**, as host molecules.²⁴ The square cavities are enclosed by aryl walls, while the hydrogen-bond donating amide units on the inner surface of the hosts offer binding sites to complementary hydrogen-bond accepting guests with suitable dimensions. Among the guests of various sizes and shapes, square **10** (see Section 2.1) binds adipamide and terephthalamide selectively because both hydrogen-bonding sites of host **10** may simultaneously interact with size-matching diamide guests. Similarly, its larger analogue **21** binds preferentially longer guest amides such as terphenyldicarboxamide, but shorter guest molecules such as adipamide and terephthalamide are not well-bound. It was also found that the introduction of different substituents (*e.g.* MeO or NO_2) onto the *para* position of the corner pyridine ring affect the electron density at the pyridine nitrogen and, accordingly, the binding strength towards amide guests.

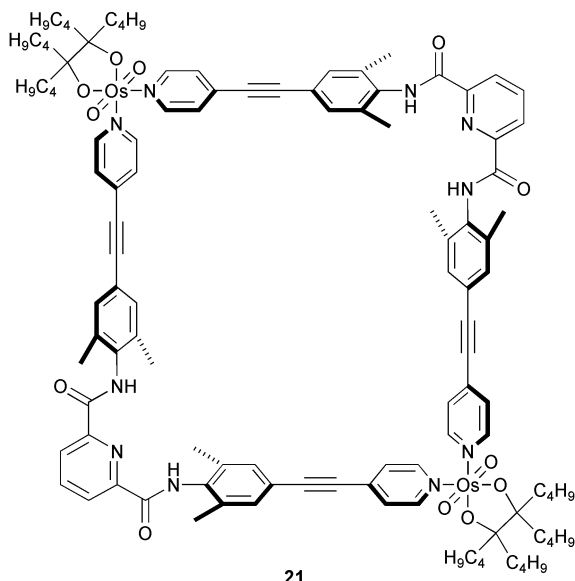
Dinuclear and mononuclear metallosupramolecular squares bearing hydrogen-bonding sites have been utilized as bead components to produce rotaxanes, in which macrocycles (beads) encircle dumbbell-like linear molecules (threads).²⁵ For examples, rotaxanes **24a–c** were obtained by mixing equimolar amounts of the respective squares **22a–c** with the thread linear component **23** in CDCl_3 , as evidenced by ^1H NMR studies.

On the basis of molecular recognition, other molecular square-containing interlocked supramolecular assemblies were produced. Kim's group has prepared the cucurbituril-based square-type molecular necklace **27** through coordination motif.²⁶ Cucurbituril (**25**) recognizes first the short-string molecule **26** in water to generate a stable pseudorotaxane complex. Under refluxing conditions, the pseudorotaxane intermediate reacts with 90° metal corner **2b** to form exclusively molecular necklace **27** ([5]MN) as the thermodynamic product, which possesses a molecular square backbone.

3.2 Chiral molecular squares

Whilst basic square-type structures possess high symmetry, chiral metallosupramolecular squares may also be derived through coordination chemistry. The construction of artificial chiral assemblies is essential not only for the understanding of the formation mechanisms of chiral entities but also to provide systems with characteristics of biomolecules for application. As demonstrated by Stang and coworkers, the introduction of chirality into molecular squares may be achieved by using metal corners bearing chiral auxiliaries, chiral linear diaza ligands, diaza ligands with hindered rotation about their linkage axis, or a combination of these methods.⁶ By employing diaza ligands which lack rotational flexibility about their linkage axis, it is possible to accomplish helicity or twist of the whole molecular square, but the formation of diastereomeric mixtures is expected. Accordingly, the introduction of chiral auxiliaries to the metal centers has proven to be the most convenient method to generate chiral molecular squares.⁶





Chiral molecular square **28**, for instance, was obtained by replacing the achiral *cis*-chelating ligands in molecular square **18** with chiral ligands 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP) and 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP).²⁷ Significant Cotton effects of the corresponding self-assembled enantiomeric macrocycles were observed. Similar to its achiral analogue **18**, coordination of silver cations by the acetylenic corners affords Lewis acidic receptors, which can further capture diheteroatomic aromatic guests such as tetramethylpyrazine and phenazine by forming inclusion complexes. Here guest binding leads to a substantial decrease in the absorption intensities and a variation of the signal shape of the initial circular dichroism signals, thus, providing a convenient method to monitor the complexation process.

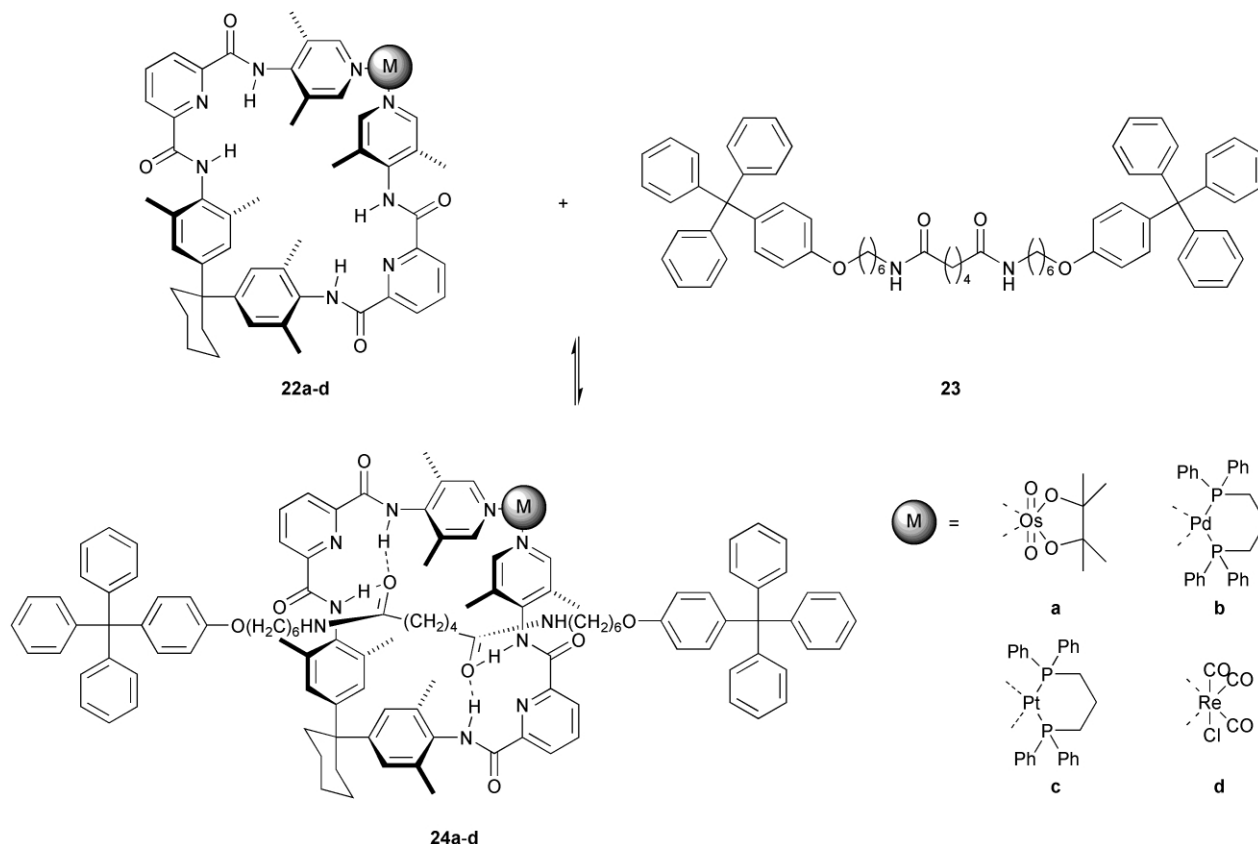
Most recently, Lin *et al.* constructed several chiral molecular squares by using atropisomeric bispyridyl bridging ligands and *fac*-

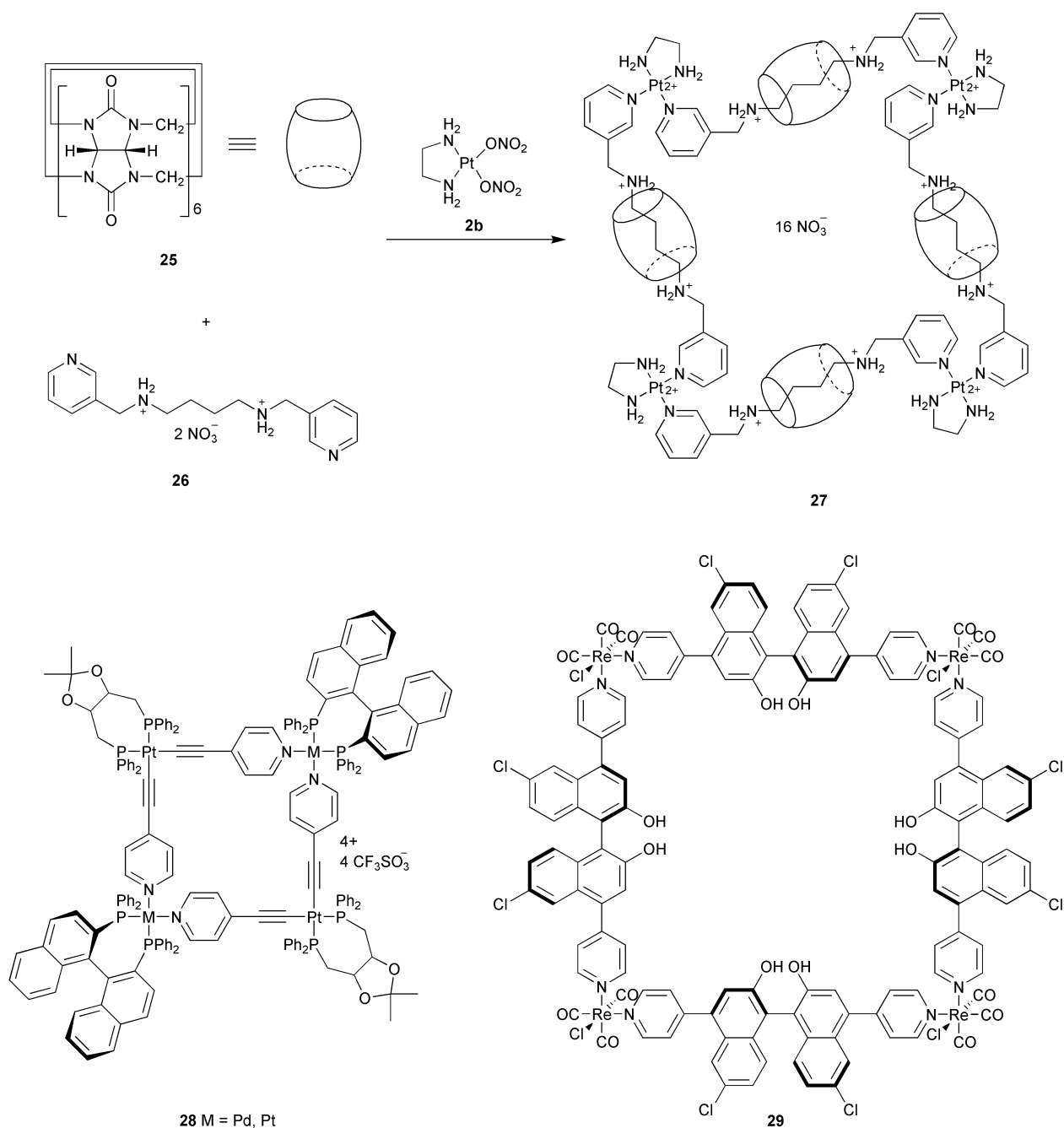
(CO)₅ReCl corners.²⁸ Metallosupramolecular square **29** exhibits luminescence signals in THF at room temperature, which can be quenched by both enantiomers of 2-amino-1-propanol, but to a significantly different extent. Accordingly, the luminescence quenching of chiral molecular square **29** by 2-amino-1-propanol is dependent on the absolute configuration of square ligands and analytes. That is, (*S*)-2-amino-1-propanol favors to quench the luminescence of the square **29** with (*R*)-configured binaphthyl ligand, while the luminescence of the antipodal assembly is preferentially quenched by (*R*)-2-amino-1-propanol. Accordingly, square ligand and analyte of opposite configuration constitute the matched pair for the effective quenching of luminescence. Additionally, the magnitude of luminescence quenching for **29** is significantly higher than that of free ligand, suggesting a better-defined chiral microenvironment conferred by molecular square **29**. Therefore, confinement of chiral ligands in metallosupramolecular squares seems to be a promising approach to enantioselective recognition, sensing, and catalysis.

3.3 Photoluminescent molecular squares

Luminescent molecular squares such as **8** and **29** were shown to be effective probes for molecular sensing.^{11,28} Furthermore, in order to mimic cyclic light-harvesting chlorophyll dye assemblies of the photosynthetic machinery of purple bacteria, square-type arrangements of organic dyes have been constructed. Owing to the structural resemblance to their natural counterparts, porphyrins have been initially selected as photoactive building blocks. Drain and Lehn have reported the first porphyrin-based molecular squares **5** and others derived from 5,15-dipyridylporphyrin and *cis*-Pt(NCPh)₂Cl₂, in which the photoluminescence of porphyrin ligands was strongly diminished upon metal coordination.⁷ However, these structures have been characterized poorly and the involvement of open-chain oligomeric by-products seems likely as *cis*-PtCl₂ units are known to isomerize easily to *trans*-PtCl₂ units.²⁹

By employing highly soluble tetra-*n*-hexyl-substituted 5,15-dipyridylporphyrin ligands in organic solvents, supramolecular



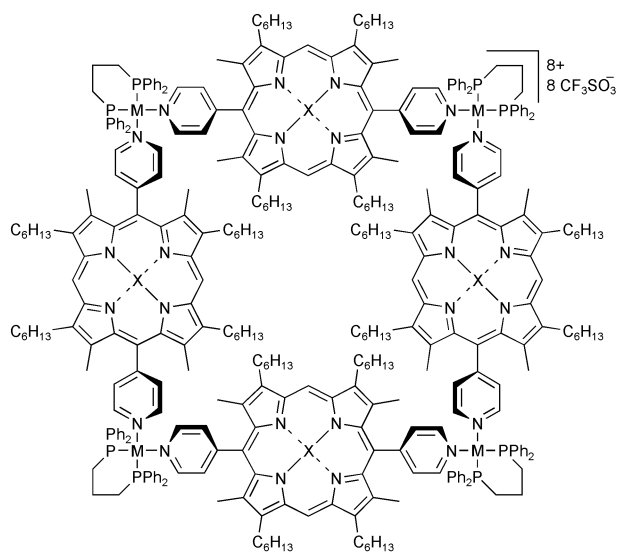


squares **30a–d** were prepared by self-assembly with *cis*-dppp metal corners **4a,b**.³⁰ These square assemblies (**30a–d**) were well-characterized. They are also stable in a wide concentration window and, accordingly, are properly suited for spectroscopic studies in highly dilute solutions. However, the initial fluorescence of porphyrins is quenched drastically by the presence of metal corners; thus, an overall 30–60% drop in fluorescence quantum yield compared to that of free ligands was observed for the macrocycles **30**. The fluorescence quenching was attributed to the heavy-atom effect.

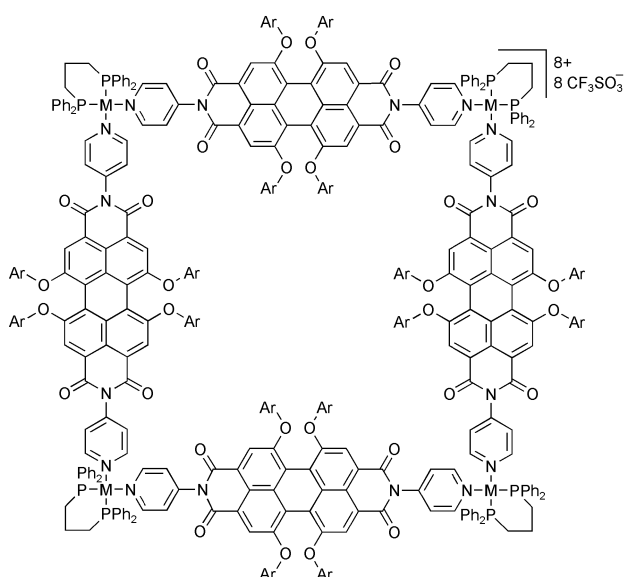
Such undesired fluorescence quenching was overcome in perylene bisimide-based squares **31** that exhibit fluorescence quantum yields of almost unity in chloroform.³¹ These squares are also the largest ones reported in the literature so far with metal–metal distances of 2.4 nm. They were prepared by coupling of 4-aminopyridine with tetraphenoxyperylene tetracarboxylic acid bisanhydrides and subsequent self-assembly with the corner units **4a,b**. Because the pyridyl moieties are located at the imide positions of the perylene core, where nodes exist in the HOMO and

LUMO orbitals, the luminescent properties of these ligands remained intact in the metal-assembled superstructures. The fluorescence quantum yields of **31a** and **31b** in chloroform are 86% and 88%, respectively. For comparison, triangles **14**/squares **15** mixtures exhibit significantly weaker emission compared to their free ligands (the quantum yield is by a factor of 10^5 to 10^6 lower than that for the corresponding free ligands) as a consequence of direct metal coordination to the chromophore.¹⁶ From these observations, it may be concluded that the binding sites of functional ligands should not be conjugated with the chromophore to preserve their inherent fluorescence upon metal binding.

Further elaboration of this functional scaffold led to the multichromophoric square **32**, which contains 16 additional pyrene dye units at the tetrameric perylene-based square.³² Such metallosupramolecular architectures are reminiscent of cyclic dye assemblies of light harvesting bacteria, where energy transfer from outer antenna dyes to the reaction center is essential for efficient capture of sun light. Indeed, for the assembly **32** an energy transfer was observed from the outer pyrenes to the inner perylene dyes



30a M = Pt, X = 2H; **30b** M = Pd, X = 2H
30c M = Pt, X = Zn; **30d** M = Pd, X = Zn



31a M = Pt, Ar = *p*-*t*BuPh
31b M = Pd, Ar = *p*-*t*BuPh

32 M = Pt, Ar =

33 M = Pt, Ar =

upon photo excitation. However, competitive photo-induced electron-transfer processes spoiled the overall efficiency, and suggest application of other antenna dyes with lower HOMO levels to construct efficient artificial light harvesting systems.

3.4 Redoxactive molecular squares and electrochemical sensing

To date, only a few redoxactive molecular squares are known. Perylene-bisimide-based molecular squares **31a,b** possess not only excellent luminescent properties, but also fascinating redox behavior.³¹ Cyclic voltammetric investigations showed that molecular square **31a** exhibits two reversible waves in the reductive cycle ($E_{1/2} = -1.01$ and -1.14 V *versus* Fc/Fc⁺), which correspond to the formation of radical anionic and dianionic perylene bisimide

species, respectively. Notably, it was possible to reversibly oxidize the perylene bisimide units in **31a** at a potential of $E_{1/2} = +0.93$ V, whereas the free ligand was irreversibly oxidized and adsorbed onto the platinum electrode at this potential. This is probably a consequence of the pyridine–platinum coordination, which blocks the nitrogen lone pairs effectively, thus, they are no longer susceptible to adsorption and facile oxidation.

Ferrocene is an excellent choice for probing electron-transfer processes at electrode surface owing to the considerable stability of ferrocenium cations. Therefore, reversible oxidation waves are expected at an electrode potential of about $+0.5$ V *versus* SCE (in CH₂Cl₂). Recently, the above-mentioned scaffold was applied to organize additional redox active ferrocene units in three-dimensional space. Starting from tetraferrocenyl-substituted perylene bipyridyl imides and Pt(II) metal corner **4b**, square **33** and its analogues containing twenty redox active units have been prepared.³³ For the inner scaffold of four perylene bisimides, two reversible four-electron reductive processes, which are little influenced by the supramolecular arrangement could be observed by cyclic voltammetry. By contrast, it has been found that the redox properties of the 16 peripheral ferrocenyl subunits are strongly affected by the sterical constraints imposed by the square-type architecture, showing signal splitting for the reduction of ferrocenium ions to neutral ferrocenes. Once all 16 ferrocene groups in squares **33** are transformed to ferrocenium ions, in total 24 positive charges are loaded onto this nanosize assembly. From the structural point of view, these assemblies exhibit similar features to dendrimers (Fig. 5) but their vacant interior might be useful to accommodate functional guest molecules.

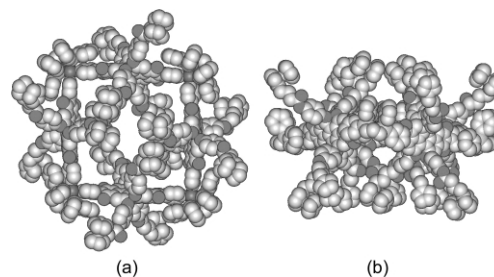
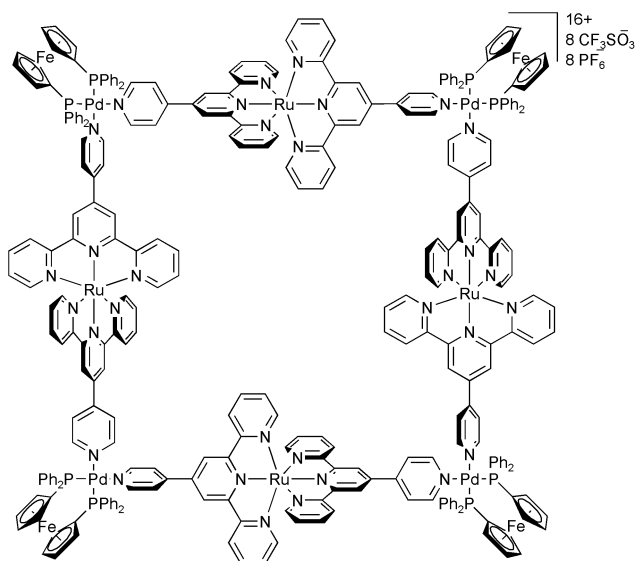


Fig. 5 Top (a) and side (b) views of energy minimized structures of molecular square **33**.

Ferrocene units have also been positioned at metal corners,^{6,17,34} or applied as linkers¹⁴ to achieve redoxactive molecular squares. The heterometallic (Pd/Ru) molecular square **34** is an attractive assembly for electrochemical sensing, since it incorporates four redoxactive terpyridyl metal complexes as bridging ligands in addition to another four ferrocene units at corners.³⁴ Cyclic voltammetric studies showed that the four Ru²⁺ were oxidized to Ru³⁺ simultaneously and reversibly in deoxygenated DMF at $E_{ox} = 0.70$ V (*versus* Fc/Fc⁺). An additional irreversible oxidation wave appeared at higher potential ($E_{ox} = 0.88$ V), which is assigned to Fc⁺/Fc²⁺. In this heterometallic system, no recognizable communication between the metal centers could be observed. Compared to the corresponding free ligand, virtually no shift of the oxidation potential for Ru²⁺/Ru³⁺ was observed in the presence of the electron-donating ferrocenylphosphine ligand, which obviously compensate the loss of electron density in the bridging metal complex through coordination. However, once the Pd(II) metal corners in **34** are replaced by *fac*-Re(CO)₃Br, the oxidation potential for Ru²⁺/Ru³⁺ was anodically shifted due to the electron-withdrawing Re(CO)₃Br moiety, the latter destabilizes the metal towards oxidation to its Ru³⁺ state.

The combination of electroactivity and complexation features of molecular squares should lead to attractive sensory materials. Willner *et al.* have recently demonstrated an interesting concept to realize electrode surfaces, which are covered with multiple layers of molecular squares.³⁵ Such stable interfaces containing defined numbers of layers were generated by stepwise treatment of



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3-aminopropyltriethoxysilane-modified indium-doped tin oxide (ITO) conductive glass with solutions of 12 nm Au nanoparticle and solutions of Pd-square **1a**.³⁵ Since molecular square **1a** may serve as a receptor for the complexation of π -donor substrates, binding of analytes such as hydroquinone to the receptor units increases its local concentration at the electrode surface, and allows its electrochemical sensing by the three-dimensional conductive Au array. Therefore, Au-nanoparticle/square **1a** layers act as a functional interface to concentrate π -donor analytes, and enable their electrochemical sensing.

Another approach was introduced by Hupp and coworkers for the electrochemical sensing of substrates by molecular square sensory layers on the basis of size-selectivity.³⁶ In their studies, thin films of neutral rhenium molecular squares (such as **8**) were prepared on inert conductive platforms, which were subsequently used as working electrodes in electrochemical cells. When the film-coated electrodes were exposed to solutions containing redox-active substances of various sizes, the electrochemical responses could be observed only for the species capable of permeating the film, depending on the cavity size of the molecular square used.

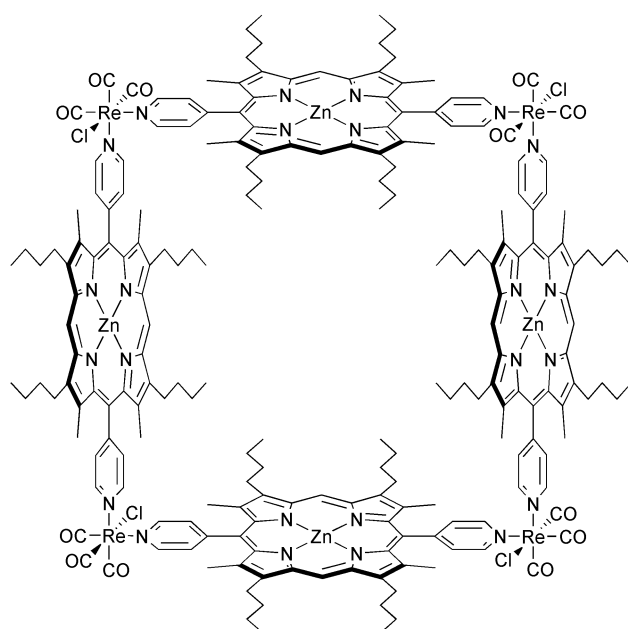
Accordingly, the square assemblies act as molecular sieves in these electrochemical sensing processes.

3.5 Molecular squares as catalysts

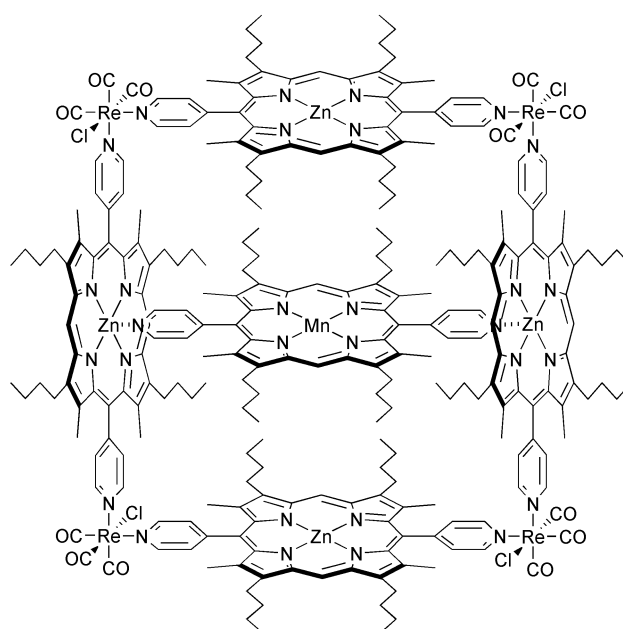
As discussed in the previous sections, many functions of molecular squares originate from their inherent cavities, such as molecular recognition, chemical sensing, and transportation of matter. In general, neutral metallocupramolecular squares seem to be superior to the more common positively charged squares for these applications, since the cavity of the latter is usually filled with counterions, while the former may furnish an elegant micro-environment for substrate encapsulation. On the basis of molecular recognition, macrocyclic compounds may be applied to enhance the product selectivity and even the reaction rate of synthetically useful transformations by selective binding of substrates. Furthermore, catalytic active centers could be introduced into functional metallocupramolecular squares and the exploitation of them as efficient microreactors seems to be feasible.

Although these rigid supramolecular assemblies have potentials as highly selective catalysts, reports on such catalyst systems are still scarce. In a representative study, Hupp and coworkers designed and prepared molecular square **35** with four zinc-porphyrin walls. The Lewis acidic receptor sites enabled encapsulation of a bispyridyl manganese-porphyrin to afford assembly **36**, which was suggested as a model for the active site of cytochrome P450.³⁷ Compared to the naked manganese-porphyrin, the lifetime of the present catalyst was increased 20-fold due to the protective environment of molecular square **35**. In addition, the half-cavity defined by molecular square **35** and the inner-bound manganese-porphyrin may affect significant substrate size-selectivity in catalytic epoxidation.³⁷ Attractively, the cavity size and shape may be easily modified by introducing various functionalities into the cavity through coordinative interactions, thus, the substrate size/shape-selectivity is eventually tunable. By following this design concept, further metallocupramolecular squares with enhanced stability and substrate selectivity should be accessible.³⁶

In their most recent studies, Fujita *et al.* have exploited more complex self-assembled coordination cages to promote the reaction between two encapsulated guest molecules.³⁸ Their results show that properly designed cavities may dramatically accelerate the [2+2] photodimerization of olefins and strictly control the configuration of the product.



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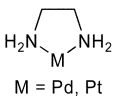
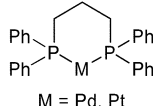
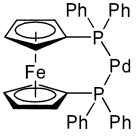
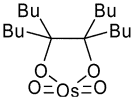


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4 Summary and outlook

Significant progress has been made over the past years in the area of metallosupramolecular squares. Here, we have presented a brief overview on the synthetic methods and functional properties of metallosupramolecular squares. As a preparation method for macrocycles, coordination-driven self-assembly proved to be superior to conventional organic routes, which usually lead to kinetically distributed product formation. Thus, structurally well-defined macrocycles can be obtained in high selectivity and quantitative yield under mild conditions through metal-mediated self-assembly. Among the macrocycles derived from this strategy, molecular squares have received the highest attention in the past. The impetus behind this rapid development is their potential application as functional materials and molecular devices. Accordingly, the focus of the current research is on featuring supramo-

Table 1 A selection of synthetically available metallosupramolecular squares (for simplicity metal corner and bridging ligand of the corresponding square are given) and their functional properties

Metal Corner	Bridging Ligand	Function
 M = Pd, Pt	4,4'-Bipyridine	Molecular recognition (in aqueous medium)
 M = Pd, Pt	4,4'-Bipyridine	Molecular recognition (in organic medium)
	5,15-Dipyridylporphyrin (2H or Zn)	Photoluminescence
	Perylene bisimide	Photoluminescence and light harvesting
	Ferrocenyl-substituted perylene bisimide	Electrochemical response
	Pyridine-terpyridyl Ru complex	Electrochemical response
(Et ₃ P) ₂ Pt	4-Pyridylacetylene	Host-guest complexation
	Pyridine-2,6-dicarboxamide (see 10)	Molecular recognition, threading
Re(CO) ₃ Cl	4,4'-Bipyridine Dipyridyl BINAP (see 29) 5,15-Dipyridylporphyrino zinc	Molecular sensing Enantioselective sensing Molecular recognition and catalysis

lecular squares with novel functional properties. In Table 1, the functional properties realized in metallosupramolecular squares are summarized.

As discussed in this review, the fundamental principles for the construction of metallosupramolecular squares are well understood. This knowledge should now be utilized to realize more diverse structures that exhibit new features. Recently, triangles as well as more complex polyhedra have become the focus of interest. However, also exploration of different metal corners seems to be important as only few well-established metal corner units limit the range of accessible metallosupramolecular macrocycles. Isothermal titration calorimetry (ITC) might be the method of choice to reveal new metal/ligand combinations with appropriate thermodynamic parameters (*e.g.* ΔH and ΔG). Improved recognition functionalities will require structures of lower symmetry to achieve structural complementarity to interesting guest molecules. Dynamic combinational chemistry could be the method of choice to select a specific ligand out of a library of ligands.³⁹ Through metal-mediated self-assembly, it should be possible to move from discrete

molecular squares to more complex infinite 2D square grids and networks, which might involve in the promising application as porous functional materials. Due to the photo- and electrochemical activities of incorporated transition metals and chromophoric ligands, metallosupramolecular squares possess also considerable potential for applications in molecular electronics.⁴⁰

Acknowledgements

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