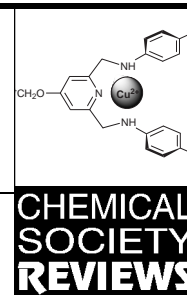


Metal-directed self-assembly of two- and three-dimensional synthetic receptors



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This article reviews recent progress in the study of the transition-metal mediated self-assembly of two- and three-dimensional synthetic receptors. Whereas macrocyclization under kinetic control is undoubtedly an unfavorable process, the self-assembly strategy offers quite efficient methods for constructing macrocycles under thermodynamic control. In particular, *cis*-protected Pd(II) and Pt(II) blocks are quite effective in obtaining the cyclic framework from simple molecules. Examples disclosed in this article are spontaneously assembled in quantitative yields by just mixing component molecules. This approach is successfully applied to the construction of cage compounds. The self-assembly of nanosized macrocycles and cages is also discussed.

thermodynamic control should be a good strategy for macrocycle (or cage) synthesis.

This principle has been realized by recently developed non-covalent syntheses. That is, spontaneous generation of well-defined structures has been achieved under thermodynamic conditions by supramolecular self-assembly. In particular, coordination chemistry has been successfully used to construct such discrete structures as helices, rods, macrocycles, and cages.¹ These structures are spontaneously generated by simply mixing component ligands and metals in solution. Among defined structures, macrocycles and cages are particularly interesting because of their potential as synthetic receptors. Exploring the function of self-assembled metal-complexes, the present article focuses on recent progress in the metal-directed self-assembly of two- and three-dimensional synthetic receptors.²

1 Introduction

Since the discovery of crown ethers, numerous studies on cyclic and cage compounds that are capable of binding atoms (ions) or molecules in their cavities have developed new fields in current chemistry such as host–guest chemistry, molecular recognition, or supramolecular chemistry. However, there seem little examples of obvious practical use for macrocycles and, in particular, cage compounds despite their remarkable potential utilities. This is partially due to synthetic difficulties encountered in their preparation. In fact, the preparation of macrocycles and cages are in general quite low yield processes and require, for example, high-dilution techniques which are not suitable for their practical syntheses. Whereas macrocyclization under kinetic conditions is an unfavorable process, macrocycles are sometimes obtained in high yields under thermodynamic conditions. Typical examples of high yield formation of macrocycles under thermodynamic conditions are provided by phenol-formaldehyde (calixarenes) or resorcinol-aldehyde cyclic oligomers which are formed under equilibrium conditions. The facile formation of such macrocycles suggests that

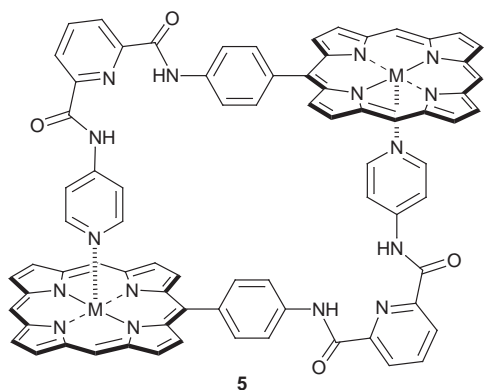
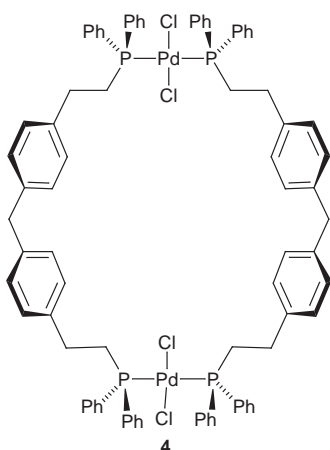
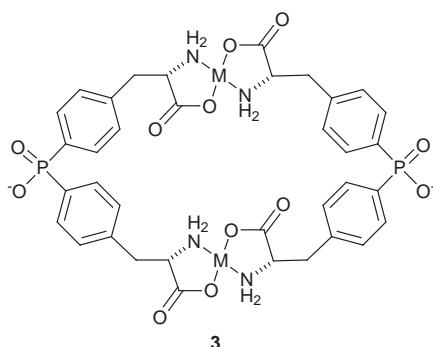
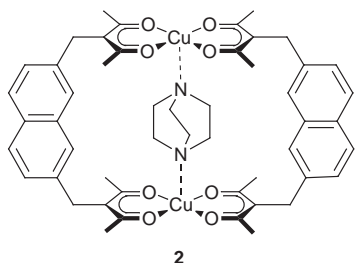
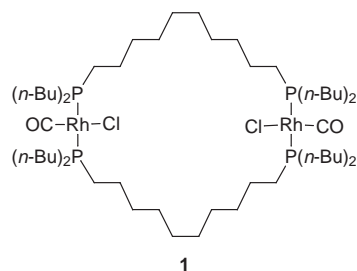
2 Macrocycles incorporating naked metals in their backbones

In the literature, several metal–ligand macrocycles have been described. An earlier example was the macrocyclic dinuclear Rh(I) complex **1**,³ which was, however, not designed as a receptor and no binding property was reported for this or related macrocycles. The first self-assembled macrocyclic host **2** containing two Cu(II) ions was reported by Maverick and Klavetter.⁴ This inorganic macrocycle showed a strong binding affinity towards 1,4-diazabicyclo[2.2.2]octane ($K_a = 220 \text{ L mol}^{-1}$) as evidenced by X-ray crystallography. Two point acid–base binding observed in the crystal structure is obviously important because little affinity was shown for monoamines such as pyridine ($K_a = 0.5 \text{ L mol}^{-1}$). Self-assembled macrocycle **3**, with a hydrophobic binding site, was shown to be effective for pyrene transport through a liquid membrane.⁵ The rate of the transport depended on the metal ion employed, and Ni(II) and Co(II) showed the highest efficiency for the cooperative binding of aromatic guests. The binding ability of hosts **2**, **3**, and **5** is summarized in Table 1. Macrocyclic dinuclear Pd(II) complex **4** also has a hydrophobic cavity.⁶ This complex was prepared by simply mixing PdCl₂ and a bis-phosphine bridging ligand and fully characterized by FABMS study. The dimerization of a zinc–porphyrin with a pyridine terminus resulted in the formation of macrocyclic complex **5** with inwardly directed hydrogen bonding sites.⁷ This macrocycle showed a binding affinity towards a terephthalic acid derivative ($K_a = \text{ca. } 40 \text{ L mol}^{-1}$) through efficient hydrogen bond formation.

Quite recently, Lehn and co-workers reported the self-assembly of circular helices whose frameworks are templated by their counter anions.⁸ That is, the self-assembly of tris-bipyridine ligand **6** with FeCl₂ salts yields pentanuclear complex **7** which incorporates a chloride ion in the cavity as evidenced by X-ray analysis, whereas the same ligand gives hexanuclear complex **8** when treated with Fe(BF₄)₂, FeSO₄, or FeSiF₆. Most probably, complex **8** carries one counter ion in the void at the center.

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A catalytic property has been reported for self-assembled macrocyclic Cu(I) complex **9**: *i.e.*, it catalyzed the hydrolysis of β -amino acid derivatives by the cooperative effect of two Cu(I)

Table 1 Association constants between self-assembled macrocycles and various guests

Host	Guest	Association constant/L mol ⁻¹
2	Pyridine	0.5
	Pyridine	5
	Quinuclidine	7
	DABCO	220
	Pyrene	14 500
3 (M = Co)	1-(Naphthoxy)acetate	6 060
	Indole	848
	Tryptamine	60
	D or L-N-Acetyltryptophan	6
	N,N'-Dihexylterephthalamide	> 1 400
5	Dimethyl terephthalate	40
	Dimethyl isophthalate	< 1
11a	N-(2-Naphthyl)acetamide	1 800
	1,3,5-Tri(methoxy)benzene	750
	p-Dimethoxybenzene	330
	m-Dimethoxybenzene	580
	o-Dimethoxybenzene	30
19	p-Bis(methoxymethyl)benzene	10
	1,4-(Dimethoxy)cyclohexane	n.c. ^a
	N-(2-Naphthyl)acetamide	15
	1,3,5-Tri(methoxy)benzene	2 500
	p-Dimethoxybenzene	2 680
	m-Dimethoxybenzene	1 560
	o-Dimethoxybenzene	1 300
	p-Bis(methoxymethyl)benzene	560
	p-Dinitrobenzene	30
	1,4-(Dimethoxy)cyclohexane	n.c.

^a n.c.: not complexed.

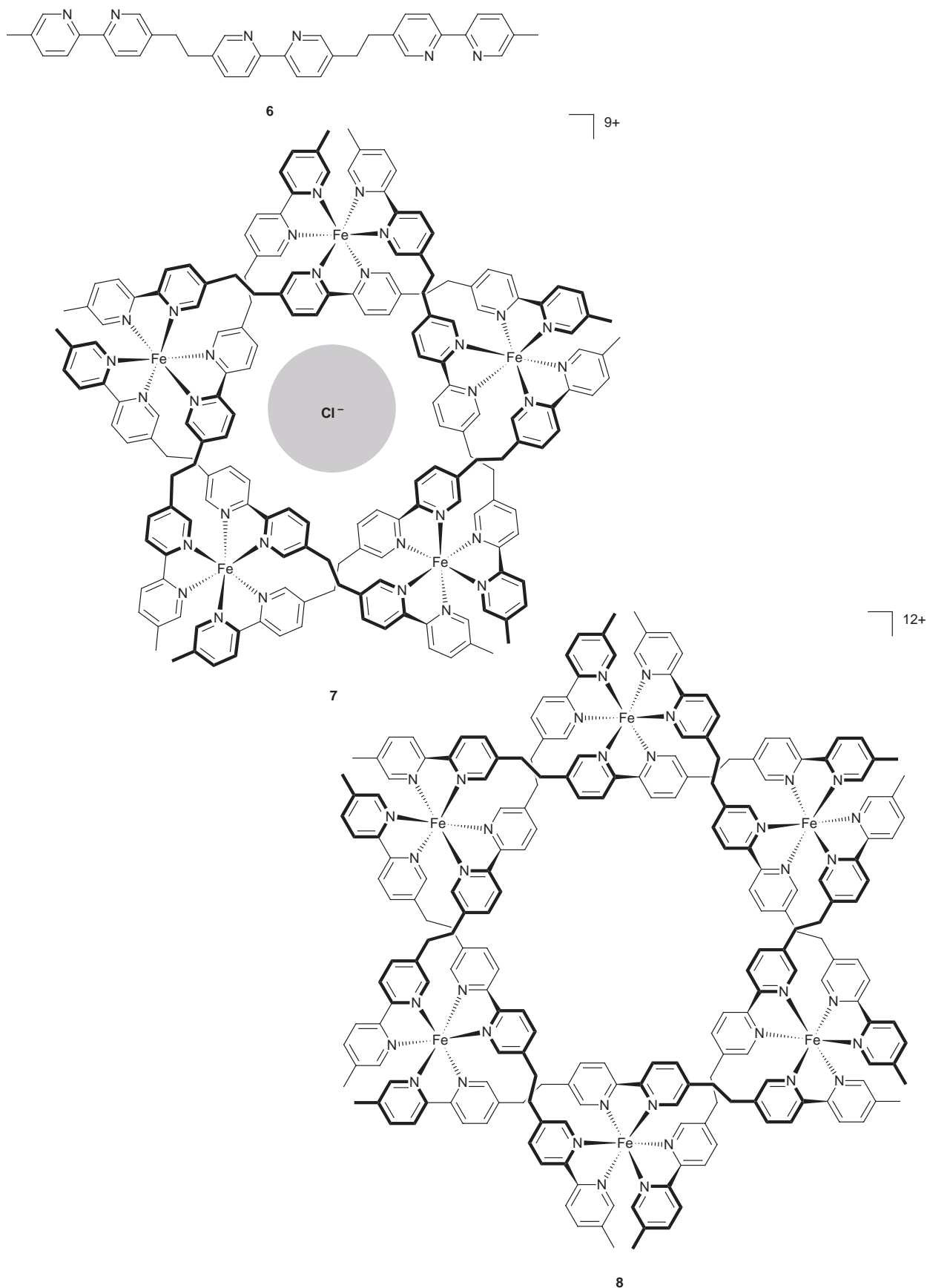
ions. Interestingly, this macrocycle inhibited the hydrolysis of α -amino acid derivatives.⁹

3 Macrocycles involving *cis*-protected Pd(II) or Pt(II) blocks

In the studies on inorganic macrocycles discussed above, naked metal ions were employed to induce the self-assembly of macrocyclic frameworks. The most frequently employed metals are tetrahedral Cu(I), octahedral Fe(II), Co(II), Ni(II), and square planar Pd(II). However, when such naked ions are employed, it is often difficult to control the number and the direction of coordinating organic ligands. If a metal ion is appropriately protected, coordination sites are limited and the number and the direction of ligands are easily controlled. Furthermore, the protection of the metal gives rise to the design of simple self-assembly from non-sophisticated monodentate ligands (*e.g.*, 4-pyridyl group). Based on such an idea, novel *cis*-protected Pd(II) and Pt(II) building blocks **10** were designed. As discussed in the following sections, these metal building blocks have shown a remarkable ability for inducing the self-assembly of a variety of macrocycles and catenanes.¹⁰

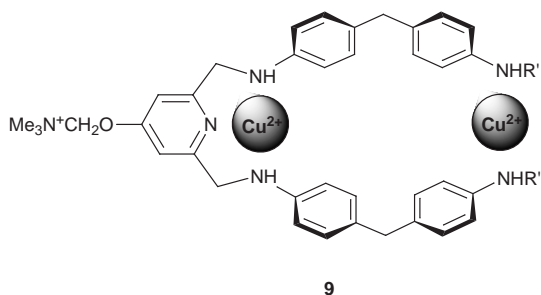
3.1 Self-assembly of Pd(II)- or Pt(II)-linked square complexes

The first example of the self-assembled complex possessing *cis*-protected Pd(II) blocks is the tetranuclear square compound **11a** (eqn. (1)).¹¹ In the design of complex **11a**, the combination of the 90 degree coordination angle of the metal with the 180 degree divergence of a linear ligand provides a square framework which has been hitherto unrealized despite its simplicity. The self-assembly takes place without losing the Pd(en) framework because the dissociation of the en ligand



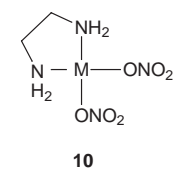
from Pd(II) is negligible under ordinary conditions but monodentate ligands undergo rapid dissociation on Pd(II) ion giving rise to the self-assembly of **11a** under thermodynamic equilibration. The procedure for the preparation of **11a** is very simple. By

just mixing an equimolar amount of **10a** and 4,4'-bipyridine in aqueous solution, the quantitative self-assembly of **11a** was observed, which was precipitated in a very pure form by adding ethanol to the reaction solution. The solution structure of **11a**



was confirmed by NMR and electrospray ionization mass spectrometry (ESI-MS) studies whereas the solid structure was determined by X-ray crystallography (Fig. 1).¹²

In the crystal structure of **11a** is found an almost perfect square framework with facial conformation of all pyridine nuclei. The interplanar surface-to-surface separation inside the



a: M = Pd; b: M = Pt

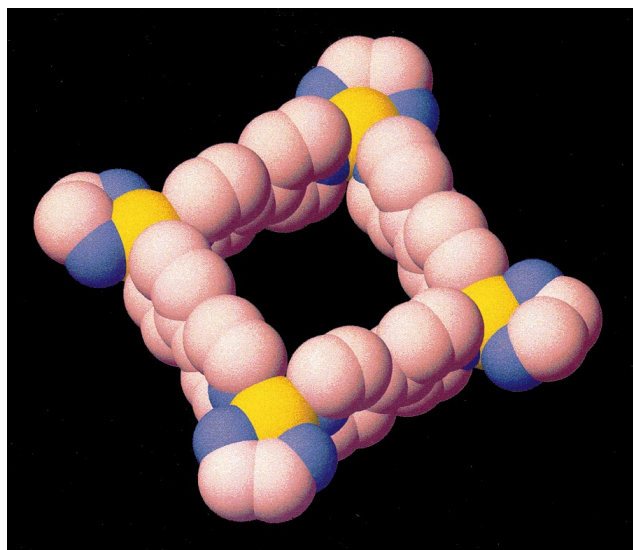
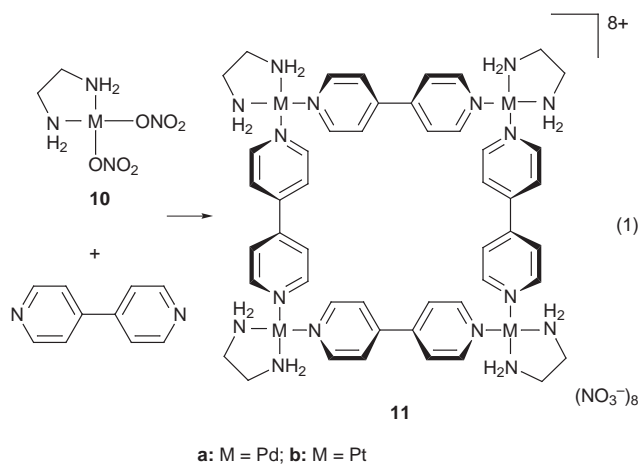
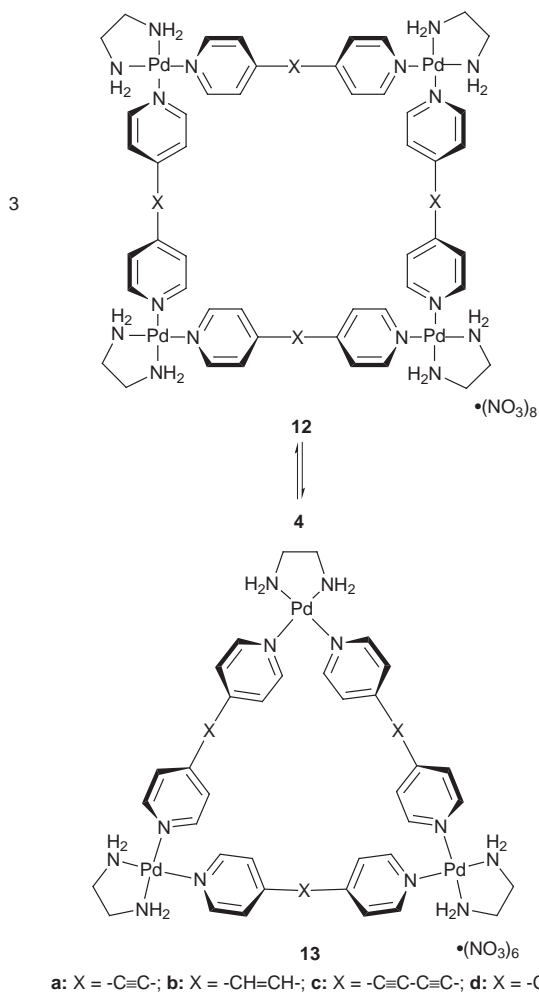


Fig. 1 The X-ray structure of **11a**



(2)

cavity is approximately 8 Å corresponding to the diameter of the cavity of β-cyclodextrin. The square structure was easily expanded by incorporating phenylene or acetylene spacers into

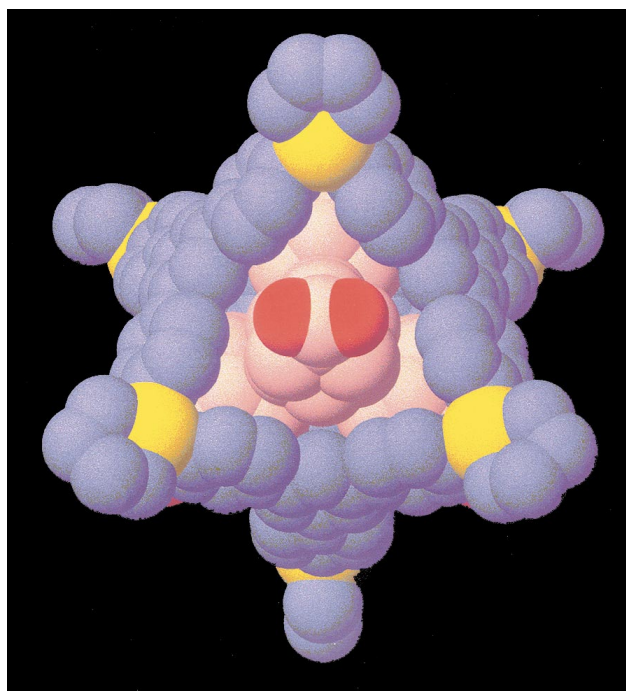
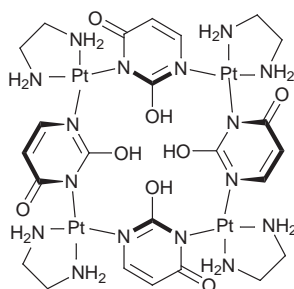
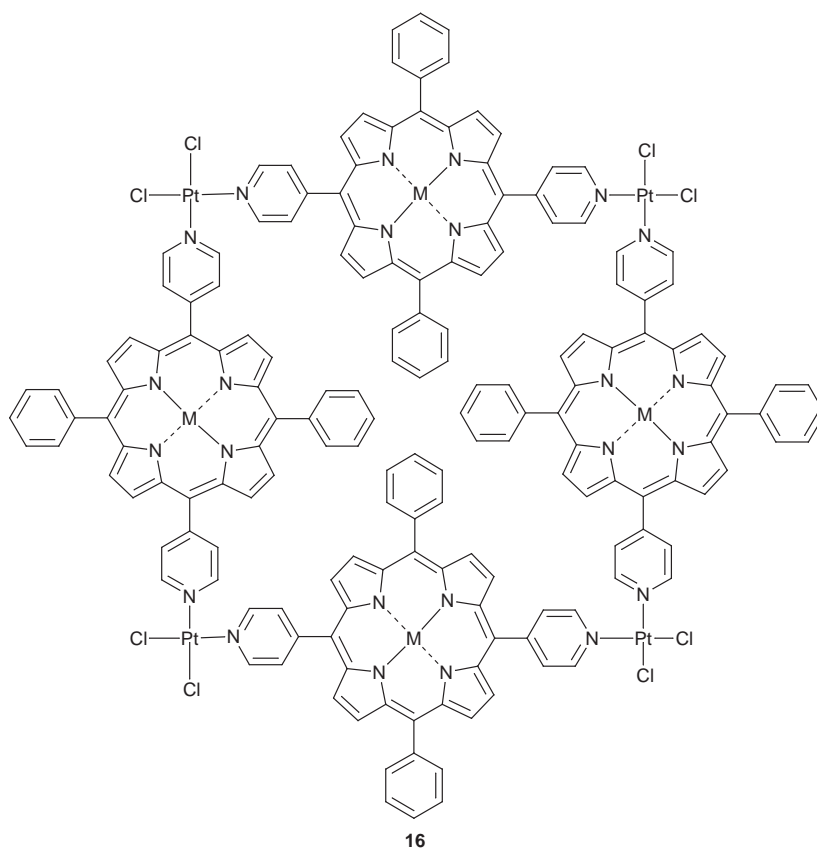
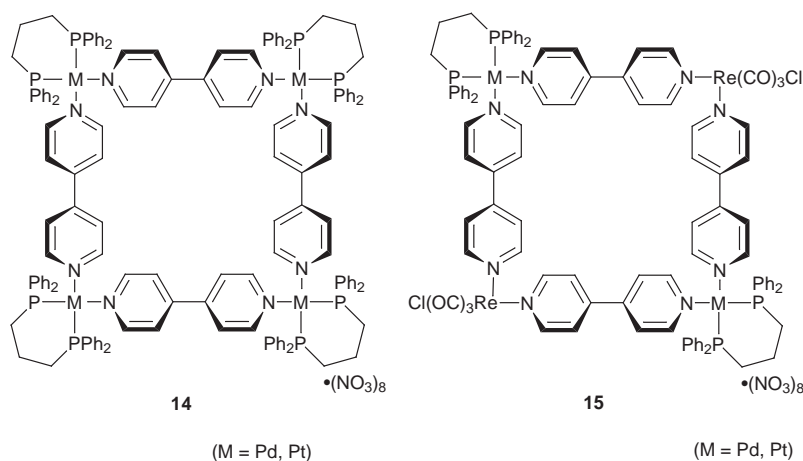


Fig. 2 The X-ray structure of **27·(G)₄** (G = adamantanecarboxylate ion)

the bipyridine framework. However, an equilibrium between square **12** and triangle **13** was observed depending on the concentration of the components (eqn. (2)).¹² Hong and co-

workers reported recently that this equilibration can be controlled by induced-fit molecular recognition. That is, the equilibrium ratio is pushed toward triangle **13b** in the presence



of a small guest. In contrast, a large guest induced the reorganization of square complex **12b**.¹³

The self-assembly of Pt(II) analog **11b** was very slow due to the inactivity of the Pt(II)–pyridine bond. Thus, upon treatment of **10b** with 4,4'-bipyridine, a kinetically distributed oligomer mixture was initially formed. However, the mixture gradually turned into the thermodynamically most stable **11b** after the solution was heated for a few weeks at 100 °C as monitored by NMR measurement.¹⁴

3.2 Molecular recognition ability of the self-assembled square complexes

Due to the cationic structure, complex **11a** is highly water soluble. In water, however, it provides a very efficient hydrophobic cavity in which neutral organic molecules are effectively recognized (Table 1).¹⁵ In addition to a hydrophobic interaction, an electrostatic or charge transfer interaction should be important for the host–guest complexation because electron-deficient host **11a** recognized electron-rich guests more efficiently. Organic carboxylates are also bound in the cavity and a significant upfield shift for guest signals (up to $\Delta\delta = -2.8$ for a (2-naphthyl)acetate ring proton) was observed. In the recognition of dimethoxybenzenes, the association constants were 30, 580, and 330 L mol^{−1} for *ortho*-, *meta*-, and *para*-isomers, respectively. The preferential recognition of *meta*- and *para*-isomers are probably due to two-point electrostatic interaction which can not be considered for the *ortho*-isomer.

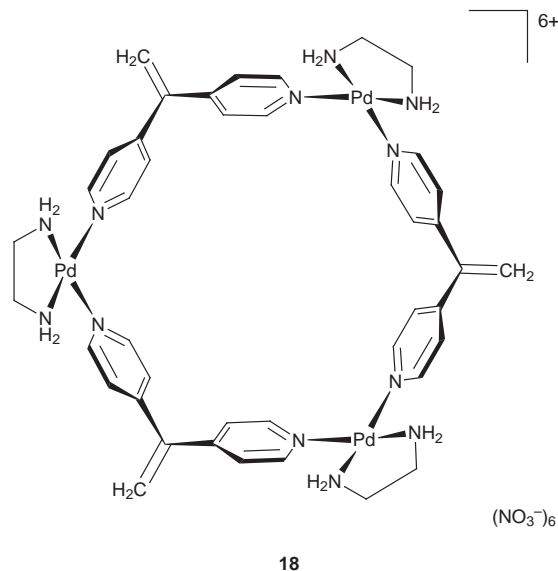
3.3 Other molecular squares

Following square complex **11**, a variety of square compounds have appeared in which transition metals provide the 90° angle at every corner of the square (Fig. 2). Stang and Cao modified the structure of **11** into organic soluble phosphine derivative **14**.¹⁶ Using the phosphine protective group, his group has been extending the chemistry of square compounds. For example, chiral squares, metal-hypervalent iodine hybrid squares, nano-sized squares, functional squares with ferrocene, crown ether, or porphyrin units have been developed.¹⁷ A similar self-assembly strategy was employed by Hupp and co-workers for the preparation of Pd(II)–Re(I) or Pt(II)–Re(I) bimetallic square complex **15** that shows a luminescent property.¹⁸ Porphyrin square **16** was also reported by Drain and Lehn,¹⁹ though its structure was deduced by inference. An “inorganic calix[4]arene” **17** was also prepared by Lippert and co-workers.²⁰

3.4 Di- and tri-nuclear macrocycles

Rigid bridging ligands give macrocyclic tetranuclear complexes on complexation with *cis*-protected metals, whereas flexible bridging ligands favor the self-assembly of fewer membered, di- or tri-nuclear macrocycles. It has been shown that the self-assembly strategy employing the *cis*-protected Pd(II) **10** unit provides a general and highly efficient synthesis of macrocycles.¹⁰ When ring strain exists in the framework to some extent, the dinuclear structure becomes in equilibrium with a trinuclear macrocycle (*e.g.*, **18**).²¹ Their structures were confirmed by X-ray crystallographic analyses and/or mass spectrometry. A macrocycle involving the 3-pyridyl group was also prepared.

The binding property of these macrocycles is worthy of note. For example, dinuclear complex **19** possessing two tetrafluorophenylene units showed a remarkable molecular recognition ability for an electron rich aromatic compound.²² Thus the association constant in aqueous media increased with increasing electron density of the guest compounds (*e.g.*, $K_a = 2680$ L

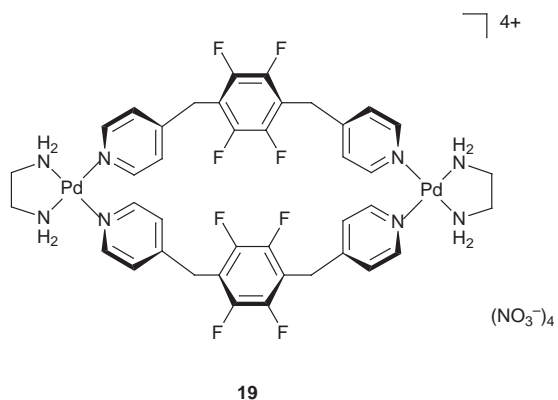


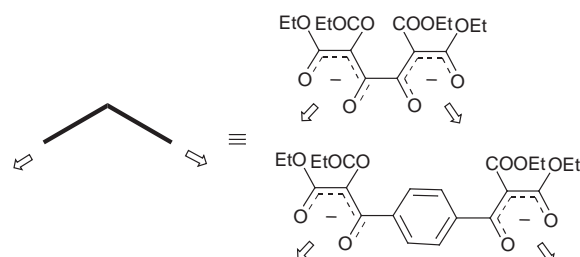
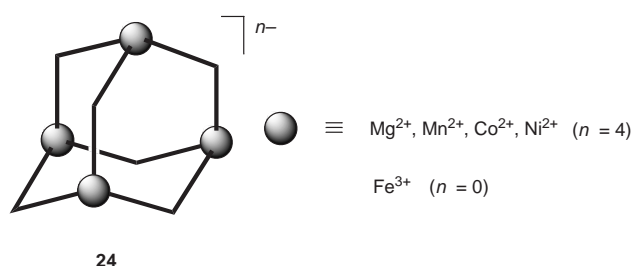
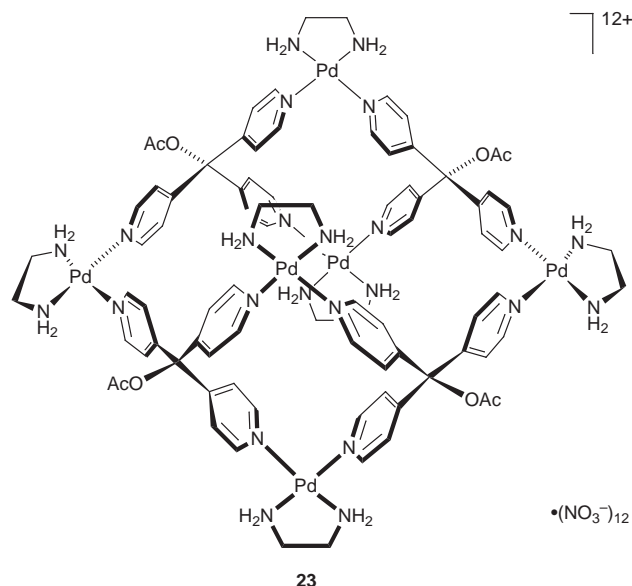
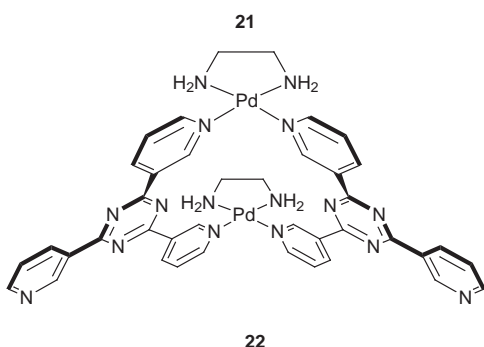
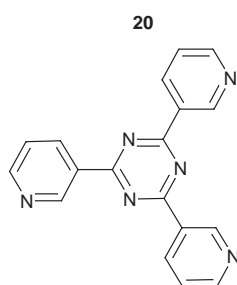
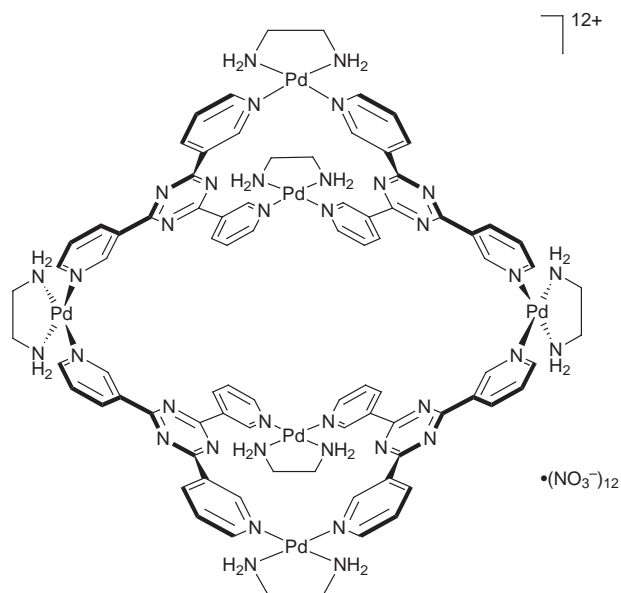
mol^{−1} for *p*-dimethoxybenzene, whereas 30 L mol^{−1} for *p*-dinitrobenzene; Table 1).

Quite recently, Lippert and co-workers reported the highly efficient assembly of a molecular triangle from (en)Pt(NO₃)₂ and 2,2'-bipyridine.²³

3.5 Self-assembly of nanometer-scale macrocycles

The construction of nanometer-scale host compounds by self-assembly is quite attractive since they can be synthetic receptors for big molecules such as C₆₀. Although there are few reports on the metal-directed self-assembly of nano-sized macrocycles, their structures have been often determined by spectroscopy and inference.²⁴ The first example of a nano-sized macrotricyclic which was prepared by metal-directed self-assembly and fully characterized by X-ray analysis was hexanuclear Pd(II) complex **20** assembling from ten small components: the treatment of tripyridyl compound **21** with **10a** gave nano-sized macrotricyclic complex **20** in which four ligand molecules were held together by six metal ions.²⁵ The molecular size of **20** is roughly 30 × 23 × 22 Å and the furthest Pd–Pd distance is 19 Å. A proposed pathway leading to **20** involves dinuclear macrocycle **22** possessing two uncoordinated pyridyl groups. Complex **20** showed selective binding properties toward dicarboxylate dianions. For example, a significant upfield shift ($\Delta\delta = -0.29$) was observed for aromatic protons of benzenediacetate in D₂O upon complexation with one equiv. of **20**. This complexation is probably due to two-point electrostatic attraction between the negative charge around COO[−] groups and the positive charge around Pd(II) ions.





Another nano-sized macrocycle **23** whose topology is the same as that of **20** also self-assembled in a quantitative yield from **10a** and tris(3-pyridyl)-1,3,5-triazine. The structure of **22** was unambiguously determined by X-ray analysis and spectroscopic studies.

4 Metal-directed self-assembly of cage compounds

4.1 Earlier examples

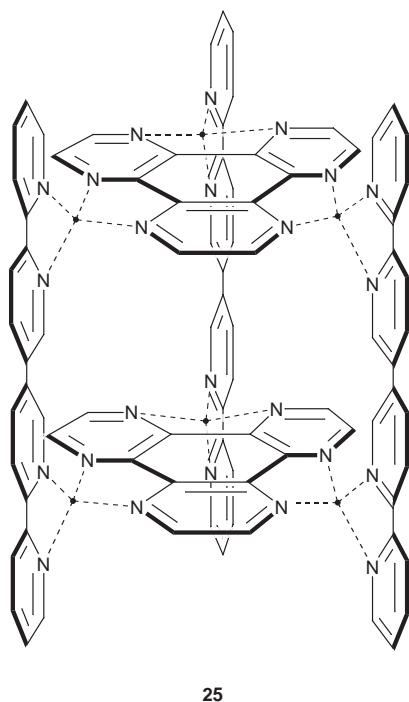
Recent progress in the self-assembly of cage compounds shows that three dimensional receptors provide a chemically localized environment.²⁶ The construction of such three-dimensional systems by metal-directed self-assembly requires a more precise design for metal–ligand recognition units. The first major advance in forming a three-dimensional cage complex may be ascribed to Saalfrank's “damantanoid” assembly **24** prepared by metallation of ethyl malonate in the presence of MgI_2 followed by the addition of oxalyl chloride. The structure

of **24** was evidenced by X-ray crystallography.²⁷ The metal center can be replaced by transition metals such as manganese, cobalt, nickel, or iron.²⁸ The three-dimensional cavity can be expanded by inserting a phenylene space into the ligand framework.²⁹ Analogous M_4L_6 cage structures have been also reported by Raymond and co-workers.³⁰

A fascinating example of the self-assembled 3D cage is Lehn's cylindrical complex **25** consisting of six Cu(I) ions and five ligands.³¹ The X-ray analysis of **25** showed that the quaterpyridine ligands are tilted by 66° with respect to the axis passing through the top and bottom of the cage. When Cu(I) is replaced by Ag(I), the quaterpyridine ligands became almost vertical.

4.2 Self-assembly of nanocages

While the 3D cage complexes discussed above possess a small cavity in their framework and thus show no significant binding property (except the recognition of inorganic anion by **25**), a nanosized roughly spherical 3D cage with an extraordinarily large cavity was recently constructed by metal-directed self-assembly.³² When coplanar exotridentate ligand **26** was complexed with *cis*-protected Pd(II) complex **10a**, ten small



molecules (four ligand and six metals) were found to self-assemble into a highly symmetric M_6L_4 type adamantanoid complex **27** in a quantitative yield (eqn. (3)). The thermodynamic stability of complex **27** is remarkable. Even if **10a** was combined with ligand **26** in a 4:2 molar ratio, complex **27** with a 3:2 stoichiometry was formed quantitatively and excess **10b** remained intact. The cage has a large spherical central void with a diameter of *ca.* 11 Å.

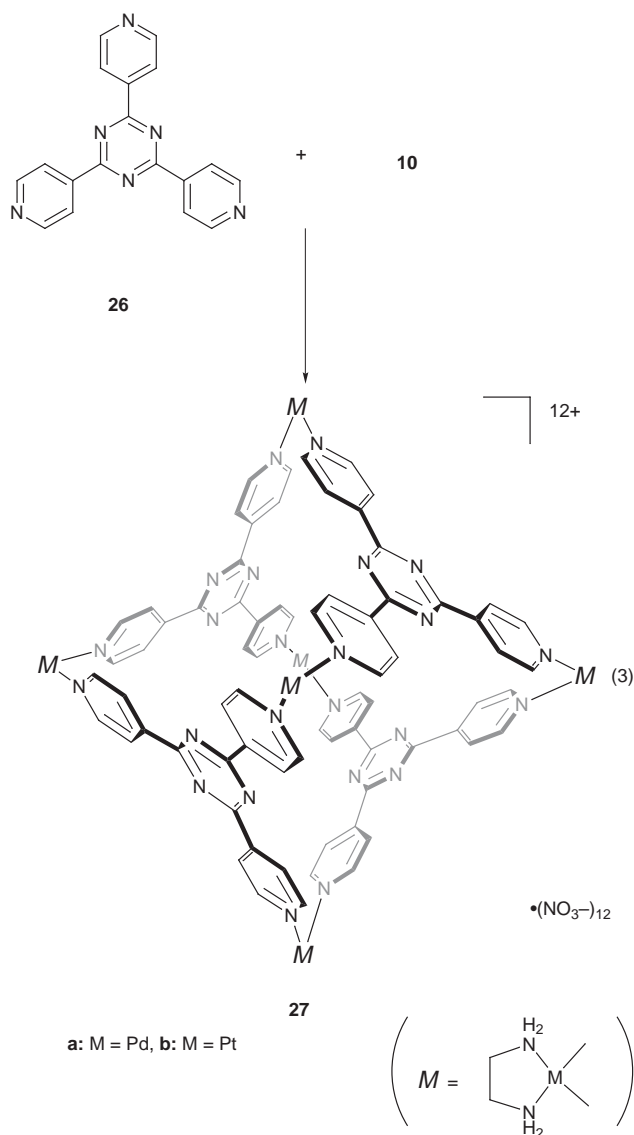
Within this self-assembling cage, four molecules of adamantane carboxylate were encapsulated and this clathrate complex was fully characterized by X-ray crystallography (Fig. 2). The inclusion geometry of the guest in the cage of **27** is very interesting. Hydrophobic adamantyl groups are located inside while hydrophilic carboxylate groups are outside. In addition, the main axes of the four guest molecules point to the corners of a tetrahedron.

A spectroscopic study based on NMR showed that the same host–guest aggregate was also organized even in solution. It is remarkable that the same 1 : 4 complexation was also observed with neutral, non-substituted adamantane. More interestingly, *o*-carborane, a more bulky spherical guest, was also encapsulated efficiently in a 1 : 4 stoichiometry.³³ Shape selectivity in the recognition was also observed: *e.g.*, *cis*-stilbene was effectively bound but its *trans* isomer was not.

Since nanocage **27a** stands as a result of thermodynamic equilibration, this structure is not stable enough to maintain its framework under forcing conditions (*e.g.*, acidic, basic, or nucleophilic conditions). In contrast, Pt(II) counterpart **27b** was shown to be very stable and it does not decompose even in the presence of an acid (HNO_3), a base (K_2CO_3), or a nucleophile (NEt_3) due to the inertness of a Pt(II)–pyridine coordinate bond. The stability of **27b** toward acid and base made it possible to design a pH controlled host–guest complexation. Thus, *N,N'*-dimethylaniline was effectively encapsulated in cage **27b** under neutral conditions, but liberated into the aqueous bulk phase by acidification (pH 1). After neutralization with K_2CO_3 , the liberated guest recapsulated in **27b**.³⁴

5 Guest-induced organization of synthetic receptors

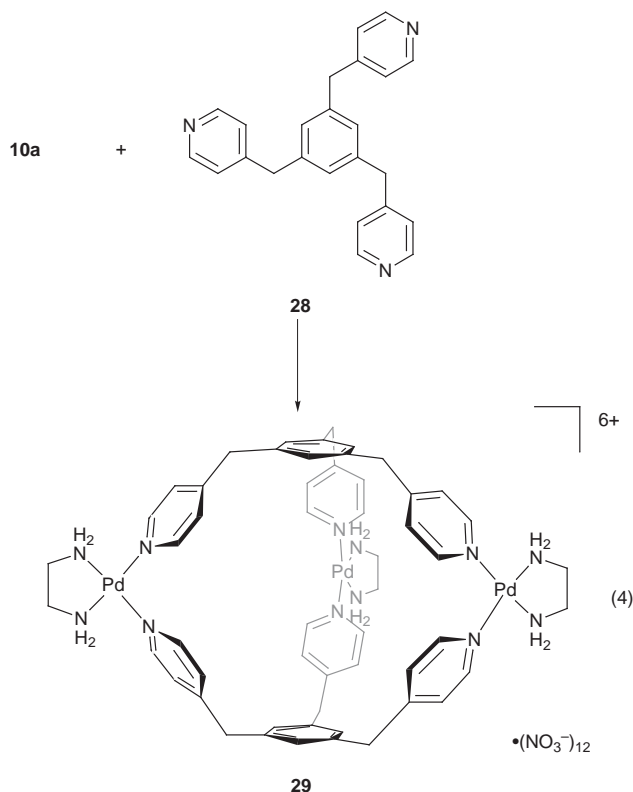
An interesting and unique example of a cage-like complex is compound **29** assembled from three molecules of **10a** and two



simple, pyridine-based ligands **28** (eqn. (4)). The behavior of this complex is quite different from that of other self-assembling receptors because **29** assembles only in the presence of an appropriate guest.³⁵ When **10a** and **28** are simply combined, an intractable mixture of oligomeric products is obtained. However, the addition of an appropriate guest induces the assembly of cage-like complex **29**. This guest-induced assembly process was monitored by a time-dependent 1H NMR measurement. NMR titration experiments showed 1 : 1 host–guest complexation between **29** and various organic carboxylates. For example, the 1 : 1 complex with 4-(methoxy)-phenylacetate ion was isolated in 94% yield. Besides anionic hosts, a neutral hydrophobic guest such as *p*-xylene was also effective for inducing the organization of **29**. Significant upfield shifts of guest signals up to *ca.* 3 ppm were observed when the guests effectively induced the organization of **29**. This guest-induced assembly can be regarded as a model for induced fit because a guest molecule induces the organization of its own receptor.

6 Summary

This article has demonstrated the effectiveness of the metal-mediated self-assembly strategy for constructing two- and



three-dimensional receptor frameworks. This strategy provides the facile preparation of synthetic receptors and, more significantly, enables the construction of nanosized, precise structures never before prepared by conventional covalent synthesis. Whereas self-assembly of helicate complexes has been studied extensively during the last decade, the area discussed in this article has been less explored and will presumably attract a great deal of attention. A more important aspect in this area is that the self-assembled complexes may exhibit new and unexpected properties particularly owing to the binding abilities of the receptor frameworks and the redox or magnetic properties of the metals. In addition, success in the construction of nano-sized receptors leads to multi guest inclusion systems which are essential to the design of an artificial micro space where a substrate and a reagent have an opportunity to be included together and to react with each other. In other words, the metal directed self-assembly of synthetic receptors will bring a variety of applications to current chemistry which have never been achieved by covalent bond chemistry.

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